POLYCATION-POLYANION COMPLEXES: PREPARATION AND PROPERTIES OF POLY(VINYLBENZYL-TRIMETHYL AMMONIUM)-POLY(STYRENE SULFONATE)

by

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B. S., University of Michigan, 1956
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Submitted to the Department of Chemical Engineering on June 19, 1961, in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical Engineering.

Abstract

High molecular weight poly(vinylbenzyltrimethyl ammonium chloride) coreacts ionically in dilute (<0.2 g/dl) salt-free aqueous solution with poly(sodium styrene sulfonate) to form a water insoluble but hydrous polysalt which contains equiequivalent quantities of the two polyelectrolytes. The reaction product is stoichiometric irrespective of whether either polymer is present in excess; the excess polymer remains dissolved in the aqueous phase. Surprisingly, the polysalt complex is found to be essentially free of microions (Na^+ and Cl^-), indicating virtually complete macro ion binding, and strongly suggesting that the molecules associate predominantly as randomly twisted pairs. In the presence of added salt (0.01-1.0 M NaBr), the polymer molecules become rather tightly coiled, and the reactions are no longer stoichiometric, complete precipitation of both polymers occurring over a considerable range of relative concentrations of the two polymers.

Mutual titrations between dilute solutions of the two polyelectrolytes can be made using a mixed dye (dichlorofluoroescein-methylene blue chloride) indicator which turns from fluorescent green to purple in the presence of a slight excess of free polycation in solution. The polymer ratio at the titration endpoints is in good agreement with the equivalent weight ratio determined by counterion titrations made on the individual polyelectrolytes.

When more concentrated (>0.6 g/dl) solutions of the two polyelectrolytes are mixed, an extremely thin, precipitated polysalt film forms at the two-solution interface which completely blocks further interpolymer reaction, making its own thickness self-limiting.

These films can be isolated, are approximately 150 Å in thickness when dry, exhibit the microadhesive properties observed for other polymer films below 0.22 microns in thickness, and show high diffusivity toward simple electrolytes (NaCl), but lower diffusivity toward larger ionic species (methylene blue chloride).

Fairly fluid solutions, containing rather high concentrations (10 g/dl) of both polyelectrolytes, can be prepared in a ternary solvent comprised of ca. 20% acetone, 20% sodium bromide, and 60% water. Dilution of these mixtures with water, or evaporation of the acetone, results in gelation. By suitable washing and drying techniques, amber, glassy solids free of extraneous electrolyte are obtained. By this route, stable complexes containing excess polycation or polyanion, as well as neutral polysalt, can be obtained. The non-stoichiometric polysalts are quite heterogeneous in structure, apparently being segregated into microscopic zones of neutral polysalt and unreacted polyelectrolyte. These complexes appear to undergo structural rearrangement by a mechanism of internal ionic bond transfer when swelled in aqueous acetone solutions, or when dried. The neutral polysalt selectively sorbs salt (NaBr) from aqueous electrolyte solutions, whereas the polyanion- and polycation-rich complexes exclude salt. Salt absorption by all of the polysalts if markedly increased when acetone (which is apparently quite strongly excluded from the polymer phase) is added to the external solutions. Polysalts gelled, but not completely hardened by precipitation from the mixed solvent system can be oriented by unidirectional stretching about 5X. Subsequent hardening (by water-washing, and drying) of the stretched gels results in noncontractile, transparent, birefringent but non-crystalline polysalts having highly fibrous structures. This fibrosity suggests that molecular pairing may occur even in polysalts precipitated from highly saline solutions.

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Department of Chemical Engineering
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June 19, 1961

Professor Philip Franklin
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

The thesis entitled, "Polycation-Polyanion Complexes: Preparation and Properties of Poly(vinylbenzyltrimethyl ammonium)-Poly(styrene sulfonate)", is herewith submitted in partial fulfillment of the requirements for the degree of Doctor of Science.

Respectfully submitted,

Richard G. Miekka

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Alan S. Michaels, whose many helpful suggestions and interpretations have been invaluable in the conduct of this investigation.

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Many thanks also to Mr. N. H. Smith for measurement of the individual polymer viscosities, to Dr. F. W. Tausch and Mr. A. Stancell for many enlightening discussions, to Mrs. B. Kaplan for her excellent typing and good humor, and to my parents for their encouragement and financial aid.

Finally, and most of all, to my wife Jeanette, for her love, her understanding, and her patience.

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I. SUMMARY

Polyelectrolytes are organo-ionic compounds, most frequently comprised of long chain hydrocarbon polymers which have ionic functional groups attached at regular intervals to their backbone chains. The precipitation reactions occurring between oppositely-charged linear synthetic polyelectrolytes in solution, and the properties of the precipitates, are of interest because of their similarities to biological systems, ion exclusion resins, and ion exchange resins and membranes. Precipitation is due to strong electrostatic attractions between oppositely-charged macromolecules which causes them to be drawn together and to react ionically, giving off their associated counterions as free salt. The precipitates can frequently be dissolved, or their formation prevented, by the addition of sufficient amounts of microionic salts (e.g., NaCl) to suppress the ionization, and thus the electrostatic charge fields, of the macromolecules.

The present study was undertaken to determine the interaction characteristics of strongly ionized oppositely-charged polyelectrolytes with high charge densities, and some of the properties of the reaction products (polysalts). The two polyelectrolytes used throughout the study were poly(sodium styrene sulfonate), NaSS, an anionic polyelectrolyte with a molecular weight of 760,000, and poly(vinylbenzyltrimethyl ammonium chloride), VBTAC, a cationic polyelectrolyte with a molecular weight of approximately 300,000. Both polymers were polymerized from the ionic monomers and were supplied by the Dow Chemical Company of Midland, Michigan.

The oppositely-charged polyelectrolytes were allowed to react under 3 distinctly different sets of conditions, each set of conditions resulting in polysalts with unique physical characteristics.

Interaction between dilute (<0.2 g/dl) aqueous solutions of VBTAC and NaSS resulted in white, hydrous, particulate polysalts similar in

appearance to the silver chloride precipitates formed by reaction between silver nitrate and the alkali chlorides. The polysalts flocculated at or near the ionic equivalence points of the mixtures. When more concentrated solutions (> 0.6 g/dl) of the polymers were mixed, extremely thin (ca. 200 Å) polysalt films formed at the two solution interfaces which completely blocked further interpolymer reactions. Finally, fairly large amounts of both polymers (5-10 g/dl) could be dissolved without interacting in a ternary solvent comprised of ca. 20% acetone, 20% NaBr, and 60% water. Dilution of these mixtures with water, or evaporation of the acetone, resulted in gelation. By suitable washing and drying techniques, these gels could be hardened into amber, glassy solids free of extraneous microions.

It was found that in dilute, salt-free aqueous solutions VBTAC and NaSS reacted in equiionic proportions regardless of the relative amounts of the two polymers being mixed. If the polymer mixtures were passed through their ionic equivalence points, the precipitates were completely flocculated, and centrifugation yielded clear supernatant liquids. The viscosity of each supernatant liquid was almost exactly equal to that of a control solution made up to contain a concentration of polymer equal to the ionic excess of the more concentrated polyelectrolyte in the mixture plus the maximum amount of salt (NaCl) which could be released from the precipitate upon complete ionic interaction of the polymers. In addition, argentometric titrations made on the supernatants of the mixtures containing excess NaSS showed that within experimental error (± 3%), all of the chloride counterions of the (precipitated) VBTAC were released into solution. Thus the experimental data showed that within very narrow limits the interactions between the polymers in dilute, salt-free solutions were both stoichiometric and ionically complete.

These rather surprising results indicate that the polymers combine in some fashion other than by random interaction between the polyions, for if this were the case, a tangled, highly matted network would be formed and one would expect that a considerable fraction of the ions of each polymer would be sterically prevented from reacting. The conclusion is that molecular pairing occurs between relatively long segments of the reacting molecules. Since VBTAC and NaSS have identical ionic spacings, pairing allows virtually complete reaction of the polyions. The conditions for pairing are most favorable at low polyelectrolyte concentrations because then the polymers are quite highly ionized and the molecules assume extended configurations because of electrostatic repulsions between neighboring polyions on the polymer chains.

In the presence of added salt (0.01-1.0 M NaBr), the dilute solution interactions between the polymers were no longer stoichiometric, but instead complete mutual precipitation of both polyelectrolytes occurred over a considerable range of relative concentrations of the two polymers (e.g., in the presence of 0.1-1.0 M NaBr, complete precipitation of both polymers occurred in all mixtures containing VBTAC and NaSS in the composition range 0.83-1.5 Meq. VBTAC/MeqNaSS). Thus, in the presence of added salts, molecular pairing was inhibited or greatly hindered, probably because the added salt diminished polymer ionization, reducing repulsive forces between like polyions which in turn allowed the chains to contract and coil, isolating many polyions from reacting.

By careful manipulation the fragile interfacial films formed between more concentrated polyelectrolyte solutions could be isolated, washed free of excess polymer, and dried. When dry, the unsupported films were transparent, but in reflected light they resembled "black" soap films. The films adhered tenaciously to any solid surface with which they came in contact, a characteristic also observed for other polymer films below 0.22 microns in thickness (3). The unsupported films were extremely fragile and almost invariably broke from shrinkage stresses shortly after drying. Films plasticized by the addition of 0.2-0.5% glycerin or dextrose to the wash water sometimes lasted for several weeks if undisturbed.

Reflectance spectrophotometer measurements made on an 11-film laminate showed a distinct first order reflectance minimum at an incident light wavelength of 480 millimicrons, corresponding to a thickness of about 160 millimicrons for the 11 films, or 145 Å per dry film. Electron photomicrographs showed the films to have a uniform pebble-grain surface texture typical of amorphous polymers.

The diffusion rate of 0.1 M NaCl through a piece of filter paper treated to contain an imbedded interfacial film was 0.33 meq/hr/sq.in., which was also the value obtained for the untreated filter paper, indicating that the diffusional resistance of the interfacial film was very low, and negligible compared to that of the supporting membrane. On the other hand, the diffusional resistance of the interfacial membrane toward methylene blue chloride was fairly high, about 1 1/2 hours being required before any blue coloration could be noted in pure water placed opposite a 0.5% solution of the intensely colored dye.

Mutual titrations between the dilute polymers were carried out using a mixed dye (dichlorofluorescein-methylene blue chloride) indicator which turned from green to purple in the presence of a small amount of free VBTAC in solution. The endpoints obtained were in good agreement with the ionic equivalent weight ratios determined by counterion titrations made on the individual polymers. Less VBTAC was needed to titrate a given amount of NaSS when the latter was mixed with low concentrations (10^{-6} - 10^{-3} molar) of $CaCl_2$ or $FeCl_3$, but the salts had no effect on titrations made in the opposite direction (VBTAC plus $FeCl_3$ or $CaCl_2$ titrated by NaSS). Apparently, the Ca^{++} and Fe^{+++} ions bridged segments of the NaSS molecules, forming kinks whose ions were sterically isolated from interaction with VBTAC. The bridging (or ion shielding) was a slow process relative to the rates of polymer interaction, so the reverse titrations were unaffected.

Stable polysalts containing excess polycation or polyanion as well as neutral polysalts could be obtained by precipitation from the mixed solvent (NaBr-acetone-water) system. Here, too, the ionic interactions between the polymers were so nearly complete after thorough water-washing that even in the neutral polysalt it was difficult to detect residual sodium (by flame test) or bromide (by reaction with silver nitrate) counterions.

Non-stoichiometric polysalts composed of 2VBTAC/1NaSS or 1VBTAC/2NaSS, although transparent when dry, were quite heterogeneous in structure as indicated by high dielectric constants and loss factors at low a-c frequencies. These polysalts were evidently segregated into microscopic regions of neutral polysalt and excess unreacted polyelectrolyte. When equilibrated with water they swelled to about 3 (VBTAC-rich polysalts) to 7 (NaSS-rich polysalts) times their original dry weights. Swelling was nearly doubled if 20-30% by weight of acetone was added to the water, even though pure acetone was incapable of swelling either polysalt at all. When placed in water immediately after being equilibrated with a 20% aqueous acetone solution, a VBTAC-rich polysalt sample swelled slightly, rather than shrinking to the swelling value obtained when the dry polysalt was equilibrated with water. After being dried and re-equilibrated with water, however, the polysalt returned to its original water swellability. These experiments showed that structural rearrangement of the polysalt into a more expanded configuration occurred when it was placed in the aqueous acetone solution, probably by a mechanism of ionic bond transfer between the previously reacted (neutral region) VBTAC and the excess unreacted VBTAC. The acetone increased the lability of the neutral regions by acting as a partial solvent for the nonionic portions of the molecules, thus enabling bond transfer to take place. Upon drying, the polysalt returned to its original, more heterogeneous micelle-like structure as the unreacted polyions were strongly drawn into the residual hydrous regions of the structure.

Because of the ion exclusion (Donnan membrane equilibrium) effect, the non-stoichiometric polysalts were found to swell far less if low concentrations of NaBr were added to the water or water-acetone mixtures. At higher NaBr concentrations (above 2-3% by weight of NaBr in the external solutions), swelling again increased as the salt was absorbed as counterions at the double polyion sites(reversal of the interaction process) thus reducing the degree of ionic cross-linking of the structures.

By contrast, the neutral polysalts (1VBTAC/ 1NaSS) were much more homogeneous, exhibiting only mildly elevated dielectric constants and loss factors at low a-c frequencies. Their swelling in water and water-acetone solutions was markedly lower than the swelling of the non-stoichiometric polysalts, being only 0.39 g. solution absorbed per g. dry polysalt in pure water, and rising to a maximum of 0.42 g. solution per g. polysalt in 20-30% aqueous acetone. Swelling was increased even at low added salt concentrations, since no Donnan effect was present.

In addition to the swelling measurements, the amounts of NaBr absorbed by some of the polysalt samples equilibrated with NaBr-acetone-water solutions were measured by increases in the dry weights of the samples. The concentration of NaBr in the internally absorbed liquid was over 3 times the external NaBr concentration for neutral polysalt equilibrated with 2% (ca. 0.2 M)NaBr, diminishing to 1.5 times the external concentration when the polysalt was equilibrated with 7% aqueous NaBr. A VBTAC-rich polysalt absorbed practically no salt from a 2% aqueous NaBr solution, but almost as much as the neutral polysalt in 7% aqueous NaBr. The high salt-binding capacity of the neutral polysalt at low external salt concentrations is attributed to absorption of NaBr at the double polyion sites, particularly those sites at which the polyion bonds are strained by steric hindrances. The Donnan exclusion effect of the non-stoichiometric polysalt inhibits salt absorption from dilute solutions, but the neutral polysalt regions are apparently able to absorb salt independently of the VBTAC regions at higher external salt concentrations.

The internal NaBr concentrations of both the neutral and quaternary-rich polysalts increased rapidly as the acetone concentrations in the external solutions were increased at constant external NaBr concentrations. These increases in salt absorption were attributed to increased NaBr activity in the external phase, coupled with exclusion of acetone from the polysalts.

When immersed in an aqueous solution 0.1 molar with respect to both KCl and NaCl, the neutral polysalt selectively sorbed K^+ over Na^+ in the ratio 1.26/1, in agreement with the selectivity obtained by Sujata (35) with Dowex 50 ion exchange resin (essentially NaSS except in the hydrogen form).

The neutral polysalt had a sufficiently high volume resistivity when dried over P_2O_5 (2.3×10^{11} ohm-cm at 100 cps) to make it potentially useful as a dielectric or insulating material, while the volume resistivities of the non-stoichiometric polysalts dried over P_2O_5 were only 1/10 (NaSS-rich) to 1/1000 (VBTAC-rich) as high. The resistivities of all of the polysalts were decreased by a factor of about 100 when the samples were equilibrated at 50% relative humidity at room temperature (12-13% moisture content).

Polysalts gelled, but not completely hardened by precipitation from the mixed solvent system could be oriented by unidirectional stretching 2-5X and then hardened to yield transparent, birefringent but non-crystalline films having highly fibrous structures reminiscent of the asbestos minerals. This fibrosity may have been a macroscopic manifestation of molecular pairing between the polymers, but may also have been due to elongation of small pores present in the structures at the time of orientation.

It is concluded that:

(1) The precipitation reactions occurring between VBTAC and NaSS in dilute (<0.2 g/dl) aqueous solutions are stoichiometric and ionically complete within ± 5%, regardless of the ratio in which the two polymers are mixed. This suggests that the molecules are able to associate predominantly as randomly twisted pairs. In the presence of 0.01 M or more of added NaBr, the polymer molecules become rather tightly coiled, and the reactions are no longer stoichiometric, complete precipitation of both polymers occurring over a considerable range of relative concentrations of the two polymers.

(2) The interfacial films formed between more concentrated (> 0.6 g/dl) solutions of the two polymers can be isolated, are approximately 150 Å in thickness when dry, exhibit the microadhesive properties of other polymer films below 0.22 microns in thickness, and show high diffusivity toward simple electrolytes (NaCl), but lower diffusivity toward larger ionic species (methylene blue chloride).

(3) Stable, transparent complexes containing excess polycation or polyanion, as well as neutral polysalts, can be obtained by precipitation from a ternary solvent (comprised of ca. 20% acetone, 20% NaBr, and 60% water) in which both polymers can be dissolved without coreacting. Polysalts containing excess VBTAC or NaSS undergo structural rearrangement by a mechanism of internal ionic bond transfer when swelled in aqueous acetone solutions, or when dried. The neutral polysalt selectively sorbs salt (NaBr) from aqueous electrolyte solutions, whereas the polyanion- and polycation-rich complexes exclude salt. Salt absorption by all of the polysalts is markedly increased when acetone (which is apparently quite strongly excluded from the polymer phase) is added to the external solutions.

The following recommendations for further study are made:

(1) It is recommended that further studies of dilute solution polyelectrolyte interactions be carried out to (a) determine more exactly the stoichiometry of VBTAC-NaSS dilute solution interactions, especially over long periods of time; (b) elucidate the mechanisms by which VBTAC and NaSS combine both in the presence and absence of a variety of added microionic salts; and (c) determine the effects of variations in polymer ionic spacing and types of polyions (and counterions) on polyelectrolyte interaction behavior. Greater measurement accuracy is needed, necessitating the use of more refined apparati such as a couette viscometer, and a sensitive conductivity bridge. The measurements should be supplemented by electron photomicrographs of the precipitate particles.

(2) It is recommended that more reliable methods be found for isolating polysalt interfacial films, and that studies be carried out to determine the factors which influence film strength, thickness, permeability, and composition. Again, special measurement techniques are required, such as the use of elliptically polarized light for determination of film thicknesses, and radiotracer analysis for measurement of film compositions.

(3) It is recommended that further studies of the properties of polysalts precipitated from ion-shielded solutions be directed toward developing practical applications for the materials, making use of their unique properties (viz., their permeability toward aqueous electrolyte solutions, and ability to absorb and/ or exchange microions).

II. INTRODUCTION

A. Terminology

The word "polyelectrolyte" as used in this writing will refer to high molecular weight polymeric substances which have ionizable groups attached at regular intervals to their hydrocarbon backbone chains. When placed in a polar solvent such as water, these groups ionize into cations (or anions) which are bonded to the polymer chains, and microanions (or microcations), which are relatively free to move about in solution. The ions bonded to the polymer chains will be referred to as "polyions", and their associated microions will be called "counterions". Polymers with cationic polyions will be referred to as cationic polyelectrolytes, while those with anionic polyions will be referred to as anionic polyelectrolytes (in contrast to the naming of cation or anion exchange resins). The complex precipitates formed by ionic reactions between anionic and cationic polyelectrolytes will be referred to as "polysalts". Unless otherwise specified, the polyelectrolytes referred to will be of the linear (not crosslinked) type.

B. Characteristic Behaviors of Individual Polyelectrolytes in Solution

Because of their unique organo-ionic structures, solvated polyelectrolytes exhibit characteristics which are in many respects different from those of both solvated nonionic polymers and solvated microionic salts. The strongly hydrophilic nature of their polyions causes most polyelectrolytes to be soluble in water, but insoluble in low-polarity organic liquids.

The behavior of polyelectrolytes in solution can be explained by considering a rough pictorial model of solvated linear polyelectrolyte molecules. In the absence of added microionic salts, an isolated molecule in dilute, aqueous solution will be quite highly ionized, and the counterions, although kept in the vicinity of the parent molecule by electrostatic forces will tend to be distributed about the parent molecule as a rather diffuse "ion-cloud" due to hydration forces and thermal agitation. The molecule will tend to assume an extended configuration* because of repulsive forces between adjacent polyions as illustrated in Figure 1.

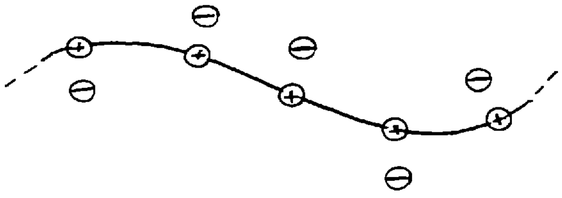

Figure 1

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* There has been considerable disagreement among various investigators concerning the degree of chain extension achieved by a fully ionized flexible-chain polyelectrolyte molecule of high charge density (i. e., at least one polyion for each 12-16 chain carbon atoms) in very dilute aqueous solutions. As recently as 1951 (13, 15) it was presumed that at or near infinite dilution the molecules of such polyelectrolytes achieved "rigid rod" configurations corresponding to maximum end-to-end extension. More recent investigations have indicated that this is probably not the case. From theoretical considerations, Kirkwood and Auer (25) have derived expressions for calculating the intrinsic viscosities of molecules in solution at maximum end-to-end extension. Eisenberg (9) found good agreement between the measured intrinsic viscosity at zero shear of sodium carboxymethyl cellulose and the value calculated from the equation of Kirkwood and Auer for maximum extension of this polyelectrolyte, which is known to be quite inflexible because of the steric configuration of the chain. However, the measured intrinsic viscosity at zero shear of the more flexible-chained polyvinylbutylpyridinium bromide (PVBuPyBr) was found to be only about 1/ 12 the value predicted by the equation of Kirkwood and Auer ($[\eta]$ measured = 9, 500 ml/ g, $[\eta]$ calculated for maximum extension = 113, 000). Since the intrinsic viscosity of a rodlike molecule is approximately proportional to the square of its length, this corresponds to an extension of about 30% of the maximum for PVBuPyBr. Using the same viscosity data, Eisenberg and Pouyet (10) have assumed that the PVBuPyBr molecules behave hydrodynamically as elongated rigid ellipsoids, and have employed the more elaborate equations of Onsager (31) and Perrin (32) to calculate

As a consequence of the foregoing, an electrical double layer will arise from the separation of the polyion and counterion charges. This double layer will extend into the surrounding solution and cause electrostatic repulsions between molecules of like charge (and electrostatic attractions between molecules of opposite charge), even when the molecules are separated at considerable distances in the solution.

If the counterion concentration is increased, either by the addition of a microionic salt such as sodium chloride, or by increasing the polyelectrolyte concentration itself, the counterions will tend to approach and surround the polyions, reducing the repulsive forces between molecules and between neighboring ions on the polymer chain. The molecule will now tend to contract and approach a randomly coiled shape which is the configuration assumed by nonionic polymers in solution* as illustrated in Figure 2.

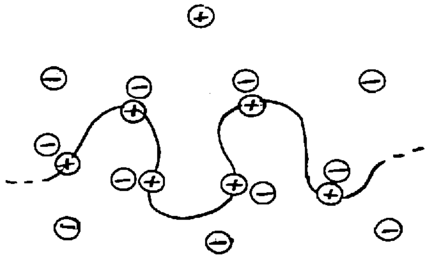

Figure 2

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an extension of 38% of maximum for the polymer. Approximately the same behavior is to be expected for the polyelectrolytes used in this study, which are similar in structure to the PVBuPyBr.

* Flory (11) gives the configuration of polystyrene in organic solvents at 25°C (determined from viscometric measurements) to be such that $(\overline{r_o^2}/M)^{1/2} = 735 \times 10^{-11}$, where $\sqrt{\overline{r_o^2}}$ is the root-mean-square end-to-end extension in centimeters of an unperturbed molecule of molecular weight M. For a polystyrene molecule of molecular weight 230,000, which corresponds to a molecular weight of approximately 500,000 for either of the polystyrene-type polyelectrolytes used in this study

If the counterion concentration is made extremely high, the polyions may become dehydrated and almost completely unionized, so that essentially no mutual repulsion remains between adjacent polyions, and the hydration tendencies of the ionic sites are barely able to keep the molecule in solution.

Under these conditions the molecules may coil to a size less than that corresponding to the statistically-kinked configuration while still remaining in solution. This hypercoiling is due to intramolecular associations, either between the nonionic portions of the molecules which, in the absence of ionic repulsions and strong hydration forces of the ions, are able to surround themselves with their own organic atmospheres so that the molecules become in effect "unimolecular micelles", and/or between the ionic groups themselves by polar associations of the same type as occur between ions of microionic salts upon crystallization from supersaturated aqueous solutions. Additional salt cannot produce any further change in molecular configuration of the polyelectrolyte, but may eventually dehydrate the polyions to the extent that the molecule is salted out of solution.

The changes in polyelectrolyte molecular configuration with changing microion concentration are reflected in the viscosities of polyelectrolyte solutions. Figure 3 is a plot showing typical polyelectrolyte viscosity behavior at infinite polymer dilution in the presence of increasing amounts of added salt.

(see Section II-E), $\sqrt{\bar{r_0^2}}$ is 354 Å. The maximum end-to-end extension of the molecule, assuming a mer unit length of 1.54 Å and carbon-carbon bond angles of 109.5°, is 2760 Å, so the root-mean-square end-to-end extension of the coiled molecule is about 1/8 of the maximum, or about 30-40% of the extension presumably achieved by PVBuPyBr at maximum ionization (see preceding footnote).

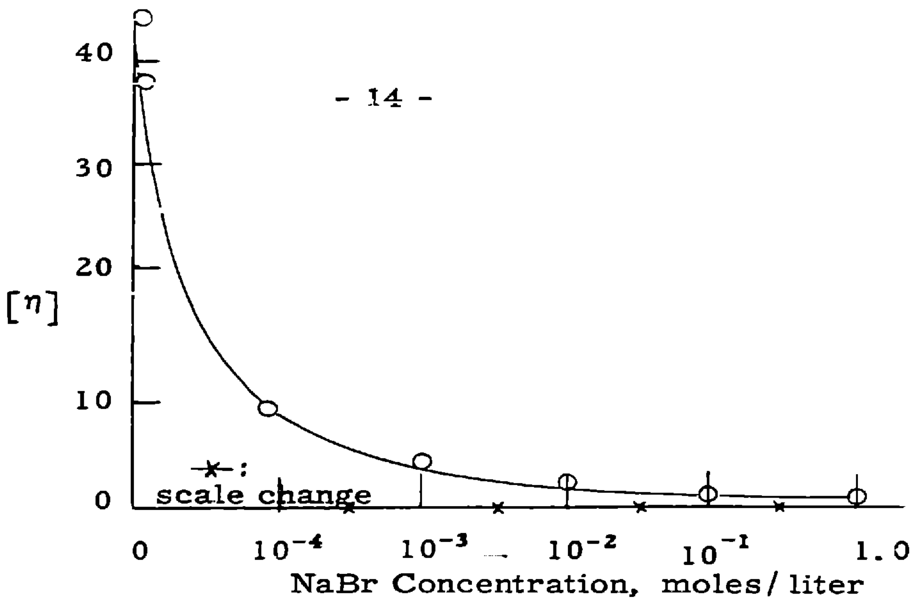


Figure 3. Effect of NaBr on the intrinsic viscosity of poly(vinylbenzyltrimethyl ammonium chloride) at 25.0°C. Data of Smith (34).

In the plot the intrinsic viscosity, $[\eta]$, is the polymer contribution to viscosity per unit polymer concentration (g. / dl) expressed as multiples of the solvent viscosity:

$$[\eta] \equiv \lim_{c_p \to 0} \frac{\eta_{sp}}{c_p} = \lim_{c_p \to 0} \frac{\eta_p - \eta_o}{\eta_o} / c_p$$

where η_p = viscosity of polymer solution
η_o = viscosity of pure solvent
η_{sp} = specific viscosity of polymer solution
c_p = polyelectrolyte concentration in g/ 100 ml.

In the absence of added salt, the polymer molecules are extended by repulsive interactions between the polyions and offer maximum resistance to shear. In the presence of added NaBr, the intrinsic viscosity decreases, indicating that the molecules have contracted and so offer less resistance to flow. At high NaBr concentrations the viscosity levels off, indicating the approach to maximum molecular coiling.

At finite polyelectrolyte concentrations, intermolecular interactions occur which tend to increase polymer viscosity, especially in the absence of added salts. Figures 4 and 5 show the changes which occur in reduced specific viscosity (η_{sp}/c_p) with varying polymer and added salt concentrations for the two polyelectrolytes used in this study. The salt-free polyelectrolyte solutions exhibit rather sharp maxima in η_{sp}/c_p at low polymer concentrations, a characteristic of most polyelectrolytes in solution. It has been suggested (4) that the maxima are due to intermolecular electrostatic reactions, and that the η_{sp}/c_p decreases at higher polyelectrolyte concentrations are due to molecular contractions with increasing counterion concentrations (which more than compensate for the increased probability of interactions with more molecules per unit volume of solution). At very low concentrations no interactions can occur because the molecules are too far apart, even when at maximum extension. It has also been suggested (34) that the interaction peaks may be due to counterion bridging between the molecules, which could arise when a counterion has diffused away from its polyion, forcing a second counterion to do double duty by partially neutralizing both its own polyion and the denuded polyion. Bridging ceases at higher polymer concentrations because of the greater availability of counterions at any point in solution.

The molecular interactions are diminished in the presence of added NaBr, disappearing completely (η_{sp}/c_p independent of c_p) at NaBr concentrations of 0.01 M and 0.10 M for the poly(vinylbenzyltrimethyl ammonium chloride) and poly(sodium styrene sulfonate) solutions, respectively. The greater viscosity suppressing effect of the salt on the quaternary polymer than on the sulfonate polymer is due at least in part to specific ion associations between quaternary nitrogens and the higher halide ions (the quaternary polymer is precipitated from solution by iodide ions).

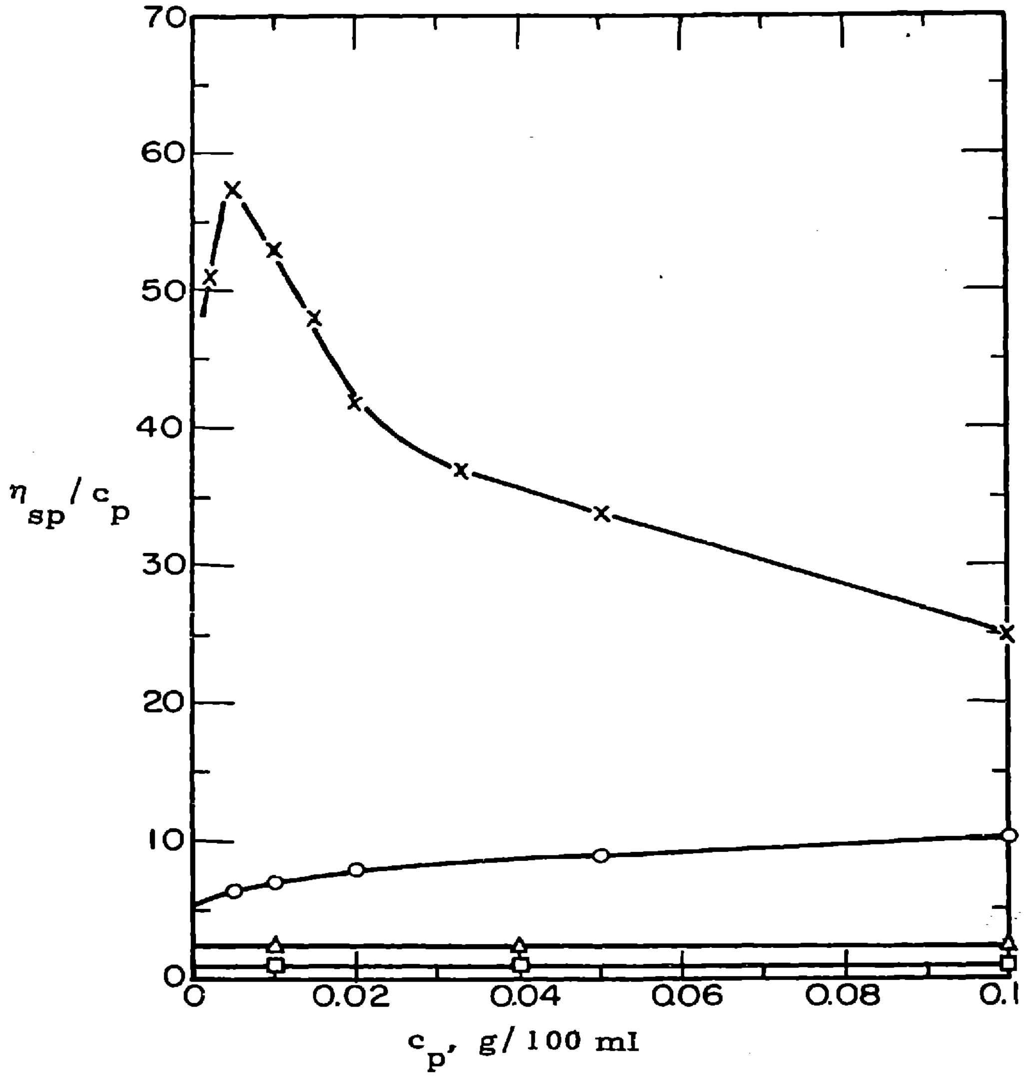


Figure 4

Reduced Specific Viscosity versus Polyelectrolyte Concentration for Poly(Vinylbenzyltrimethyl Ammonium Chloride) in:
(x) pure water, (o) 0.001 M NaBr,
(△) 0.01 M NaBr, and (□) 0.10 M NaBr

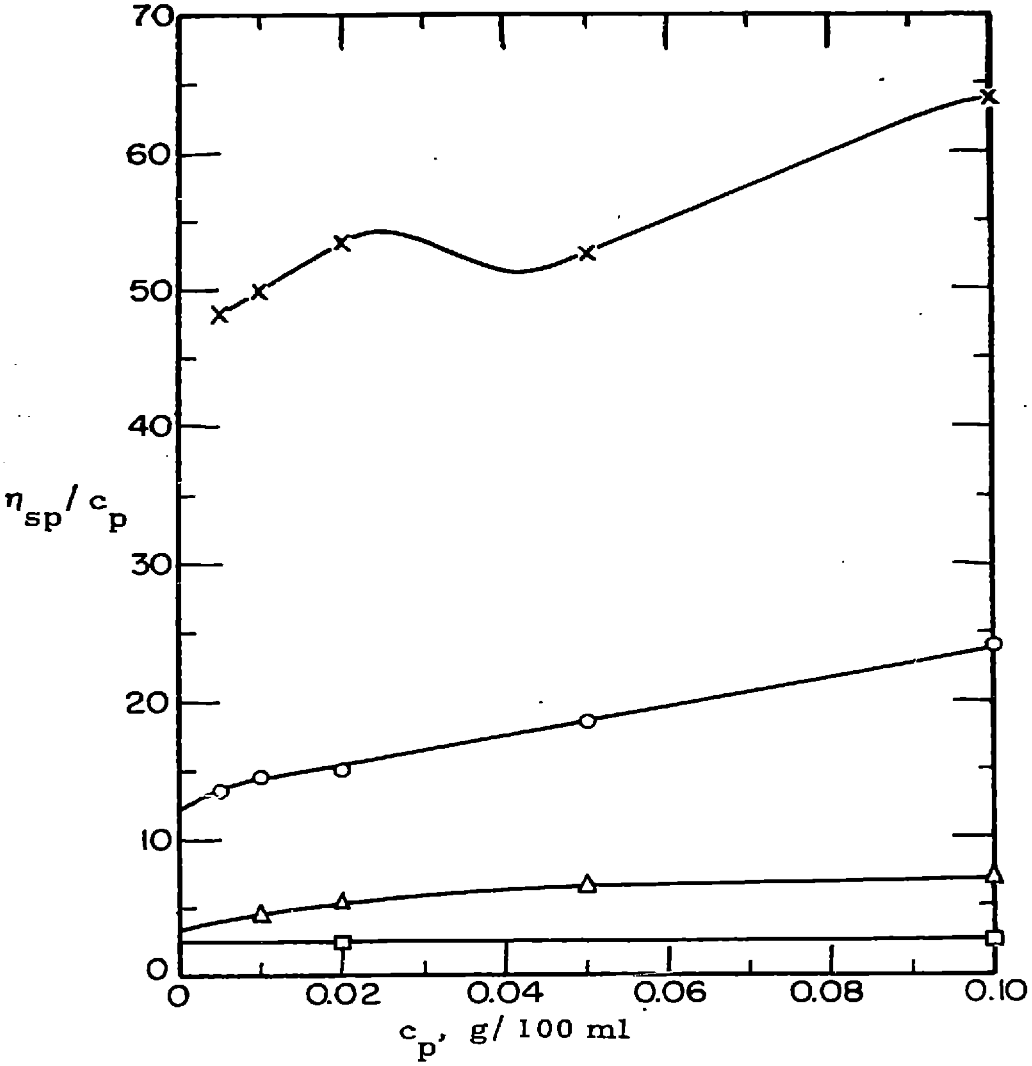


Figure 5

Reduced Specific Viscosity versus Polyelectrolyte Concentration for Poly(Sodium Styrene Sulfonate) in:
(x) pure water, (o) 0.001 M NaBr,
(Δ) 0.01 M NaBr, and (□) 0.1 M NaBr

C. Interactions Between Oppositely-Charged Polyelectrolytes

When aqueous solutions of oppositely-charged polyelectrolytes are mixed under proper conditions of concentration and temperature, the polyions unite ionically to form polysalts, giving off their associated counterions as free salt. The polysalts, although often quite hydrous, are usually insoluble in water and so precipitate from solution. The electrical double layers surrounding the macromolecules in dilute, salt-free solutions (see previous discussion) cause the oppositely-charged molecules to be electrostatically attracted together, even when initially separated at considerable distances in solution. The free energy reductions resulting from the release of counterions into solution as free salt (increases in system entropy), coupled with the mutual anihilation of the electrostatic fields of both reacting species, constitute a strong thermodynamic driving force for interpolymer reactions. Tendencies for ionic association between the corresponding monomers, or between one polyelectrolyte and the monomer of the oppositely-charged polyelectrolyte, are not nearly as great, since the above-mentioned driving force is absent or greatly diminished in intensity.

At sufficiently high concentrations of some polyelectrolyte pairs, the polysalts take the form of thin, continuous films which form rapidly at the two-solution interfaces (37). These films are impermeable to either polymer species, and so completely block further interpolymer reactions, making their own thickness self-limiting.

In the presence of added microionic salts (e.g., NaBr), or at high polyelectrolyte concentrations, the degree of polyion ionization is reduced, resulting in diminution of the electrical double layers and of the intramolecular repulsive forces causing molecular extension. This results in decreased electrostatic attraction between oppositely-charged macromolecules, and the more coiled molecular configurations may result also in increased steric hindrance to polyion associations.

Polysalts can frequently be dissolved, or their formation prevented, by the addition of sufficient amounts of microionic salts to almost completely suppress ionization of the macromolecules. The more strongly ionic the polyelectrolytes, and/or the more strongly the polyions associate with one another, the more difficult the suppression of interpolymer reactions becomes. Conversely, the stronger the association between the polyions and the ions of the added salt, the easier it is to suppress polymer ionization. Because of their smaller size/charge ratio and relatively weaker hydration tendencies, doubly and triply charged counterions are generally more effective polyion shielders than univalent ions. Thus, neglecting special micro-ion-polyion affinities, considerably more than twice as much sodium chloride is required to give the same shielding effect as a given concentration of magnesium sulfate. On the other hand, monovalent ions, being more strongly hydrated than polyvalent microions, are better able to deprive polyions of water. This greater dehydrating ability of monovalent ions may in some instances make them better than polyvalent microions (at very high concentrations) for completely suppressing polymer ionization. The salt concentrations required to cause salting out of polyelectrolytes are sometimes increased if small amounts of water-miscible low polarity organic liquids (e.g. acetone) are added to the aqueous polymer solutions, presumably because the organic liquids help to increase the solvent affinity of the organic portions of the molecules.

D. Previous Polyelectrolyte Interaction and Polysalt Property Studies

Precipitation reactions between oppositely-charged polyelectrolytes were studied as early as 1896 when Kossel (26) precipitated egg albumin with protamine. Since that time interactions between naturally occurring polyelectrolytes, particularly the proteins, have been studied to try to gain information about their functions in biological systems. Synthetic polyelectrolytes have also been investigated in connection with these studies in hopes that the information obtained from examining the behaviors of compounds with known and controllable structures could be used to gain insight into the nature of the interactions occurring between the more complex, natural polyelectrolytes whose structures are difficult to evaluate (8, 23, 24).

Bungenburg de Jong and his associates (1, 27, 28) have made extensive studies of polyelectrolyte ionic interactions, particularly in the system gelatin-gum aribic-water, and have done much to explain the reaction mechanisms. Their work has been one of the principal sources of information for the preceding discussion of polyelectrolyte interaction behavior and will not be repeated here.

A study of the precipitation of pectic acid by polyethylene imine, together with an excellent review of much of the previous literature has been given by Deuel, et al (8). They found that precipitation occurred only in a narrow range of relative concentrations of these two weakly ionic polyelectrolytes. At the maximum precipitation point, the polyacid and polybase were quantitatively reacted, and no polyelectrolyte could be found in the supernatant liquid (the liquid was clear and had the viscosity of pure water). Electron microscope studies indicated that the precipitates formed at this optimum reacting ratio had a crosslinked structure. Polyethylene imine was found to have considerably greater affinity for pectic acid than for its monomer, galacturonic acid.

Fuoss and Sadek (16) made turbidity measurements while titrating dilute (2.5×10^{-6}N) polyvinyl-N butylpyridinium bromide (PVBuPyBr) with 0.001 N sodium polyacrylate (NaPA). They found that turbidity increased linearly with the amount of NaPA added to a fixed amount of PVBuPyBr until shortly beyond the equivalence point, then increased very sharply to a maximum, and decreased slowly thereafter. They also investigated the stoichiometry of reactions occurring between 0.018 N PVBuPyBr and approximately 0.005 N sodium polystyrene sulfonate in mixtures containing excess cationic polymer. They found a considerable variation in the weight of precipitate obtained (1.30 - 2.40 mg. of precipitate per cc of sulfonate polymer solution), and the percentage of the total bromide ion trapped in the precipitate (5-10%), depending on the relative amounts and order of addition of the polyelectrolyte solutions. Although the results of the present investigation indicate more nearly equivalent stoichiometry between a pair of polyelectrolytes with similar structures (at lower concentrations), we too have found considerable deviations from complete stoichiometry at polyelectrolyte concentrations above about 0.005 N, which we have attributed to the beginnings of interfacial film forming tendencies.

In a previous study by the author (29), a series of polysalts of different compositions were precipitated in membrane form and some of their physical and chemical properties were investigated. The membranes were formed as follows. Aqueous solutions were made up to contain approximately equiionic amounts of two oppositely charged polyelectrolytes with sufficient magnesium sulfate added to prevent polysalt precipitation. These mixed-polyelectrolyte solutions were then contacted with pure water to allow the charge-shielding $MgSO_4$ to diffuse out of the mixture so that the polymers could interact and precipitate into continuous films.

Eleven different films were made by utilizing all but one of the possible polyanion-polycation pairs from the list below (no film was made from the CMC-PEI pair).

Polycationics:

1. Polydimethylxylylene ammonium chloride (PDMXAC)
2. "Separan CR 70" (quaternary ammonium polymer)

3. Polyethylene imine (PEI)
4. Poly (N-ethoxymethacrylyl, N, N dihydroxyethyl methyl ammonium) dihydrogen phosphate (PEMDAP)

Polyanionics:

1. Carboxymethyl cellulose (CMC)
2. Polyvinylmethyl ether-maleic anhydride copolymer (PVM/ MA)
3. Polyvinylpyrrolidone (PVP)

Without exception the films were brittle but quite strong when dry, but rubbery or cheezy and very weak when wet. Water absorption varied from 0.9 to 2.8 grams per gram of dry solid, depending on the film tested. X-ray studies showed the films to be amorphous.

Practical uses of polysalts or polyelectrolyte interactions have been rather limited until very recently. Because of their reversible nature, polyelectrolyte interactions have been used in the separation (by fractional precipitation) and purification of proteins (7, 8), and for precipitation and deactivation of viruses (2).

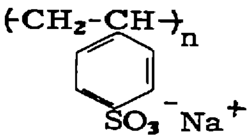
B. K. Green (17) of the National Cash Register Co. has recently patented a process utilizing polyelectrolyte interactions in the production of oil-containing microscopic capsules which have oil impermeable, shell-like gelatin coatings. In the process gum arabic (polyanion) is added to gelatin (polycation when kept below its isoelectric pH) to form a "complex coacervate", a polysalt which is so hydrous that it separates from the main solution as a second liquid phase. The coacervate is finely dispersed throughout the main liquid phase by rapid agitation. Next, an oil is added which becomes emulsified or vacuolized within the coacervate droplets, and is permanently entrapped when the mixture is cooled to gel the gelatin. In subsequent treatment, the pH of the gelled material is adjusted so that the (amphoteric) gelatin becomes polyanionic, and the gum arabic, which does not enter into the gel structure (1), probably diffuses out of the gel and does not appear in the final product.

The first commercially useful direct utilization of polysalts has been the recently developed "snake-cage" ion retarding resins made by the Dow Chemical Company (21). A typical resin of this type consists of a standard ion exchange resin into which a polyelectrolyte of opposite charge has been introduced. This is accomplished by soaking the resin in a solution containing the monomer of the polyelectrolyte to be introduced, and then polymerizing the ionic monomer in situ inside the resin phase. The original resins are crosslinked and the added polyelectrolytes are linear, but are so entwined with the crosslinked molecules that they cannot escape by diffusing out of the structure--a snake in a cage. Hence the name "snake-cage" resins. The double polyion sites weakly and reversibly absorb microionic salts (as counter-ions), thus retarding their passage through a column filled with the resin. The ability of the resins to absorb microionic salts was found to be quite sensitive to their polyanion/polycation ratios, the neutral resins being much better salt absorbers than those containing even small excesses of polyanions or polycations.

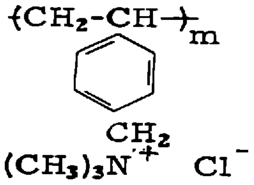
E. Present Investigation

The present investigation was undertaken to determine the ionic interaction behavior under various conditions of strongly ionic oppositely-charged polyelectrolytes with similar structures and equal ionic spacings, and to measure some to the properties of their interaction products (polysalts). Particular attention was given to relating interaction behaviors to the individual polymer concentrations and probable molecular configurations at the time of interacting, to ionic bond rearrangements (if any) after initial interaction, and to investigation of those physical and chemical properties which are peculiar to polymeric electrolytes, and which might lead to practical applications for the polysalts.

The strong electrolyte character and equal ionic spacings were desired in order that the interpolymer ionic associations be intense enough to yield stable, fairly strong polysalts whose properties could be studied in the presence of water with substantial concentrations of added microionic salts and organic solvents. The two polyelectrolytes used throughout the study were (1) poly(sodium styrene sulfonate), NaSS, an anionic polyelectrolyte with a molecular weight of about 760,000, having the mer unit structure



where n = approximately 3,200, and (2) poly(vinylbenzyltrimethyl ammonium chloride), VBTAC, a cationic polyelectrolyte with a molecular weight of approximately 300,000, having the mer unit structure



where m = approximately 1200. The polymers were supplied as dry "purified" powders by the Dow Chemical Company of Midland, Michigan. Both polyelectrolytes were polymerized from the ionic monomers, so the structures were presumably quite uniform.

Preliminary investigations of the viscometric behaviors of the individual polyelectrolytes in dilute aqueous solutions were made by Smith (34). He obtained the plots of reduced specific viscosity (η_{sp}/c_p) vs. polyelectrolyte concentration shown in Figures 4 and 5, using a modified Ostwald capillary viscometer at 25.0°C.

The polyelectrolyte interaction and polysalt property studies of the present investigation were carried out in three stages:

1.) Investigation of the stoichiometry and extent of the ionic reactions occurring between VBTAC and NaSS in dilute (<0.2g/dl) aqueous solutions at varying relative amounts of the two polyelectrolytes and in the presence of varying concentrations of added salt (NaBr). In this concentration region the polysalts took the form of white, hydrous, particulate precipitates which were similar in appearance to the silver halide precipitates formed by reaction between dilute solutions of silver nitrate and alkali halides. The precipitates flocculated at or near the VBTAC-NaSS ionic equivalence points of the mixtures.

2.) Measurement of some of the physical properties (after isolation) of the extremely thin, transparent polysalt films which formed rapidly at the interfaces between more concentrated (>0.6 g/dl) aqueous solutions of VBTAC and NaSS and completely blocked further interpolymer reactions.

3.) Measurement of some of the physical and chemical properties of thicker, transparent polysalt films formed by precipitation from a ternary solvent (NaBr-acetone-water) in which substantial amounts (5-10 g/dl) of both polymers could be dissolved without coreacting.

III. EXPERIMENTAL PROCEDURES

A. Purification of the Polyelectrolytes

400-600 ml of a 5% aqueous solution of VBTAC or NaSS was placed in a large beaker, and a quantity of demineralizing resin (a mixture of anion exchange resin in hydroxide form and cation exchange resin in hydrogen form) was added. This type of resin, while completely removing microionic salts from solution, does not remove ionic polymers since the latter are too bulky to enter the resin phase. The polymer solution-resin mixture was stirred to keep the resin suspended, and after sufficient time (8-12 hours) had been allowed to assure good solution-resin contact, the mixture was filtered through a coarse fritted glass funnel to remove the resin plus any large impurity particles which might be present. Since the demineralizing resin partially ion-exchanged VBTAC into the hydroxide form, and NaSS into the hydrogen form, it was necessary to treat the purified polyelectrolytes further to put them into the desired ionic forms. This was accomplished by passing the VBTAC solutions through a column of Dowex I or Dowex II anion exchange resin in the chloride form, and the NaSS solutions through a column of Dowex 50 in the sodium form. The solutions were then evaporated to dryness, and the dry polymers coarsely ground with a mortar and pestle and set aside for further use.

Some earlier polymer samples were purified by countercurrent dialysis against distilled water, using regenerated cellulose dialysis tubing. The high degree of polymer dilution caused by osmotic absorption of water, coupled with the slow rates of polymer purification (ca. 1 g/ day) made this process undesirable. This is especially true in the light of the strong suspicion that the VBTAC became degraded by bacterial attack upon long standing in solution. The dialyzed polymer samples were used for the viscosity measurements (on the individual polyelectrolytes) made by Smith.

using a modified Ostwald capillary viscometer at 25.0°C.

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2.) Measurement of some of the physical properties (after isolation) of the extremely thin, transparent polysalt films which formed rapidly at the interfaces between more concentrated (>0.6 g/dl) aqueous solutions of VBTAC and NaSS and completely blocked further interpolymer reactions.

3.) Measurement of some of the physical and chemical properties of thicker, transparent polysalt films formed by precipitation from a ternary solvent (NaBr-acetone-water) in which substantial amounts (5-10 g/dl) of both polymers could be dissolved without coreacting.

B. Determination of Polyelectrolyte Equivalent Weights

The ionic equivalent weights of the polyelectrolytes were determined by (a) potentiometric titration of the chloride counter ions of VBTAC against silver nitrate, and (b) standard base titrations of NaSS which had been ion exchanged into the hydrogen form.

a.) Dilute solutions (< 0.01 M) of VBTAC were titrated by silver nitrate solutions standardized against 0.00300 M NaCl. The endpoints were determined potentiometrically using a Beckman pH meter with hydrogen and silver wire electrodes. The solutions were buffered to pH 4 to assure constant hydrogen electrode potential during the titrations. The silver nitrate solution was delivered from a 5 ml microburette calibrated to 0.01 ml, while the VBTAC solution was delivered from the same pipette (4 or 5 ml) as the NaCl used for the silver nitrate standardization.

b.) Samples of NaSS were converted to the hydrogen (HSS) form in earlier measurements (Batch A) by passing purified polymer over a bed of Dowex 50W (X8) cation exchange resin in the hydrogen form, and in a later instance (Batch B) by repeatedly stirring a solution of the polymer with small amounts of fresh demineralizing resin until no sodium ion could be detected by visual flame test on the solution. The hydrogen form of the polymer was titrated by sodium hydroxide (standardized against potassium acid phthalate) to a phenolphthalein or methyl orange endpoint. The initial measurements were made on HSS which had been dried, weighed, and redissolved. Later measurements were made on HSS solutions which had not been evaporated to dryness. These samples were evaporated to dryness after being titrated, and were then weighed to determine the quantities of polymer present.

C. VBTAC-NaSS Dilute Solution Interaction Stoichiometry

The stoichiometry and extent of ionic (precipitation) reactions occurring between NaSS and VBTAC in dilute (< 0.2 g/dl) aqueous solutions were studied viscometrically and titrimetrically at varying polymer ratios, both in the presence and absence of added sodium bromide. The studies were carried out in three stages: (1) viscometric studies on polyelectrolyte mixtures in the absence of added salt; (2) volumetric analysis of chloride ion released upon interpolymer reaction in these mixtures; and (3) viscometric investigation of reaction stoichiometry in the presence of 0.01, 0.1, and 1.0 molar added sodium bromide.

1.) Sodium bromide-free mixtures were made up by placing a measured amount of a 2.000 g/dl aqueous solution of one of the polyelectrolytes in a 100 ml volumetric flask fitted with a magnetic stirrer, diluting to a concentration of 0.1-0.15 g/dl, and adding a 0.1-0.2 g/dl solution of the oppositely-charged polyelectrolyte dropwise from a 50 ml burette until the ionic equivalence point was reached. The mixture was stirred at this point for 30 seconds or more to insure thorough mixing and precipitate flocculation, and then the desired excess (if any) of one of the polyelectrolytes was added, and the mixture diluted to 100.0 ml. The total amount of more concentrated polyelectrolyte in the mixtures varied from 0.342 - 0.427 meq (0.08-0.1 g/dl). An aliquot of each freshly-made mixture was centrifuged to settle the precipitate, and the viscosity of the clear supernatant liquid measured at 25.0 ± 0.02°C in a Cannon-Fenske type modified Ostwald capillary viscometer (size No. 100, with a flow time of 70.1 or 75.7 seconds for water at 25.0°C with a 10 ml sample in the viscometer). Next, a control sample was made up to contain the ionic excess of the more concentrated polyelectrolyte in the mixture, plus the amount of NaCl which would have been released from the precipitate into the supernatant liquid upon complete ionic reaction between the polymers.

The viscosity of this solution was measured under the same conditions as described above for the corresponding mixture supernatant liquid. These measurements were repeated for mixtures containing VBTAC: NaSS in the approximate ionic ratios 5:1, 5:2, 5:3, 1:1, 3:5, 2:5, and 1:5. Some of the measurements were repeated for mixtures deliberately kept from being passed through their equivalence (flocculation) points. The supernatant liquids of these mixtures were all somewhat turbid in appearance, since the precipitates could not be completely settled by centrifugation. For these mixtures, the control samples were mixtures of the same composition which had been passed through their equivalence points.

2.) The cloride ion concentrations in the supernatants of mixtures containing VBTAC:NaSS in the ionic ratios 1:1, 3:5, 2:5, and 1:5 were measured by titrating aliquots of the liquids against 0.003-0.005 M $AgNO_3$. The endpoints were determined potentiometrically using the same equipment and procedure (described in Section III-B) as was used for equivalent weight determinations. The measured supernatant chloride concentrations were compared directly to similar titrations made on the VBTAC stock solutions used for making up the mixtures, or to the amount of chloride corresponding to the measured equivalent weight of the VBTAC batch.

3.) Viscometric measurements were also made on the supernatants of mixtures containing 0.01, 0.1, and 1.0 M added NaBr. The 0.1 M NaBr mixtures were made up by placing a measured amount of a 0.2 g/dl solution of one of the polyelectrolytes, 0.1 M in NaBr, in a 100 ml volumetric flask, and adding a 0.2 g/dl solution of the oppositely-charged polyelectrolyte, also 0.1 M in NaBr, dropwise from a 50 ml burette. All of the mixtures were passed through their flocculation points. The compositions at the observed flocculation points, all of which occurred before the mixture equivalence points had been reached, were recorded. After the desired amounts of the polymer solutions had been mixed, the mixtures were diluted to 100.0 ml with 0.1 M aqueous NaBr. After centrifugation, the viscosities of the supernatant liquids of these mixtures were measured at 25.0 ± 0.02°C in the same manner as described previously for the NaBr-free mixtures. Since at these salt concentrations the reduced specific viscosities (η_{sp}/c_p) of both polyelectrolytes are independent of polymer concentration, and essentially unchanged by the additional amounts of salt released into solution by interpolymer reaction, it was not necessary to make up direct-comparison control samples. Instead, for each polyelectrolyte a series of mixtures containing from 0.0 to 0.1 g/dl of polymer were made up, and their viscosities measured to determine the reduced specific viscosities.

The mixtures containing 0.01 M NaBr and 1.0 M NaBr, made prior to the 0.1 M NaBr measurements, were prepared as follows: For each mixture, 2% aqueous solutions containing the desired (final) amounts of each polyelectrolyte were diluted separately to approximately equal concentrations, and with a combined volume of 80 ml. The total amount of salt desired in the final mixture was divided approximately proportionately between the two solutions. The solutions were then poured slowly together, with no attempt being made to pass the mixture through, or to keep it from being passed through, its flocculation point. After centrifugation, the viscosities of aliquots of the supernatant liquids (some of which were turbid) were measured at 25.0 ± 0.05°C in one of the same viscometers (70.1 sec flow time for water) described previously for the salt-free mixtures. In addition to the mixtures, the viscosities of 0.1 g/dl solutions of both polymers were measured at the prevailing salt concentrations to determine the reduced specific viscosities of the polymers.

D. NaSS-VBTAC Dilute Solution Mutual Titrations

Mutual titrations between dilute (≤ 0.1 g/dl) solutions of the polyelectrolytes were made with endpoints indicated by a mixed dye (dichlorofluorescein-methylene blue chloride) indicator which turned from fluorescent green to purple in the presence of a slight excess of free VBTAC in solution. In most cases, titrations were made in both directions (i.e., NaSS titrated by VBTAC and VBTAC titrated by NaSS) and the endpoint differences noted. The effects of small amounts of added $FeCl_3$, $CaCl_2$, and NaBr on the endpoints were also determined for titrations made in both directions. For the titrations, the polymer solutions were delivered from 10 ml burettes calibrated to 0.05 ml. One to three drops of indicator solution containing approximately 0.1% by weight of each dye was used for each titration.

E. Interfacial Films

The thin interfacial films which formed spontaneously at the interfaces between sufficiently concentrated (>0.6 g/dl) aqueous solutions of VBTAC and NaSS were formed, isolated from their polyelectrolyte solution environments, and treated in the following ways.

1. Unsupported films formed across the holes in 3/4" I.D. Plexiglas rings

a. Formation and Isolation

A plexiglas annulus of dimensions 3/4" I.D., 1" O.D., and approximately 1/16" thick was dipped into a 3% aqueous solution of NaSS in such a way that a film of the solution formed (in soap bubble fashion) across the hole in the ring. The ring was then turned over and dipped into a 3% aqueous VBTAC solution to form a film of the latter in contact with the NaSS solution film from the first dipping. A coprecipitated complex polyelectrolyte membrane formed almost instantaneously at the interface between the two liquid films. After some of the excess solutions were blotted from the plastic rim, the washer containing the polyelectrolyte film was attached to a micromanipulator and carefully lowered edgewise into a beaker of quiescent distilled water to wash the excess polyelectrolyte solutions from the film surfaces. Since the wash water could not be stirred without rupturing the delicate interfacial membranes, it was necessary to rely on molecular diffusion and natural convection currents in the water to wash the films. These processes were aided by the fact that the polyelectrolyte solutions were denser than the wash solutions, so they tended to slough off the film surfaces and drift to the bottom of the wash vessel. 0.25 to 2.0% of glycerine or dextrose was sometimes added to the wash solutions to plasticize the films during subsequent drying. After the films had been washed for 1/2 to 24 hours, the rings were removed and the films either laminated wet onto solid supporting surfaces or placed to dry in a horizontal position in a dessicator kept at 50% relative humidity by a sulfuric acid-water solution. In most cases the solid supporting surfaces to which the wet films were laminated were convex (e.g., 1/2" diameter glass magnifying lenses). The domed surfaces facilitated application of the films by eliminating the problem of undue film breakage from contact with sharp edges. When more than one film was to be laminated to a single surface, the previously applied films were allowed to dry before each succeeding film was added. The laminations were accomplished by carefully lowering the rings containing the films over the solid surfaces until the films coated the surfaces and were sheared off at the edges.

b. Electron Photomicrographs of Interfacial Films

Samples of several dried interfacial films were laminated to 300 mesh nickel screens and electron photomicrographs made through the courtesy of Professor C. E. Hall of the M.I.T. Biology Department. The samples were chrome shadowed at an elevation of 1/3. The negatives were obtained at a magnification of 6250X.

c. Film Thickness Measurements

The approximate thickness of the unplasticized interfacial films formed between 3% aqueous solutions of the polyelectrolytes was determined by light reflectance measurements made on an 11 film laminate, using the reflectance spectrophotometer of the M.I.T. color measurements laboratory under the direction of Professor A. C. Hardy. The machine gives a continuous recording of per cent light reflected from a sample surface vs. incident monochromatic light wavelength in the range from 400-700 millimicrons. Since preliminary experimentation indicated that the individual films were too thin to give any reflectance reinforcements or cancellations in the range of light wavelengths used, a multiple layered laminate was built up by carefully lowering wet, washed, interfacial films one after another onto a silvered convex glass surface until distinct interference colors were visible in reflected sunlight.

d. Film Surface Ionic Anisotropy

To test for the presence of residual polycations or polyanions on the film surfaces, several films were laminated to glass surfaces and rinsed with either a 1/2% methylene blue chloride solution (cationic) or a 2% anionic kaolin suspension at pH 9. Since each film was initially contacted by VBTAC solution on one side and NaSS solution on the other side, a distinction was made between the sides of the films originally in contact with the oppositely-charged polyelectrolytes, and the film orientation was noted at the time of lamination. Before being rinsed with the mixtures, the films were allowed to dry to assure good film adhesion to the supporting glass lens surfaces.

2. Films Formed within Sheets of Filter Papers or Millipore Filters

To measure the diffusivity of the interfacial films toward simple electrolytes (NaCl) it was necessary to support them quite intimately to prevent breakage. The films were therefore formed within supporting membranes composed of filter paper or millipore filters and treated as follows:

A sheet of filter paper (S & S No. 576) or Millipore filter (Type SM) was clamped vertically in a diffusion cell in such a way as to form a barrier between the two compartments of the cell. A diagram of the cell arrangement used is shown in Figure 6.

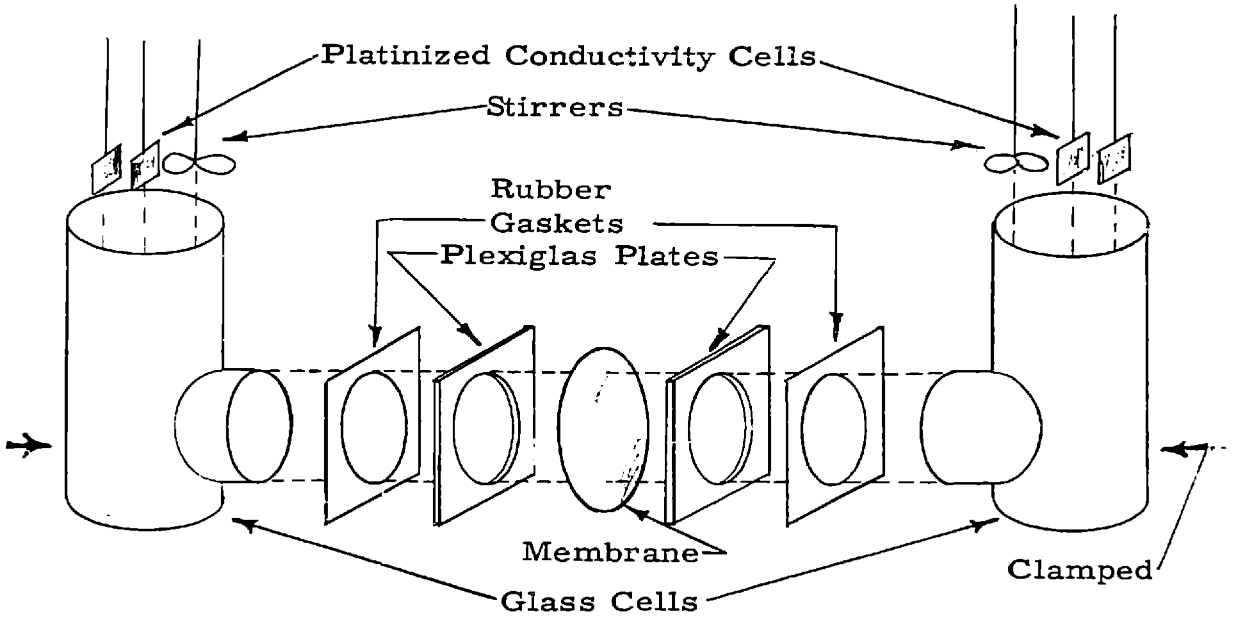

Figure 6. Apparatus Used for Measuring Diffusivity of Polysalt Interfacial Films

The cell was then placed in a constant temperature bath regulated to 25.0 ± 0.02°C. A measured volume of 0.001 M NaCl was placed in one compartment of the cell, and 0.1 M NaCl in the other, with the liquid heights adjusted so that no appreciable hydraulic gradient existed across the membrane. The compartments were fitted with stirrers and conductivity cells previously calibrated for conductivity vs. NaCl concentration. The rate of diffusion of NaCl through the membrane was determined by measuring the rates of change of conductivity of the solutions in the two cell compartments. The conductivity measurements were made at 1000 cps using a conductance bridge with a sensitivity of ± 1 %. After completion of the conductivity measurements, the cell was emptied and washed with distilled water. Opposite sides of the wet membranes were then contacted by 3% aqueous NaSS and VBTAC solutions by pouring the solutions simultaneously into the two cell compartments, with the liquid heights adjusted so that no hydraulic gradient existed across the filter paper or millipore filter. After 8-24 hours time had been allowed for the polyelectrolyte solutions to diffuse into the supporting membranes and form imbedded interfacial films, the polymer solutions were poured out and the membranes washed thoroughly (in situ) with water to remove the excess polyelectrolyte solutions. The diffusion rate of NaCl (0.1 M NaCl diffusing into 0.001 M NaCl) through the membranes was then measured in the same manner as described above for the untreated membranes.

In addition to the NaCl diffusivity measurements, a qualitative measurement of the diffusional resistance of the interfacial films toward a larger molecular species, methylene blue chloride, was made by noting the times required for the first visible streamer of the blue solution to appear in pure water placed opposite a 1/2% solution of the intensely colored dye, both in the presence and absence of an impregnated interfacial film. The solutions were intentionally not stirred in these tests, in order to make the initial appearance of the dye more readily discernable.

F. Polysalt Solubilities in NaBr-Acetone-Water Mixtures

To determine the range of sodium bromide, acetone, and water concentrations in which both polyelectrolytes could be completely dissolved at room temperature without coreacting, the solution compositions at which polymer precipitation began to occur were measured as follows: Approximately 0.5 g/dl of each polyelectrolyte was dissolved in a NaBr-acetone-water mixture of known composition in the solubility region. Acetone was added until the development of turbidity indicated the onset of polymer precipitation. The mixture was weighed, a measured amount of water added to reclarify the solution, and acetone again added until turbidity redeveloped. This alternate acetone-water addition was continued, working stepwise around the phase diagram, until a point was reached where the addition of water no longer reclarified a mixture made turbid by acetone (minimum NaBr concentration). Additions were then continued using water as the precipitating agent and NaBr as the dissolving component, until a point was reached at which NaBr was no longer able to redissolve a precipitate formed by the addition of water (minimum acetone concentration). Addition was continued using acetone as the solvating agent and NaBr as the precipitant until the minimum water concentration was reached. New mixtures were made up whenever the polymer concentration fell to about 0.2 g/dl. Weighings were made on a Mettler automatic balance accurate to ± 0.1 g. Measurements were repeated at selected points on the precipitation curve to eliminate the possibility that systematic errors in the additions were causing appreciable errors in the position of the curve. Next, a similar series of measurements were made with NaSS as the only polyelectrolyte to determine which portions of the precipitation curve were due to salt-out of NaSS rather than polyelectrolyte interaction. Other series of measurements were made on mixtures containing VBTAC/NaSS in the ionic ratios 2/1 and 1/2 to determine whether there was any effect of polyelectrolyte ratio on the position of the precipitation points. Finally, some measurements were made on mixtures containing more than 0.5 g/dl of each polyelectrolyte. In this polymer concentration range the polymers reacted to form gels or very viscous solutions before any turbidity could be observed in the mixtures.

G. Formation of Polysalts by Precipitation from NaBr-Acetone-Water Solutions

The following procedures were used to obtain fairly large samples (2-5 g) of salt-free polysalts in the form of amber, transparent solids.

1.) Solutions were made up at room temperature containing 10-15% by weight of polymer dissolved in a solvent comprised of 60% water, 20% NaBr, and 20% acetone. Three different polyelectrolyte ratios were used: VBTAC/ NaSS in the ionic ratios 2/ 1, 1/ 1, and 1/ 2.

2.) After the polymers were completely dissolved, portions of the solutions were poured into paraffin wax-lined petri dishes and allowed to gel at room temperature by evaporation of acetone.

3.) The gelled mixtures were placed in an oven at 50-60°C to evaporate acetone and water, and allowed to remain until, or shortly before, a slight opacity developed at the periphery of the gels due to salt-out of NaSS. The gels were then washed briefly with water to extract some of the NaBr, and replaced in the oven to again allow water evaporation to the point of insipient NaSS precipitation. This alternate washing and drying procedure was continued until the NaBr content was low enough so that the samples could be completely dried without becoming opaque, * after which the polysalts were washed with demineralized water until no more salt could be extracted from them, cut into samples of the desired size, and dried at 50% relative humidity over a sulfuric acid-water mixture to yield amber, transparent solids.

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* The purpose of this rather elaborate wash-dry procedure was to remove as much salt, water, and acetone as possible from the polysalts while keeping the overall solvent composition near the region of polysalt solubility. If too much salt was extracted from the dilute gels by prolonged contact with water, internal porosity developed due to contraction of the polymer volume, and the final polysalts were microporous sponges rather than continuous solids.

H. Oriented Polysalt Fibers and Films

During the alternate washing and drying process used in the formation of the polysalts, the samples were rubbery, elastic solids until the polymer content became about 40% of the total sample weights. Samples of these gels were oriented by unidirectional stretching 2-5X, hardened by water washing, and dried. The dry, transparent solids were examined for birefringence by crossed polarizing lenses, and X-ray photographs were taken to determine if they were crystalline.

It was also found that monofilaments of the polysalts could be drawn by dipping a spatula or other solid object into a solvated mixture of the polymers, and withdrawing it at a uniform rate. The filament of liquid drawn out by the spatula gelled rapidly in air by evaporation of acetone, thus preserving its uniform diameter. After being washed briefly with water, the filaments were dried, rewetted, and oriented by stretching about 2X. These filaments were also examined for birefringence and crystallinity. The tensile strength of an oriented filament was measured by suspending it from a metal rod, and attaching a beaker to its free end. The beaker was slowly filled with water until the filament broke, after which the beaker of water was weighed, and the diameter of the filament at the break point measured by microscopic examination.

I. Electrical Properties of Polysalts

Dielectric constants, loss factors, and volume resistivities were measured as a function of applied a-c frequency for polysalt samples containing NaSS/ VBTAC in the ionic ratios 2/ 1, 1/ 1, and 1/ 2 after the samples had been equilibrated at both 50% and 0% relative humidity and room temperature. The measurements were made on conductivity and capacitance bridges at the M.I.T. Laboratory for Insulation Research. The samples varied from 0.085 to 0.17 inches in thickness and from 0.80 to 1.0 inches in diameter, and were clamped between 1.0 inch diameter brass electrodes for the measurements. After being mounted between the electrodes and equilibrated at 50% relative humidity (over a sulfuric acid-water mixture) or at 0.0% humidity (over phosphorus pentoxide), the samples were sealed from external humidity changes with electrical tape. Electrical measurements were made in the frequency range of 100 to 10^7 cps at applied potentials of less than 1.0 volt.

J. Swelling of Polysalts in NaBr-Acetone-Water Solutions

Swelling measurements were made at room temperature to determine the equilibrium amounts of various NaBr-acetone-water solutions which would be absorbed by polysalts composed of VBTAC/ NaSS in the ionic ratios 2/ 1, 1/ 1, and 1/ 2. The measurements were made by immersing 0.2-0.8 gram samples of the polysalts in 40-50 ml volumes of various NaBr-acetone-water solutions, and allowing them to swell until the rate of weight increase was not over 0.5% in a 24 hour period. The samples were weighed on an analytical balance to ± 1 milligram in a closed vessel after their surfaces were blotted briefly with tissue paper to remove excess superficial liquid. Since the polysalts tended to shatter when exposed to room air after being dried over P_2O_5, most of the samples were dried only to 50% relative humidity before being immersed in the liquids. One sample from each batch was dessicated over P_2O_5 to determine the residual moisture content of samples dried to 50% humidity.

K. Swelling Hysteresis of a Quaternary-Rich Polysalt in Water and Water-Acetone Solutions

Swelling measurements were made on a polysalt sample composed of VBTAC/ NaSS in the ionic ratio 2/ 1 to determine whether the polysalt would return to its normal water swellability after being equilibrated in a 20% aqueous acetate solution, and dried at 50% humidity. The sample, originally dried over P_2O_5, was equilibrated with water, then 20% acetone in water, then again in water (without intermediate drying), and then dried at 50% relative humidity over a sulfuric acid-water solution. This cycle was repeated twice, and then the sample was redried over P_2O_5. After each equilibration, the sample was blotted with tissue paper to remove superficial liquid, and weighed in a closed vessel to ± 1/10 milligram.

L. Sodium Bromide Absorption by Polysalts Equilibrated with Sodium Bromide-Water-Acetone Solutions

Some of the neutral and quaternary-rich polysalts equilibrated with NaBr-acetone-water solutions were dried at 50% humidity without being washed, and reweighed to determine the concentrations of NaBr in the absorbed solutions. The difference in sample weights at 50% humidity before and after equilibration with the salt solutions, after being corrected for the moisture content of pure NaBr at 50% humidity, was taken to be the amount of NaBr present in the samples.

M. Potassium/ Sodium Ion Sorption Selectivity of Neutral Polysalt

The K^+/ Na^+ cation absorption selectivity of a polysalt containing equal amounts of VBTAC and NaSS was measured in the following manner: An 0.964 gram sample of the polysalt was equilibrated with a solution 0.1 molar with respect to both KCl and NaCl. The absorbed ions were then displaced by 0.1 M magnesium bromide solution and their concentrations measured with a Beckman Model B flame photometer calibrated at varying sodium and potassium ion concentrations in the presence of 0.1 M magnesium bromide.

N. Minimum NaSS and VBTAC Concentrations for Gelation of Shielded Mixtures

The following measurements were made in attempts to determine the limiting ratios of VBTAC/ NaSS and minimum concentrations of each polyelectrolyte at which gelation of shielded solutions could be induced at room temperature: Separate 5% (by weight) solutions of VBTAC and NaSS dissolved in a solvent composed of 20% acetone, 20% NaBr, and 60% water were mixed together in varying ratios, and gelation induced by dilution with water, or evaporation of acetone. Some of the mixtures were diluted (at constant VBTAC:NaSS) with additional solvent before gelation was induced, to distinguish between limiting polymer ratios and limiting polymer concentrations. Aliquots of water contacted with some of the gels for brief periods of time (20-30 minutes) were tested for the presence of free VBTAC and NaSS by adding dilute, salt-free solutions of the polyelectrolytes and observing whether or not polysalt precipitation occurred.

IV. RESULTS

Table I: Summary or VBTAC and NaSS equivalent weight determinations

VBTAC Equivalent Weight			NaSS Equivalent Weight		
Batch	Eq. wt.	No. of determinations	Batch	Eq. wt.	No. of determinations
A	234 ± 10	6	A	234 ± 8*	5*
B	264 ± 10	2	B	224 ± 4	5

* These titrations made on polymer kept in the H^+ form. longer than the major portion of Batch A, so may not be completely representative of the batch.

Table II: Supernatant liquid and control sample specific viscosities for NaBr-free dilute solution VBTAC-NaSS mixtures passed through their ionic equivalence points

	Mixture Composition		Control Sample Compositions							
Mix-ture	meq/dl VBTAC*	meq/dl NaSS*	meq/dl ionic excess VBTAC	meq/dl ionic excess NaSS	Max. meq/dl super-natant NaCl	Mix-ture η_{sp}	Control sample (theo.) $\eta_{sp_{theo}}$	$\eta_{sp}/\eta_{sp_{theo}}$	$\eta_{sp}-\eta_{sp_{theo}}$	Mixture ion fraction NaSS
1	0.0855	0.427	--	0.342	0.0855	5.94	5.95	0.998	-0.01	0.832
2	0.171	0.427	--	0.256	0.177	2.68	2.69	0.996	-0.01	0.715
3	0.256	0.427	--	0.171	0.256	1.20	1.22	0.984	-0.02	0.625
4	0.342	0.342	0.00	0.00	0.342	0.001	0.00	--	+0.001	0.500
5	0.384	0.249	0.135	--	0.249	0.198	0.206	0.965	-0.008	0.393
6	0.384	0.166	0.218	--	0.166	0.442	0.456	0.97	-0.014	0.302
7	0.384	0.0829	0.301	--	0.0829	0.943	0.949	0.994	-0.006	0.178

* VBTAC Batch A used for mixtures 1-4, Batch B for 5-7;

NaSS Batch A used for all mixtures.

Figure 7: Supernatant Liquid and Control Sample Specific Viscosities for NaBr-Free Dilute Solution VBTAC-NaSS Mixtures

Solid line: Control sample (stoichiometric and ionically complete VBTAC-NaSS reaction) values

Plotted points (o): Mixture supernatant values

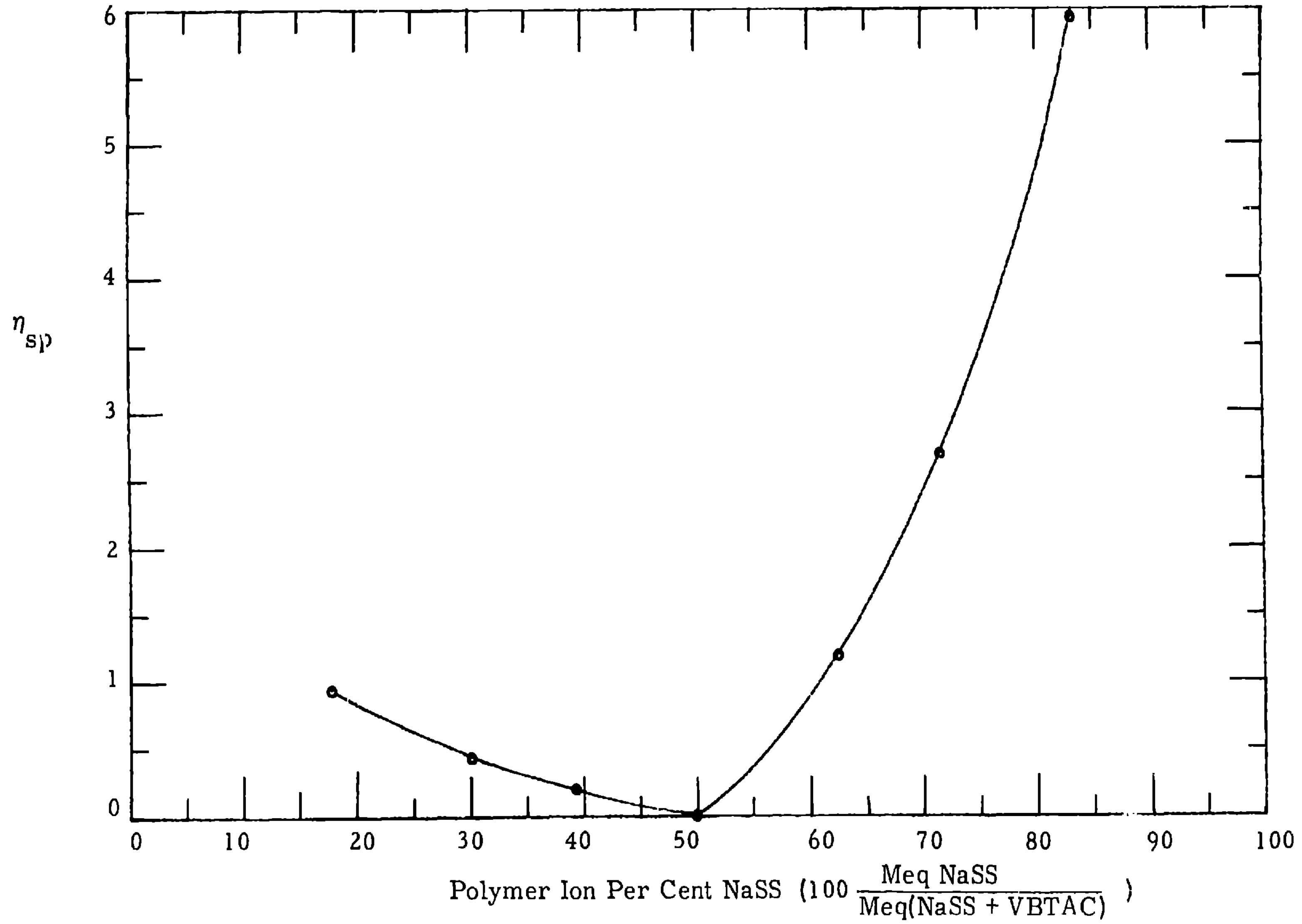


Table III: Chloride concentrations in dilute VBTAC-NaSS mixtures compared to concentrations expected for maximum NaCl release from precipitates

Mixture Number	$\dfrac{\text{Cl}^- \text{ in supernatant/ g VBTAC in mixture}}{\text{Cl}^- \text{/ g VBTAC in stock solution}}$	Apparent equiv. wt. of VBTAC in mixture	$\dfrac{\text{Cl}^- \text{ in supernatant/ g VBTAC in mixture}}{\text{Cl}^- \text{/ g VBTAC (eq. wt. = 234)}}$
8 (1)*	1.03	Not measured	--
9 (2)	1.02	Not measured	--
10 (3)	1.02	237	0.99
3 (3)	stock soln. not measured	234	1.00
4 (4)	stock soln. not measured	242	0.97

* Numbers in parentheses signify mixtures of the same composition in Tables II and IV.

Table IV: Deviations from stoichiometric interaction of VBTAC-NaSS mixtures passed through their ionic equivalence points

Mixt. No.	$\eta_{sp}-\eta_{sp_{theo}}$ (measured)	$\eta_{sp}-\eta_{sp_{theo}}$ for 3% of NaCl retained in precipitate	$1/\frac{\partial \eta_{sp}}{\partial c_p}$ (c_p = meq/dl excess VBTAC or NaSS in solution)	Max. deviation from stoich, meq/dl excess VBTAC or NaSS	% max. deviation from stoich, excess VBTAC or NaSS in soln	% error, total polymer in mixture	$\frac{\text{meq VBTAC}}{\text{meq NaSS}}$ in ppte for max. deviation
1	-0.01	+0.089	0.022	2.2×10^{-3}	0.6	0.4	0.97
2	-0.01	+0.041	0.044	2.3×10^{-3}	0.9	0.4	0.99
3	-0.02	+0.018	0.086	3.3×10^{-3}	1.9	0.5	0.99
5	-0.006	+0.0031	0.69	6.3×10^{-3}	4.7	1.0	1.03
6	-0.014	+0.0068	0.31	6.4×10^{-3}	3.0	1.2	1.04
7	-0.008	+0.014	0.14	3.1×10^{-3}	1.0	0.7	1.04

Table V: Supernatant liquid and control sample specific viscosities for NaBr-free dilute solution VBTAC-NaSS mixtures deliberately kept from being passed through their ionic equivalence points

Mixture	Meq/ dl VBTAC	Meq/ dl NaSS	Meq/ dl ionic excess VBTAC	Meq/ dl ionic excess NaSS	Mixture η_{sp}	Control sample η_{sp}	$\frac{\eta_{sp}}{\eta_{sp_{theo}}}$
11	0.256	0.427	--	0.171	0.979	0.912(1)	1.07
12	0.0427	0.427	--	0.384	9.45	9.00(1)	1.05
13	0.427	0.0427	0.384	--	1.58	1.50(1)	1.05
14	0.427	0.086	0.341	--	1.33	1.01(2)	1.32(2)

(1) Control samples made from mixtures of the same composition passed through their flocculation compositions

(2) Both VBTAC and NaSS concentrations 0.2 g/ dl at time of mixing. Interfacial film formation may have prevented complete interaction. The control sample for this mixture was made in the same manner as those in Table II.

Table VI: Measured and theoretical (stoichiometric) supernatant liquid specific viscosities, flocculation points, and supernatant liquid and precipitate compositions for dilute VBTAC-NaSS mixtures containing 0.1 M NaBr. NaSS Batch 1 and VBTAC Batch 2 used for the mixtures

Mixture	VBTAC Meq/dl	NaSS Meq/dl	Ionic excess VBTAC or NaSS Meq/dl	Polymer ion % NaSS = meqNaSS(100) / meq(NaSS + VBTAC)	Mixture Supernatant η_{sp}		η_{sp} for stoich. Reaction(1)		Measured excess of VBTAC or NaSS, Meq/dl(1)		MeqVBTAC/ Meq NaSS in precipitate		Floc. point MeqVBTAC Meq/NaSS
					Initial	10 days	Initial	10 days	Initial	10 days	Initial	10 days	
0.1-1	0.379	0.0	0.379	0.0	0.101	0.101	0.101	0.101	0.379	0.379	--	--	--
0.1-2	0.379	0.085	0.294	18.4	0.0746	0.0728	0.0788	0.0788	0.278	0.272	1.19	1.26	0.807(2)
0.1-3	0.379	0.171	0.208	31.1	0.0456	0.042	0.056	0.056	0.170	0.158	1.22	1.29	0.817(2)
0.1-4	0.379	0.171	0.208	31.1	0.0415	0.038	0.056	0.056	0.155	0.143	1.31	1.38	1.53(3)
0.1-5	0.379	0.256	0.123	40.3	0.025	0.0146	0.033	0.033	0.095	0.055	1.11	1.27	0.817(2)
0.1-6	0.379	0.427	0.048	53.0	0.0025	0.0026	0.030	0.029	0.004	0.004	0.89	0.89	0.824(2)
0.1-7	0.379	0.427	0.048	53.0	0.046	0.026	0.030	0.029	0.074	0.043	1.07	0.99	1.48(4)
0.1-8	0.227	0.427	0.200	65.3	0.127	0.119	0.125	0.122	0.203	0.194	1.01	0.97	1.49(4)
0.1-9	0.152	0.427	0.275	73.8	0.153	0.146	0.172	0.168	0.244	0.238	0.83	0.80	0.816(5)
0.1-10	0.152	0.427	0.275	73.8	0.177	0.163	0.172	0.168	0.282	0.266	1.05	0.94	1.53(4)
0.1-11	0.0758	0.427	0.351	85.0	0.227	0.218	0.220	0.215	0.362	0.341	1.16	0.88	1.37(4)
0.1-12	0.0	0.427	0.427	100.0	0.271	0.263	0.268	0.261	0.432	0.428	--	--	--
0.1-13	0.141	0.171	0.030	54.8	0.00	0.00	--	--	0.0	0.0	0.83	0.83	0.826(2)
0.1-14	0.304	0.197	0.107	39.4	0.00	0.00	--	--	0.0	0.0	1.54	1.54	1.54(4)

(1) Values calculated assuming η_{sp}/c independent of polymer concentration for both polymers, and equal to the average of values measured for 0.04, 0.06, and 0.1 g/dl solutions of each polymer in 0.1 M NaBr.

(2) VBTAC added to NaSS

(3) NaSS added to an equivalent amount of VBTAC, then excess VBTAC added

(4) NaSS added to VBTAC

(5) VBTAC added to an equivalent amount of NaSS, then excess NaSS added

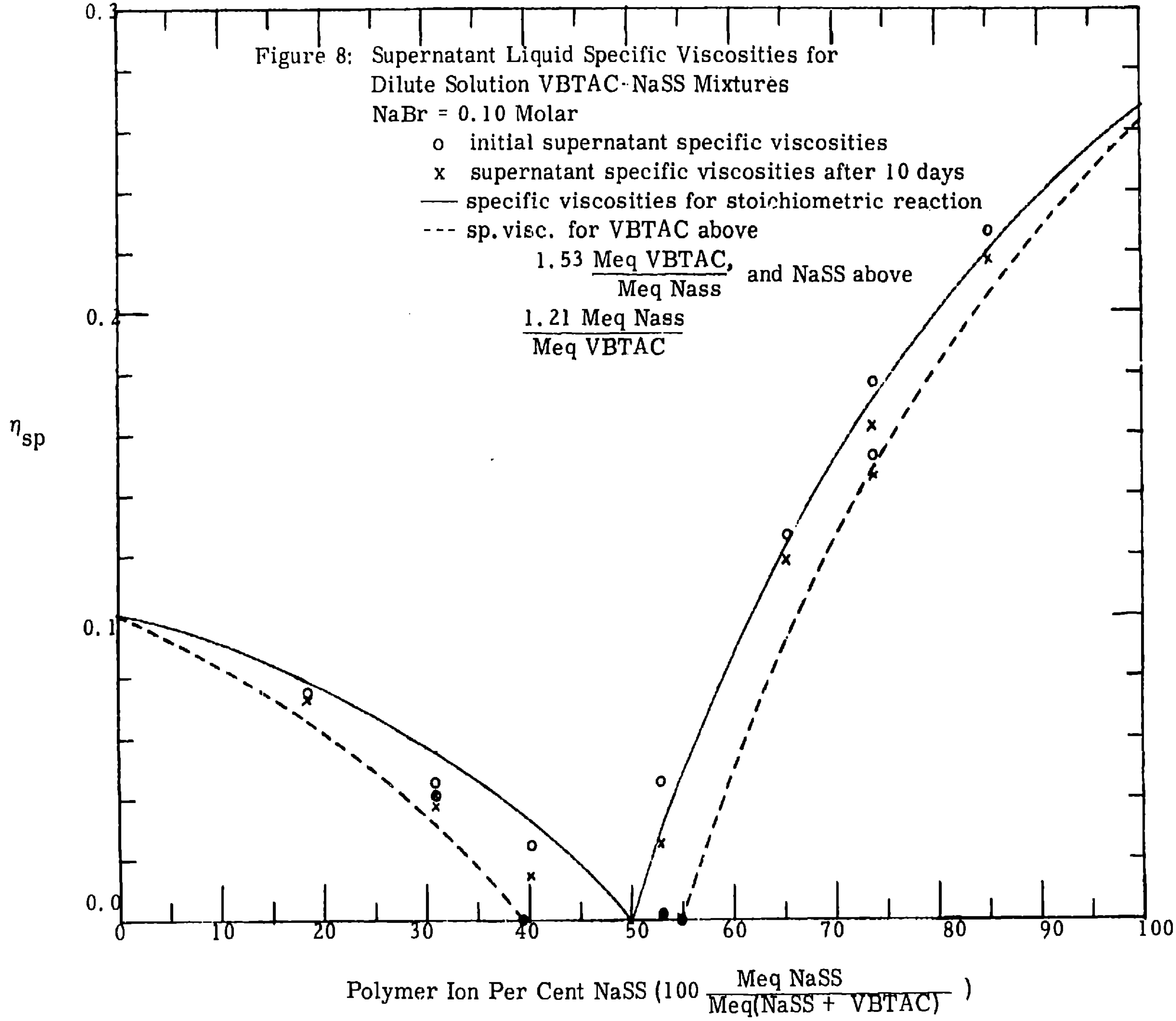


Figure 8: Supernatant Liquid Specific Viscosities for Dilute Solution VBTAC-NaSS Mixtures

NaBr = 0.10 Molar

- o initial supernatant specific viscosities
- x supernatant specific viscosities after 10 days
- —— specific viscosities for stoichiometric reaction
- - - - sp. visc. for VBTAC above $1.53 \frac{\text{Meq VBTAC,}}{\text{Meq Nass}}$ and NaSS above $\frac{1.21 \text{ Meq Nass}}{\text{Meq VBTAC}}$

Table VII: Measured and theoretical (stoichiometric) supernatant liquid specific viscosities of dilute VBTAC-NaSS mixtures containing o. 01 M NaBr. VBTAC Batch A, and NaSS Batch A used for all mixtures.

Mix-ture	VBTAC Meq/ dl	NaSS Meq/ dl	Ionic excess of VBTAC or NaSS Meq/ dl	Ion % NaSS $\frac{\text{MeqNaSS}}{\text{Meq(NaSS+VBTAC)}}$	η_{sp} Measured	η_{sp}* Stoich.	$\frac{\eta_{sp}}{\eta_{sp}\text{stoi.}}$	Excess* polymer in super-natant	$\frac{\text{MeqVBTAC}}{\text{MeqNaSS}}$ in preci-pitate
0. 01-1	0. 427	0. 00	0. 427	0. 0	0. 294	0. 294	--	0. 427	--
0. 01-2	0. 427	0. 0855	0. 342	16. 7	0. 219	0. 222	0. 986	0. 337	1. 06
0. 01-3	0. 427	0. 171	0. 256	28. 6	0. 142	0. 160	0. 888	0. 227	1. 17
0. 01-4	0. 427	0. 256	0. 171	37. 5	0. 073	0. 103	0. 71	0. 121	1. 19
0. 01-5	0. 427	0. 342	0. 086	44. 4	0. 014	0. 050	0. 281	0. 024	1. 18
0. 01-6	0. 427	0. 427	0. 0	50. 0	0. 024	0. 0	--	0. 020(NaSS)	1. 05
0. 01-7	0. 342	0. 427	0. 086	55. 6	0. 127	0. 104	1. 25	0. 107	1. 07
0. 01-8	0. 256	0. 427	0. 171	62. 5	0. 240	0. 241	1. 00	0. 171	1. 00
0. 01-9	0. 171	0. 427	0. 256	71. 4	0. 391	0. 390	0. 99	0. 254	1. 00
0. 01-10	0. 0855	0. 427	0. 342	83. 3	0. 568	0. 560	1. 01	0. 345	1. 00
0. 01-11	0. 00	0. 427	0. 427	100. 0	0. 776	0. 776	1. 00	0. 427	--

* η_{sp} - concentration relationships calculated assuming ratio of η_{sp} at the polymer and salt concentrations in question to η_{sp} of same polymer at 0. 427 Meq/ dl is the same as obtained by Smith (34). (See appendix B, Section A).

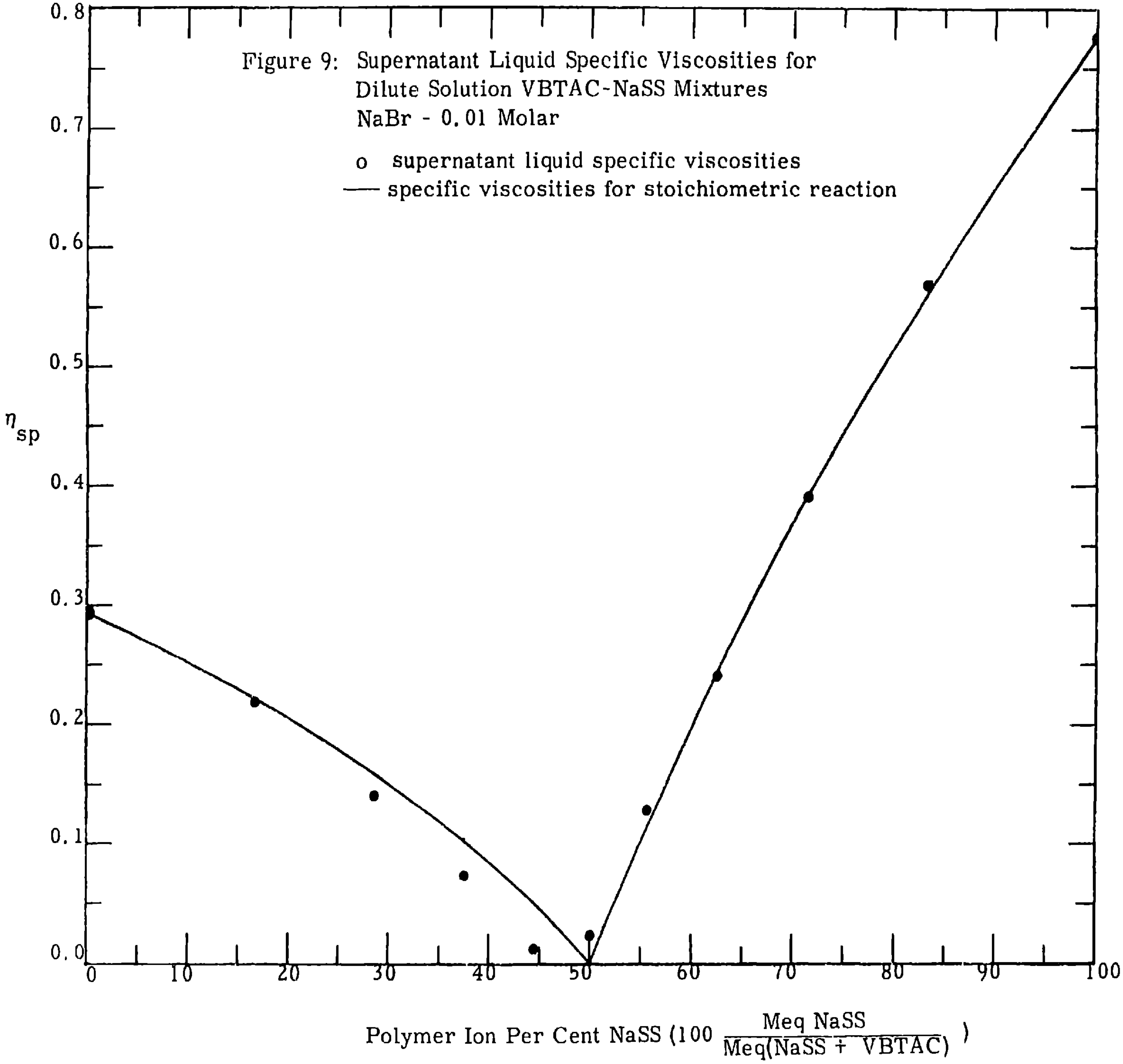


Figure 9: Supernatant Liquid Specific Viscosities for Dilute Solution VBTAC-NaSS Mixtures NaBr - 0.01 Molar

Table VIII: Measured and theoretical (stoichiometric) supernatant liquid specific viscosities for dilute VBTAC-NaSS mixtures containing 1.0 M NaBr. VBTAC Batch A, and NaSS Batch A used for all mixtures.

Mixture	VBTAC Meq/dl	NaSS Meq/dl	Ionic excess of VBTAC or Nass, Meq/dl	Ion% NaSS $\frac{\text{meqNaSS}}{\text{meq(NaSS+VBTAC)}}$	η_{sp} measured	η_{sp}* stoich.	$\frac{\eta_{sp}}{\eta_{sp}\text{ stoi.}}$	Excess* polymer in supernatant Meq/dl	$\frac{\text{MeqVBTAC}}{\text{MeqNaSS}}$ in precipitate
1 - 1	0.427	0.0	0.427	0.0	0.0438	0.0438	1.00	0.427	--
1 - 2	0.427	0.086	0.342	16.7	0.0309	0.035	0.881	0.301	1.42
1 - 3	0.427	0.171	0.256	28.6	0.017	0.026	0.662	0.170	1.50
1 - 4	0.427	0.256	0.171	37.5	0.002	0.0175	0.141	0.0240	1.57
1 - 5	0.427	0.342	0.086	44.4	0.002	0.0088	0.247	0.0214	1.19
1 - 6	0.427	0.427	0.0	50.0	0.00	0.00	--	0.00	1.00
1 - 7	0.342	0.427	0.086	55.6	0.002	0.0159	0.138	0.0119	0.825
1 - 8	0.256	0.427	0.171	62.5	0.035	0.0317	1.11	0.189	1.07
1 - 9	0.171	0.427	0.256	71.4	0.039	0.0475	0.83	0.212	0.795
1 - 10	0.086	0.427	0.342	83.3	0.058	0.063	0.925	0.315	0.77
1 - 11	0.0	0.427	0.427	100.0	0.079	0.079	1.00	0.427	--

* Values calculated assuming η_{sp}/c independent of concentration for both polymers, and equal to the values obtained for 0.427 Meq/dl of each polymer (Mixt. 1-1&1-11)

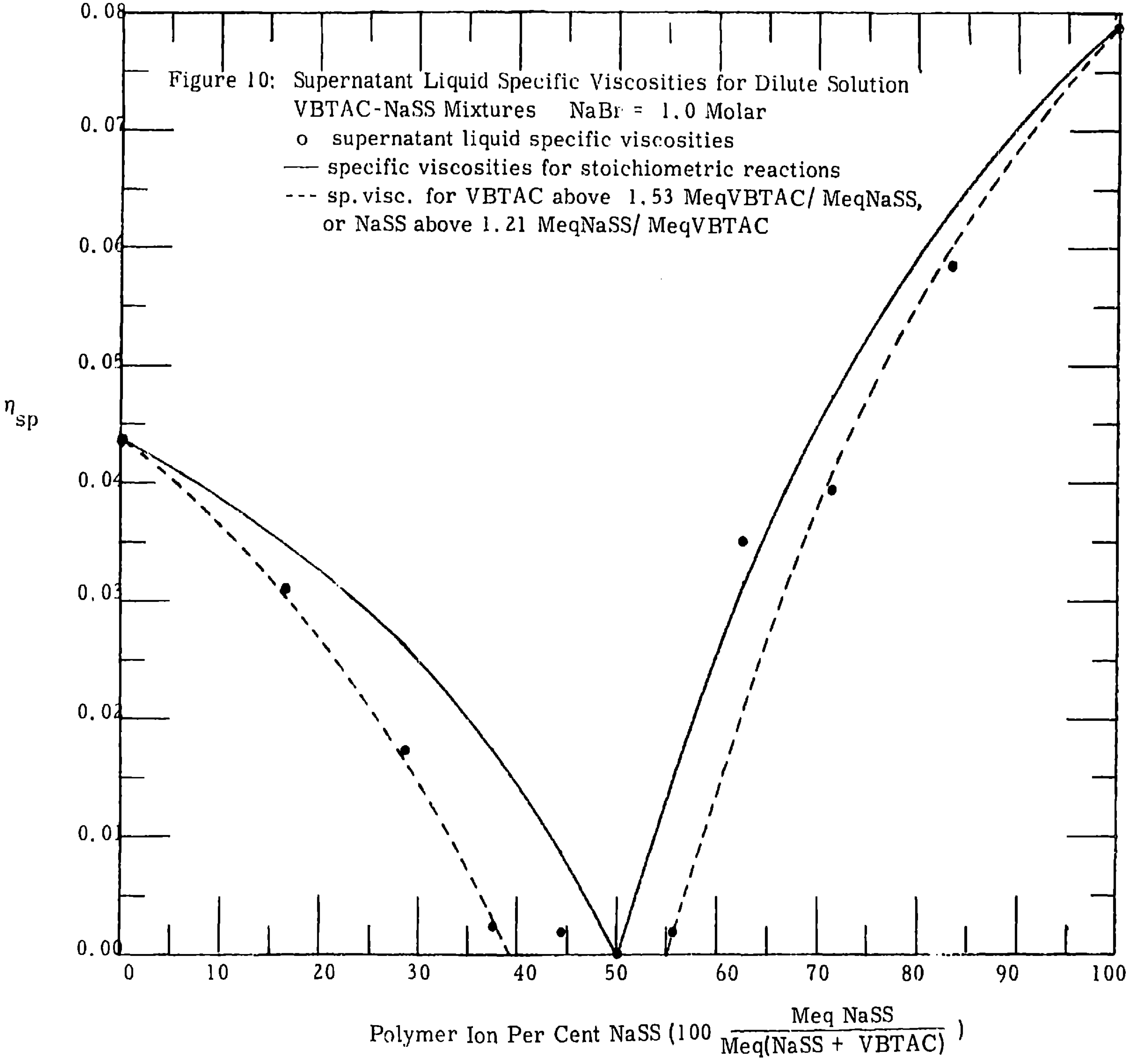


Figure 10: Supernatant Liquid Specific Viscosities for Dilute Solution VBTAC-NaSS Mixtures NaBr = 1.0 Molar

o supernatant liquid specific viscosities
— specific viscosities for stoichiometric reactions
--- sp. visc. for VBTAC above 1.53 MeqVBTAC/ MeqNaSS, or NaSS above 1.21 MeqNaSS/ MeqVBTAC

Table IX: Endpoints of VBTAC-NaSS mutual titrations (No salt added)

VBTAC Batch	NaSS Batch	Average endpoints, g VBTAC/ g NaSS		Apparent Equiv. wt. ratio	Eq. wt. ratio from counter-ion titrations
		VBTAC tit. by NaSS	NaSS tit. by VBTAC		
A	A	--	1.00 (3)[1]	1.00	1.00
A&B(?)	A	1.07 (4)	1.05 (7)	1.06	--
impure, not dried	impure, not dried	1.00 (5)	0.975 (6)	1.01[2]	--
"	"	1.00 (2)[3]	0.90 (3)[3]	--	--
B	A	1.11 (3)	1.10 (3)	1.10	1.13
B	A	1.12 (3)	1.11 (2)	1.11	1.13

[1] Numbers in parentheses are number of titrations made

[2] Corrected for moisture contents of undried VBTAC and NaSS

[3] Measurements made using tap water instead of distilled water as diluent

Table X: Endpoints of VBTAC-NaSS mutual titrations in the presence of added $FeCl_3$ and $CaCl_2$ (NaSS Batch A, VBTAC Batch B)

Meq $FeCl_3$	Meq $CaCl_2$	Meq NaSS	Endpoint g VBTAC/ g NaSS (NaSS+ salt titrated byVBTAC)	Meq VBTAC/ MeqNaSS at end-point	Apparent Eq. NaSS titrated per mole salt
0	0	-	1.09	1.0	-
1.22×10^{-3}	-	6.84×10^{-3}	1.03	0.948	0.884
2.43×10^{-3}	-	7.09×10^{-3}	0.992	0.912	0.758
4.86×10^{-3}	-	6.98×10^{-3}	0.890	0.819	0.758
7.32×10^{-3}	-	7.01×10^{-3}	0.804	0.739	0.742
9.72×10^{-3}	-	7.59×10^{-3}	0.731	0.672	0.765
0	0	-	1.12	1.0	-
-	8×10^{-3}	5.13×10^{-3}	0.984	0.877	0.158
-	12×10^{-3}	5.13×10^{-3}	0.94	0.839	0.137
-	16×10^{-3}	5.13×10^{-3}	0.866	0.774	0.145

Figure 11: Effects of Calcium Chloride and Ferric Chloride on VBTAC-NaSS Mutual Titration Endpoints

-x- NaSS + $CaCl_2$ titrated by VBTAC
-o- NaSS + $FeCl_3$ titrated by VBTAC
--- VBTAC + $FeCl_3$ or $CaCl_2$ titrated by NaSS

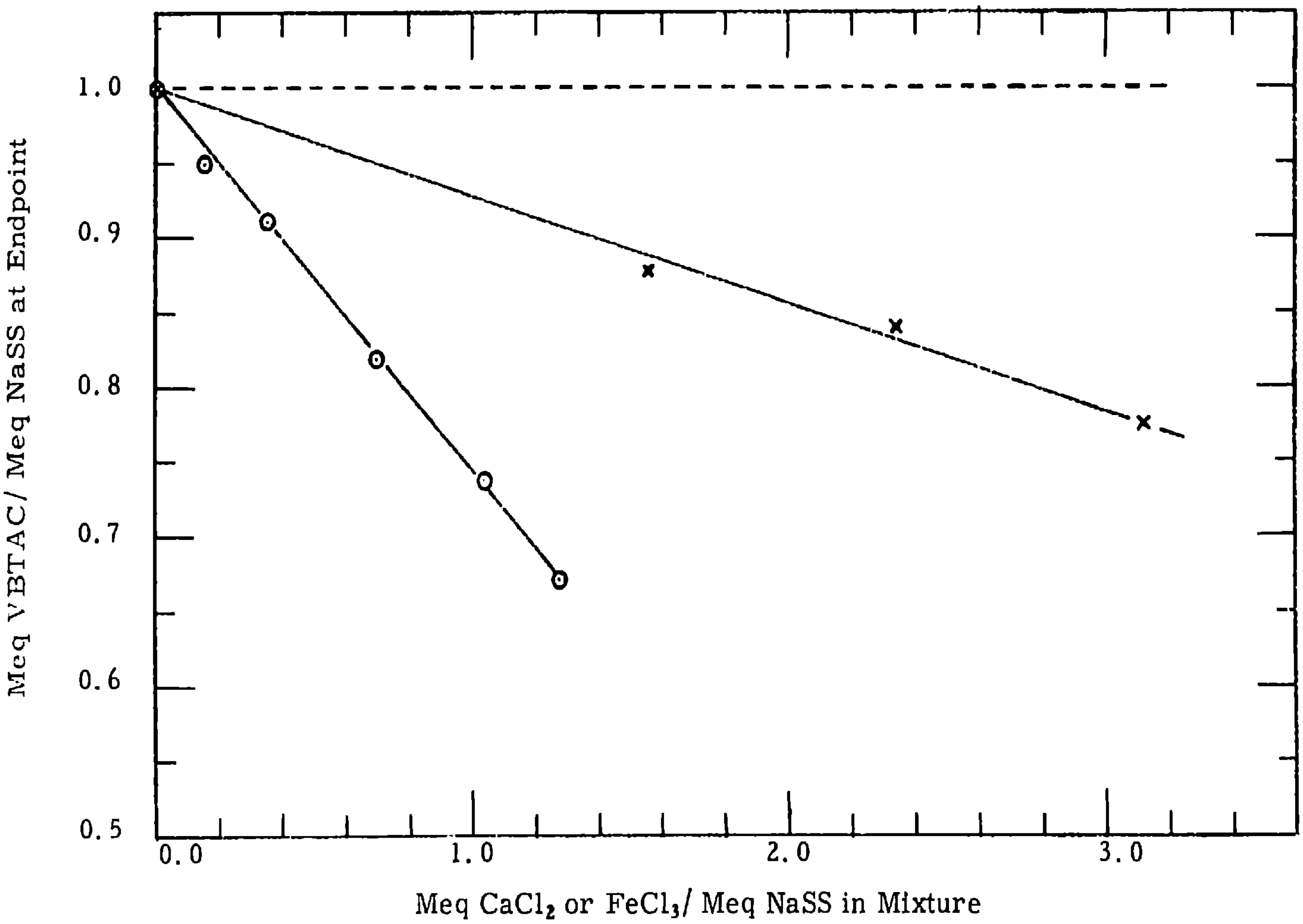


Table XI: Diffusion rates of NaCl through interfacial films imbedded in filter paper or millipore filters

Run No.	Supporting membrane	Polysalt Interfacial film	Avg. NaCl conc. grad across membrane, m/l	Diffusion rate of NaCl thru membrane, moles/hr/sq. in. per 0.1 M conc. gradient
1-a	filter paper, S&S 576	No	0.0964	3.0×10^{-4}
1-b		Yes	0.0963	3.0×10^{-4}
2-a	filter paper, S & S 576	No	0.096	3.2×10^{-4}
2-b		Yes	0.096	3.2×10^{-4}
3-a	Type "SM" cellulose acetate millipore filter	No	0.079	9.5×10^{-4}
3-b		Yes	0.084	9.5×10^{-4}

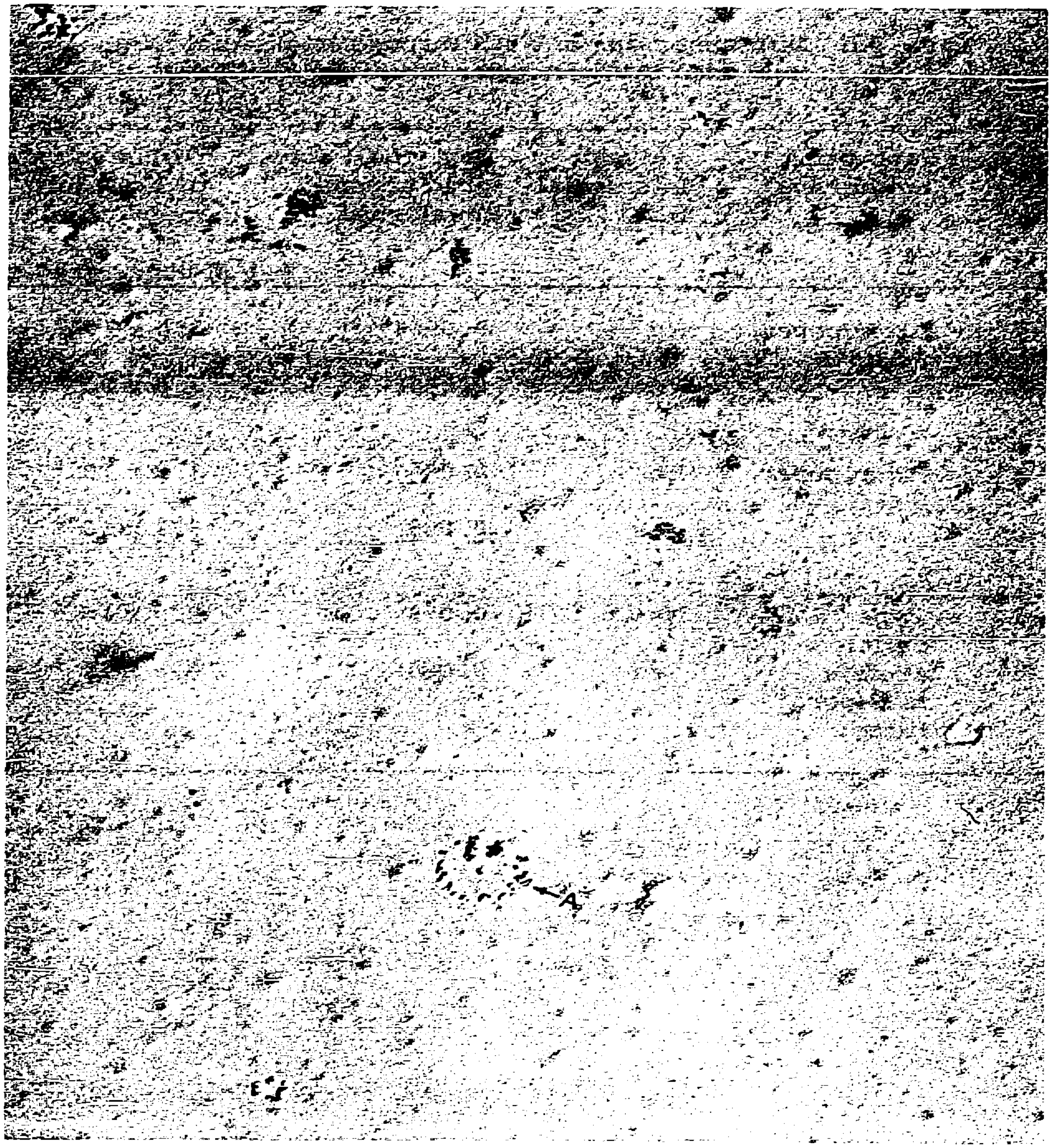


Figure 12: Electron Photomicrograph of Polysalt Interfacial Film Surface, Magnification = 34,250 X (292 Å/ mm) Shadow Length/ Object Height = 3/ 1

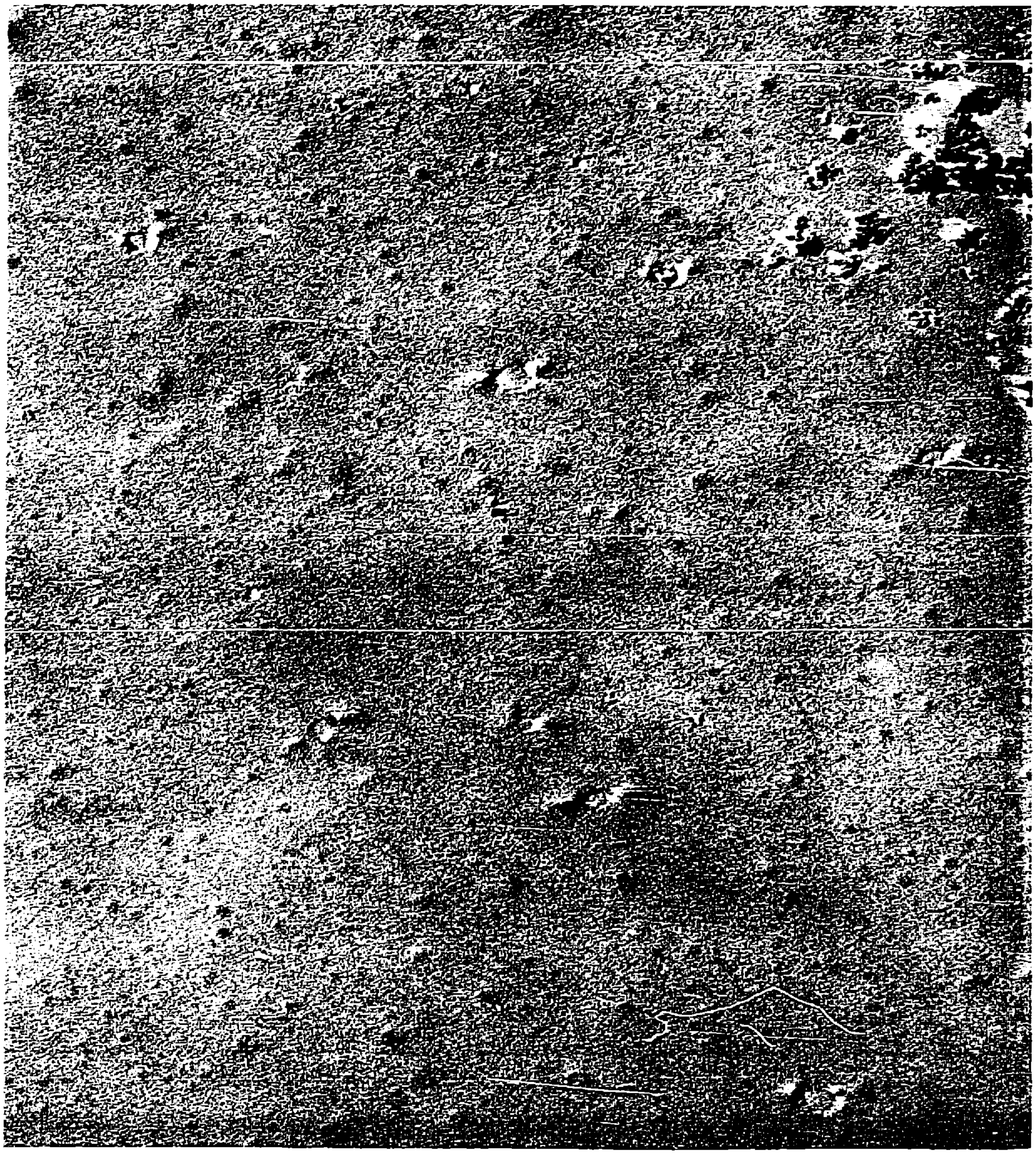
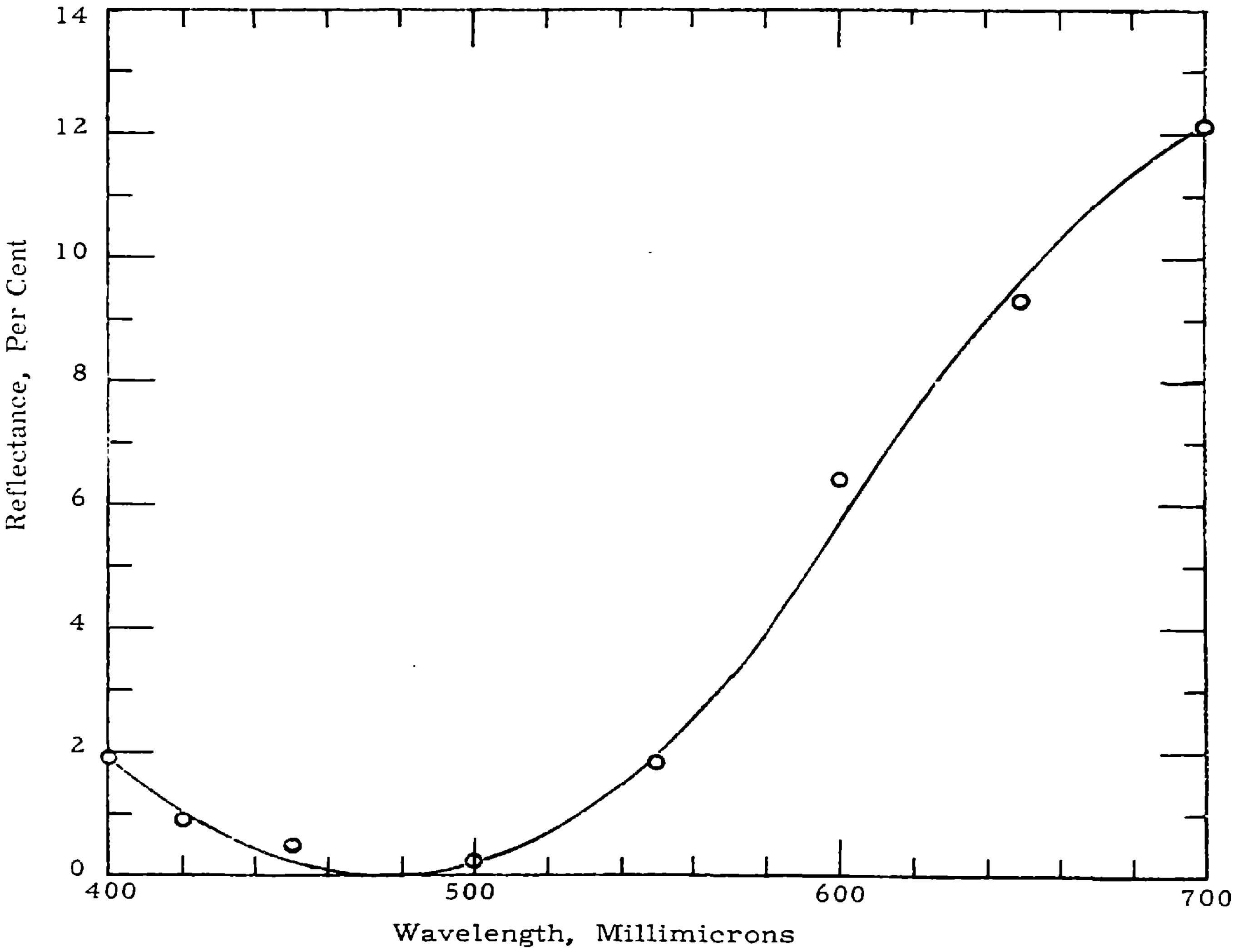


Figure 13: Electron Photomicrograph of Polysalt Interfacial Film Surfaces, Magnification - 34,250 X (292 Å/mm) Shadow Length/Object Height = 3/1

Table XI: Diffusion rates of NaCl through interfacial films imbedded in filter paper or millipore filters

Run No.	Supporting membrane	Polysalt Interfacial film	Avg. NaCl conc. grad across membrane, m/l	Diffusion rate of NaCl thru membrane, moles/ hr/ sq. in. per 0.1 M conc. gradient
1-a	filter paper, S&S 576	No	0.0964	3.0×10^{-4}
1-b		Yes	0.0963	3.0×10^{-4}
2-a	filter paper, S & S 576	No	0.096	3.2×10^{-4}
2-b		Yes	0.096	3.2×10^{-4}
3-a	Type "SM" cellulose acetate millipore filter	No	0.079	9.5×10^{-4}
3-b		Yes	0.084	9.5×10^{-4}

Figure 14: Net Reflectance of an 11-Film Polysalt Interfacial Film Laminate vs. Wavelength of Incident Monochromatic Light



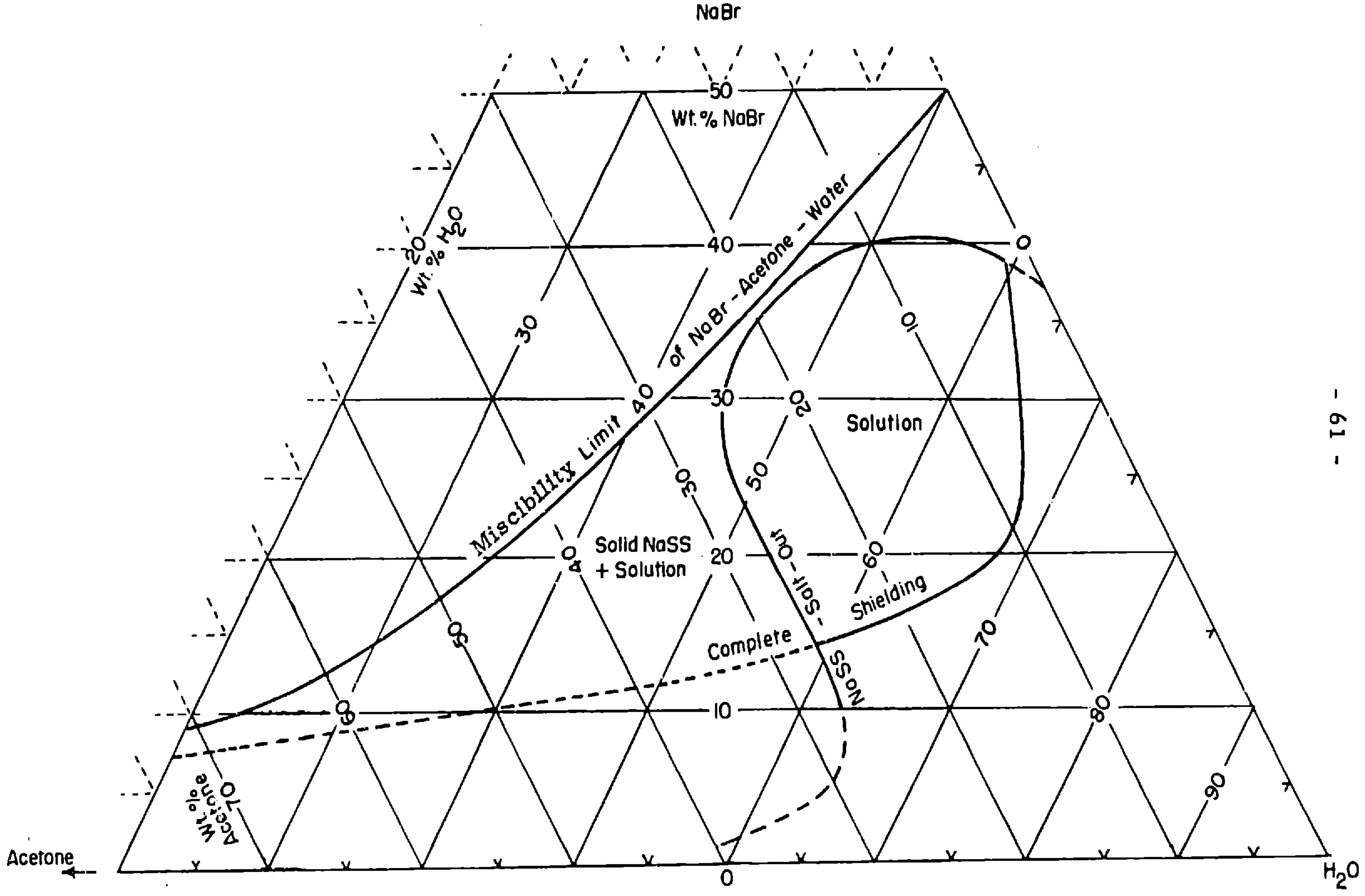


Figure 15

Shielding and Dissolving of Polysalts, and Salt-out of NaSS in NaBr-Acetone-H_2O Mixtures at Room Temperature (25-30°C). Total Polymer Concentration <1.0 g/ 100 ml

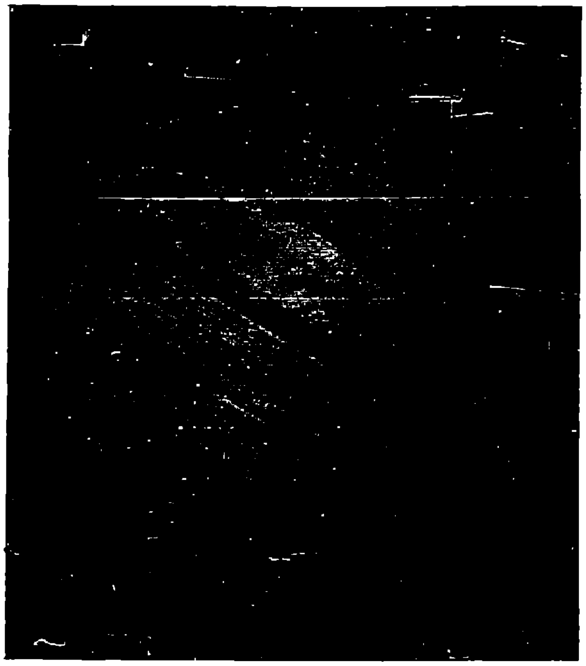


Figure 16: Oriented Polysalt Film at 200X
Showing Fibrous Structure
Each Small Division on Scale = 10 Microns

Table XII: Dielectric constants, volume resistivities, and loss factors of polysalts equilibrated at 50% relative humidity and room temperature (22-27°C), and at 0% relative humidity

Composition, Equivalents VBTAC / Equivalents NaSS		2/1			1/1			1/2		
Moisture Content at 50% Humidity, Wt. Percent H_2O		13%			12%			13%		
Freq. cps	Rel. Hum. %	Dielec. Const. ϵ'	Vol. Resistivity, R ohm-cm	Loss Factor ϵ''	ϵ'	R, ohm-cm	ϵ''	ϵ'	R, ohm-cm	ϵ''
10^2	50	--	--	--	--	--	--	--	--	--
10^3	50	2580	99x10^4	1820	14.0	7.0x10^8	2.52	137.5	12x10^6	150
10^4	50	1120	21.2 "	890	12.5	2.2 "	0.83	49.8	4.7 "	36.1
10^5	50	314	5.1 "	355	11.8	1.9 "	0.95	25.3	1.6 "	11.4
10^6	50	101.5	1.6 "	116	11.3	0.46 "	0.40	--	--	--
10^7	50	40.5	0.55 "	32.5	--	--	--	--	--	--
10^2	0.0	--	--	--	6.16	23x10^{10}	0.0782	6.71	17.1x10^9	1.05
10^3	0.0	73.4	31x10^6	61	5.94	2.3 "	0.0773	5.80	3.4 "	0.53
10^4	0.0	29.5	9.4 "	20.4	5.86	0.19 "	0.0944	5.20	0.67 "	0.268
10^5	0.0	13.6	2.8 "	7.1	5.71	0.14 "	0.131	4.97	0.099 "	0.137
10^6	0.0	8.9	0.78 "	2.4	--	--	--			
10^7										

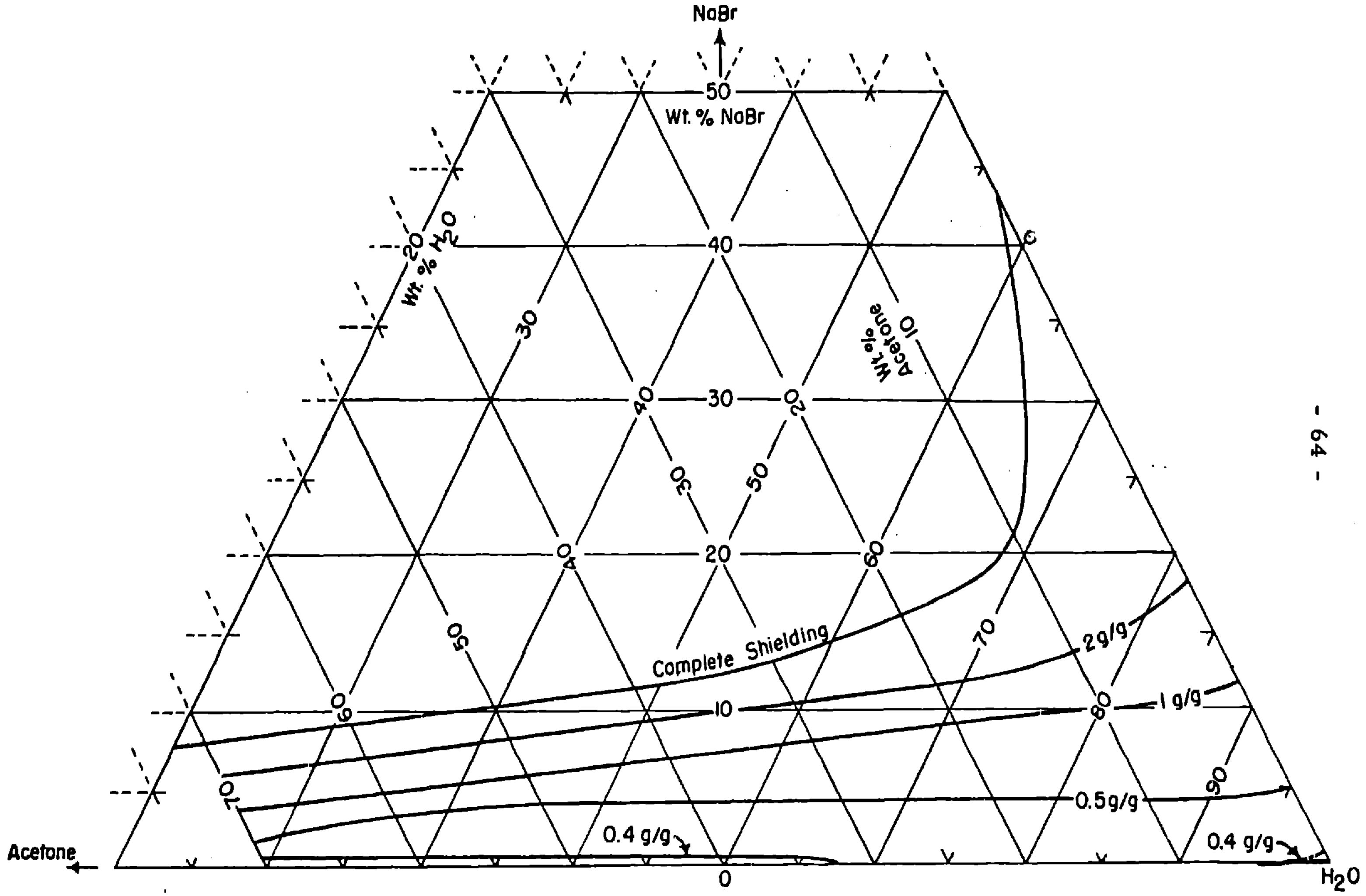


Figure17

Swelling (g solution absorbed per g dry polysalt) of Neutral Polysalt in NaBr-Acetone-H_2O Solutions at Room Temperature

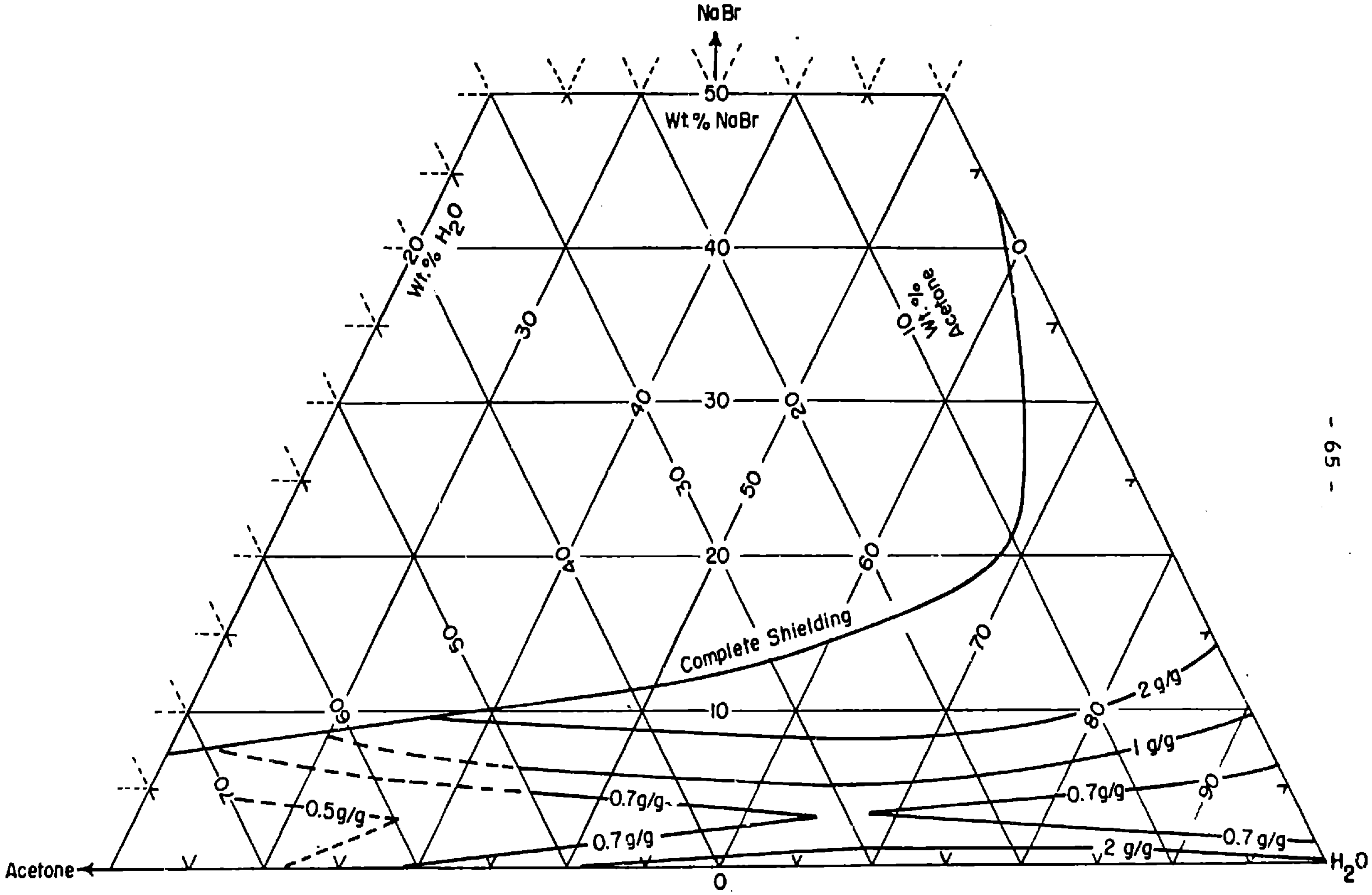


Figure 18

Swelling (g solution absorbed per dry polysalt) of Polysalt Composed of 2 VBTAC/ 1 NaSS in NaBr-Acetone-H_2O Solutions at Room Temperature

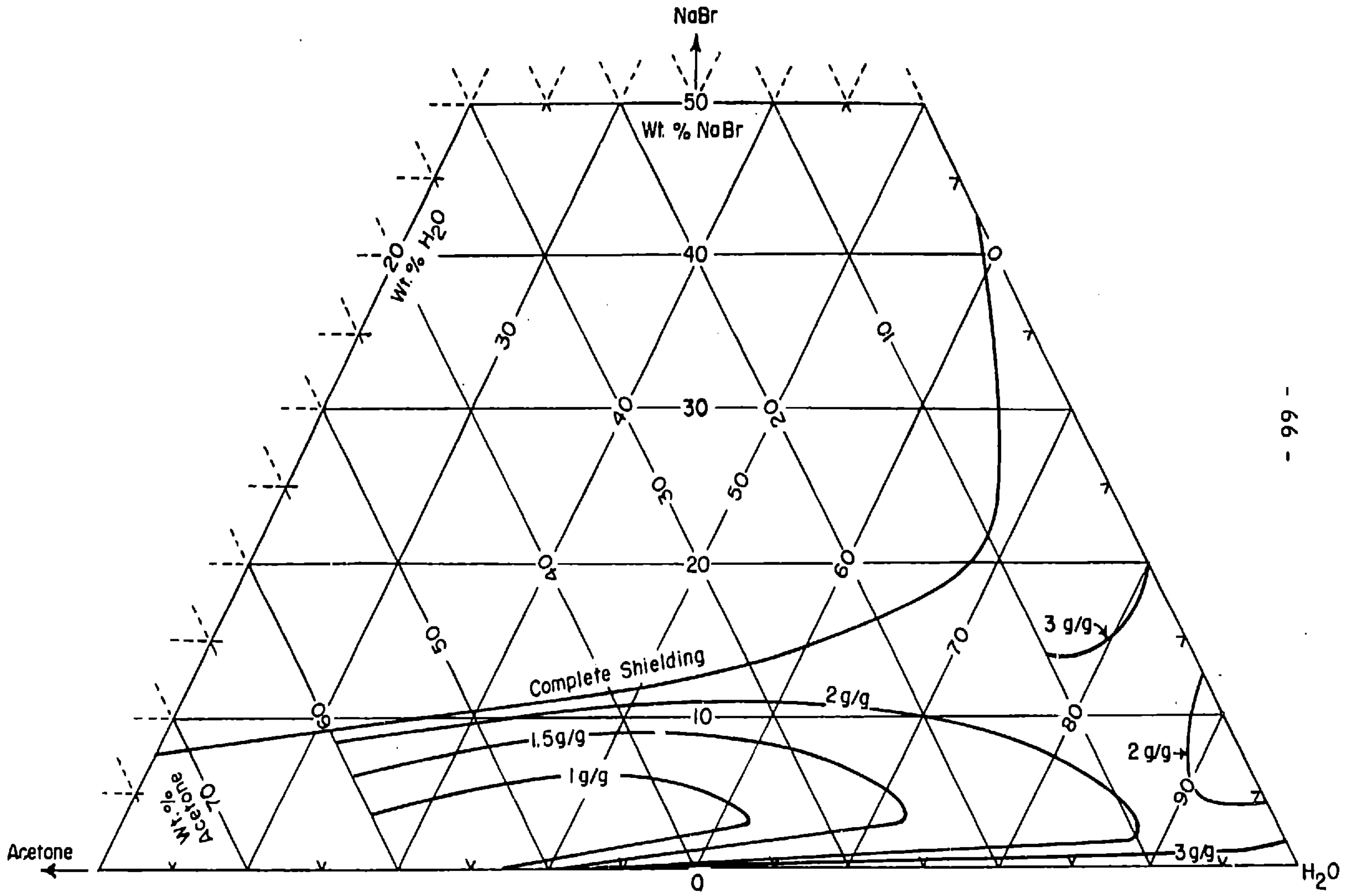


Figure 19

Swelling (g solution absorbed per g dry polysalt) of Polysalt Composed of 2 NaSS/ 1 VBTAC in NaBr-Acetone-H_2O Solutions at Room Temperature

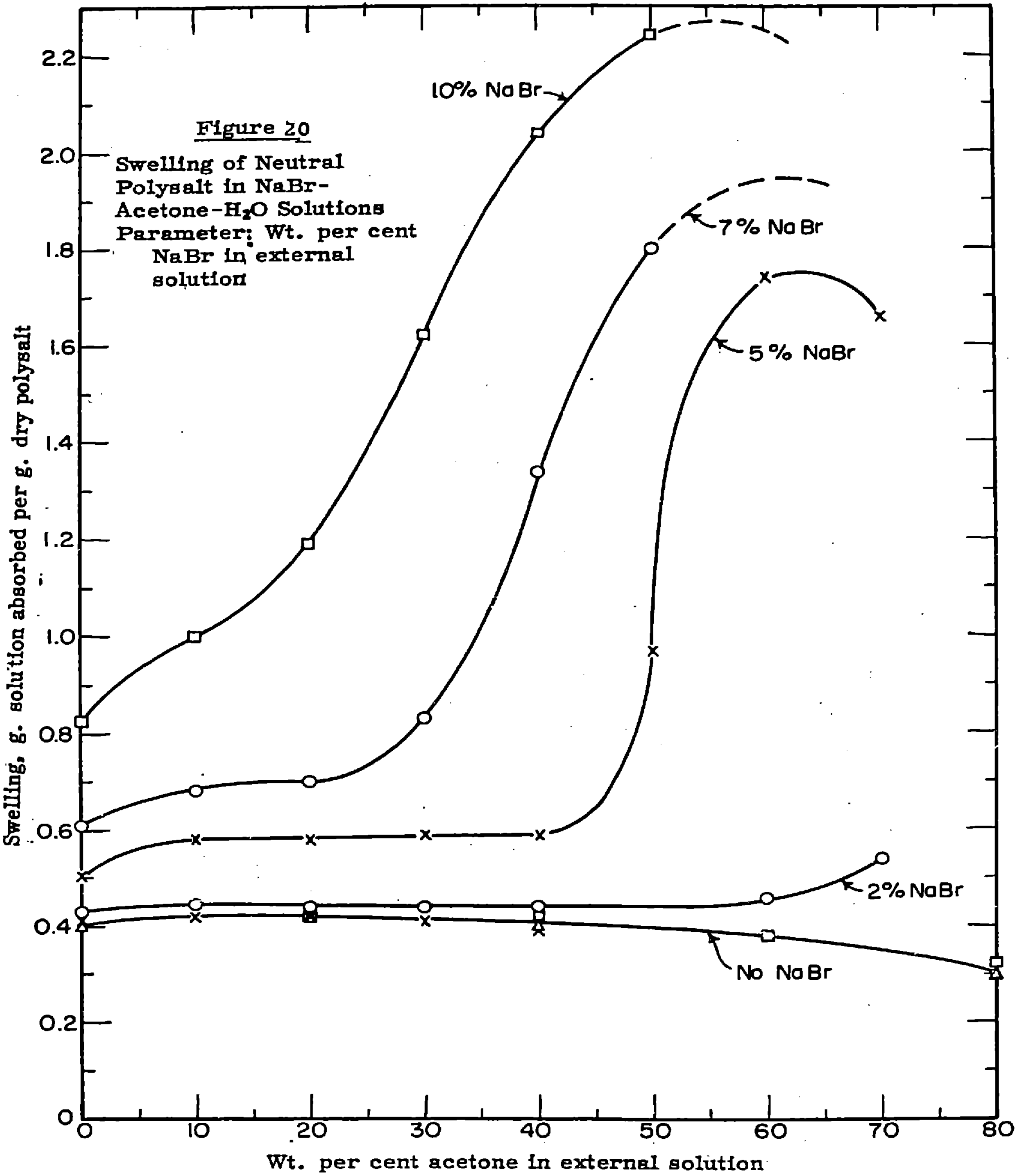


Figure 20

Swelling of Neutral Polysalt in NaBr-Acetone-H_2O Solutions
Parameter: Wt. per cent NaBr in external solution

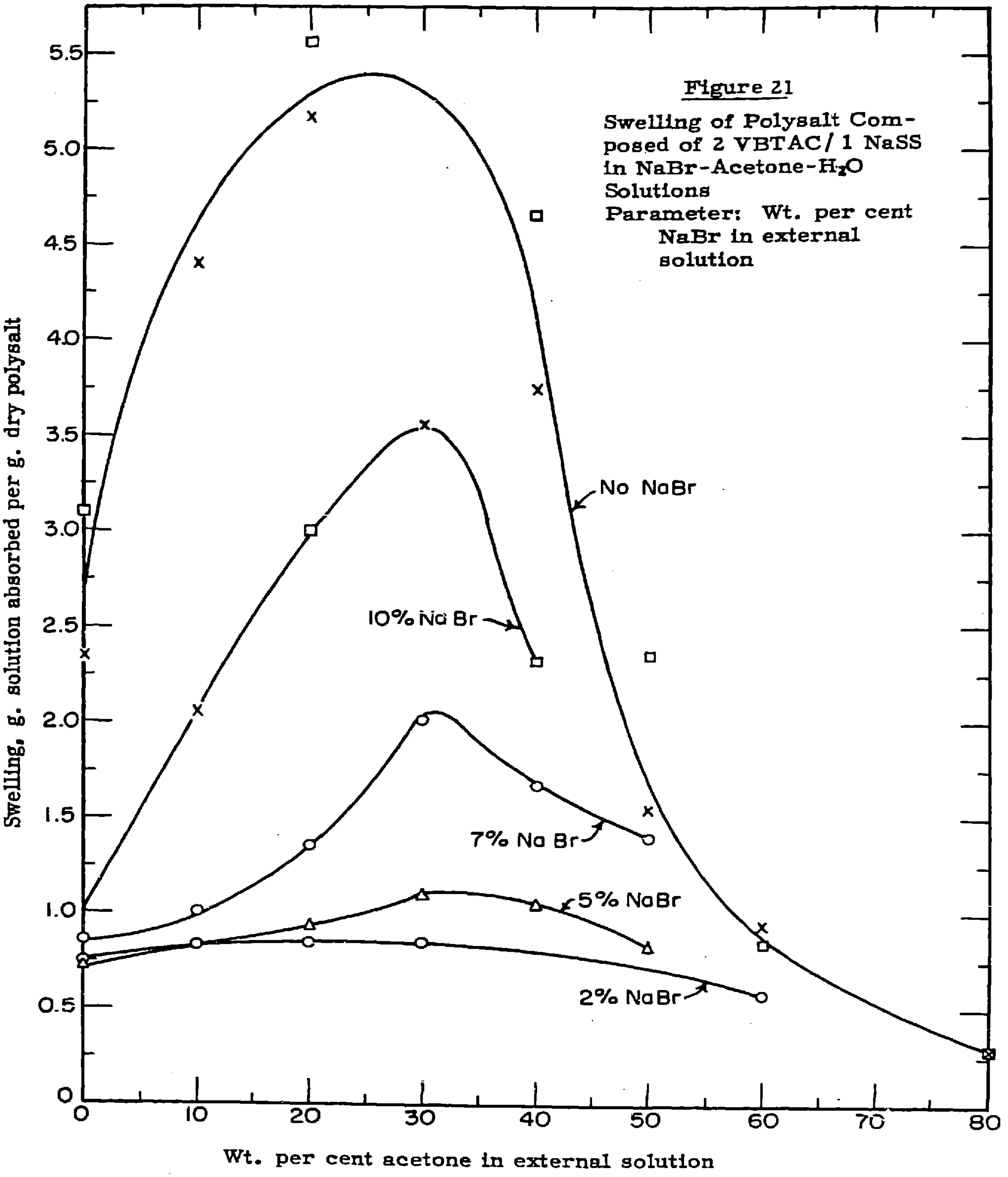


Figure 21

Swelling of Polysalt Composed of 2 VBTAC/ 1 NaSS in NaBr-Acetone-H_2O Solutions

Parameter: Wt. per cent NaBr in external solution

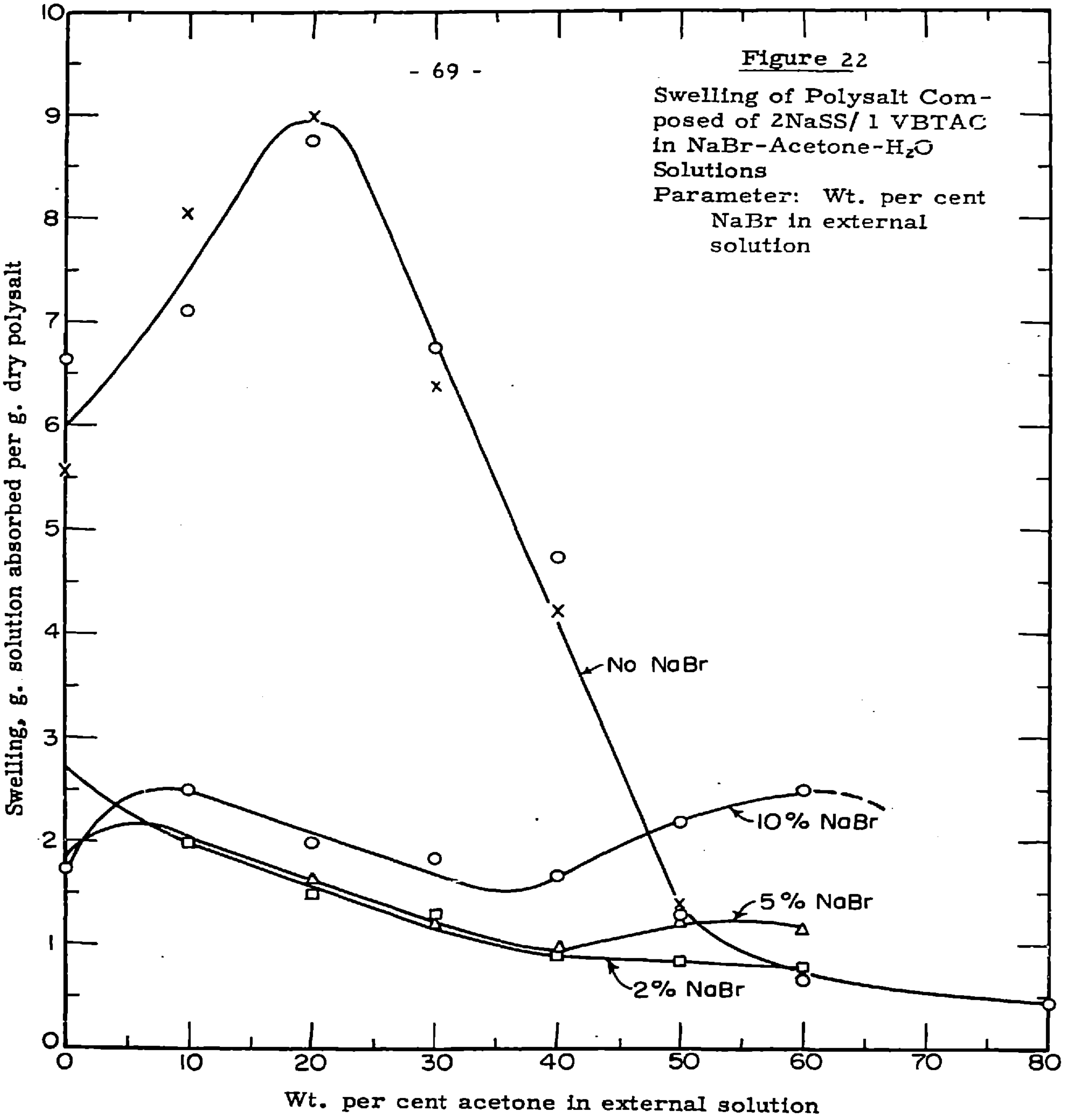


Figure 22

Swelling of Polysalt Composed of 2NaSS/ 1 VBTAC in NaBr-Acetone-H_2O Solutions
Parameter: Wt. per cent NaBr in external solution

Table XIII: Swelling hysteresis of polysalt containing VBTAC/ NaSS in the ionic ratio 2/ 1; dried, in water, and in 20% aqueous acetone at room temperature

Sample No.	Step	Treatment	Weight, steady state	Swelling or moisture content, g/ g
A_6 - A	1	Dried over P_2O_5	0.450 g	0.0
A_6 - B		Dried over P_2O_5	0.376 g	0.0
A_6 - A	2	Equilibrated, 50% hum	0.516 g	0.146
A_6 - B		Equilibrated, 50% hum	0.438 g	0.165
A_6 - A	3	in 20% acetone	1.535	2.41
A_6 - B		in H_2O	0.843	1.24
A_6 - A	4	in H_2O	1.568	2.48
"	5	dried, 50% hum	0.516	0.146
"	6	in H_2O	1.463	2.25
"	7	in 20% acetone	2.231	3.95
"	8	in H_2O	2.281	4.07
"	9	dried, 50% hum	--	--
"	10	in H_2O	1.922	3.27
"	11	in 20% acetone	2.538	4.64
"	12	dried, 50% hum	0.510	0.132
"	13	in H_2O	1.931	3.29

Figure 23: Effects of Swelling and Drying History on Swelling of Polysalt Composed at 2 VBTAC/ 1 NaSS at Room Temperature

(0. 0 swelling) dried over P_2O_5

dried at 50% relative humidity

steady state swelling in water

steady state swelling in 20% aqueous acetone

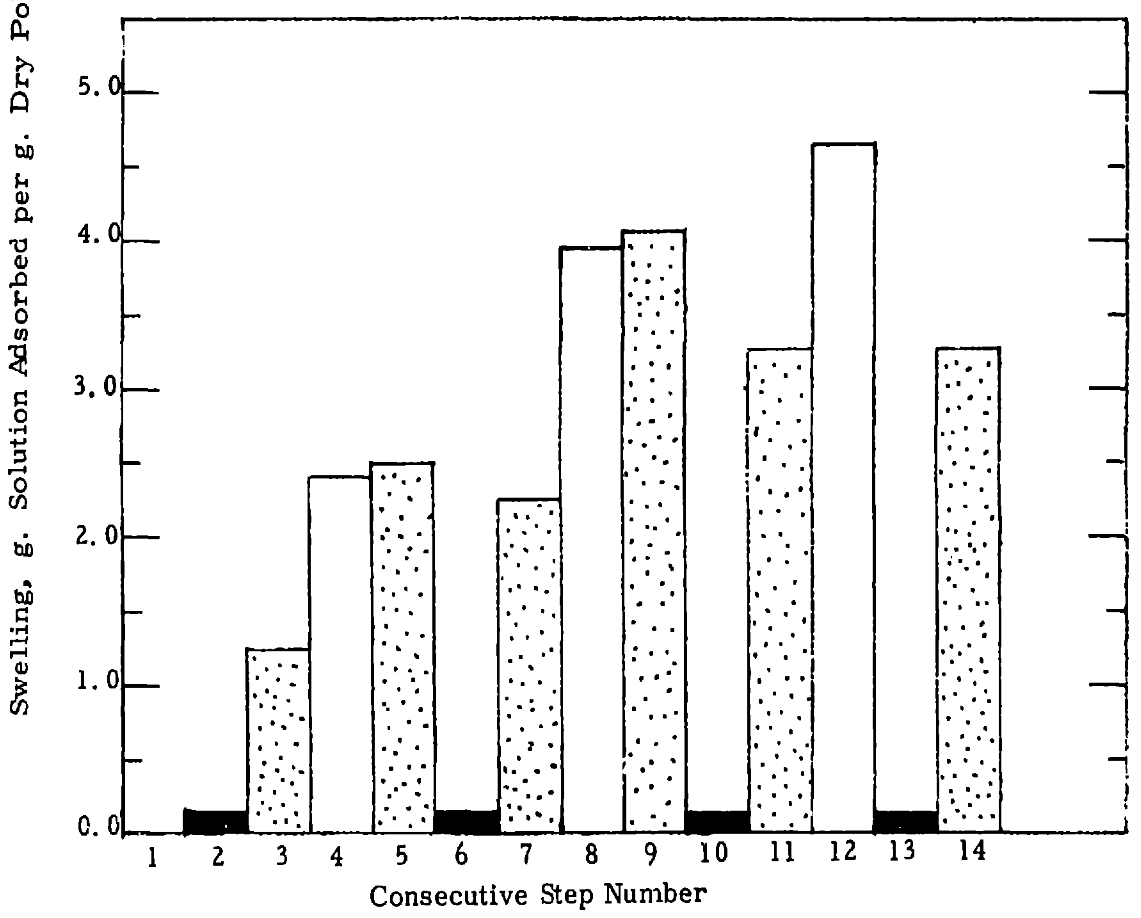


Table XIV: NaBr absorption by neutral polysalt equilibrated with NaBr-acetone-water solutions

Sample	Soln. wt.% NaBr	Soln. wt.% acetone	Dry weight, g.	g. NaBr absorbed	g. NaBr / g. polysalt	g soln absorbed / g polysalt	Wt.% NaBr in absorbed liquid	Wt.% NaBr in swollen polysalt	Wt.% NaBr in abs. liq. / wt.% NaBr, external solution
B_5-A	2	0	0.655	0.019	0.030	0.43	6.9	2.0	3.5
B_5-B	2	10	0.719	0.024	0.034	0.445	7.6	2.3	3.8
B_5-C	2	20	0.312	0.010	0.031	0.435	7.2	2.1	3.6
B_5-D	2	30	0.382	0.020	0.053	0.435	12.2	3.7	6.1
B_5-E	2	40	0.369	0.021	0.058	0.44	13.1	4.0	6.6
B_5-G	2	60	0.430	0.042	0.097	0.46	21.1	6.7	10.6
B_5-A	7	0	0.655	0.048	0.073	0.61	11.9	4.6	1.7
B_5-B	7	10	0.719	0.059	0.083	0.68	12.1	5.0	1.7
B_5-C	7	20	0.312	0.029	0.093	0.70	13.3	5.5	1.9
B_5-D	7	30	0.382	0.056	0.15	0.83	17.6	8.0	2.5
B_5-E	7	40	0.369	0.079	0.21	1.34	15.9	9.1	2.3
B_5-G	7	50	0.430	0.142	0.33*	1.81	18.2	11.7	2.6

* Maximum quaternary-sulfonate site capacity = 0.25 g. NaBr/g. polysalt

Table XV: NaBr absorption by polysalt composed of VBTAC/ NaSS in the ionic ratio 2/ 1, equilibrated with NaBr-acetone-water mixtures

Sample	Wt.% NaBr (sol'n)	Wt.% acetone (sol'n)	Dry weight, (g)	g. NaBr absorbed	g. NaBr / g. polysalt	g. solution absorbed / g. polysalt	Wt. % NaBr in absorbed liquid	Wt.% NaBr in swollen polysalt	Wt.% NaBr in abs. liq. / wt.% NaBr, external solution
A$_5$-A	2	10	0.321	0.00	0.00	0.83	0.0	0.0	0.0
A$_5$-B	2	20	0.320	0.00	0.00	0.85	0.0	0.0	0.0
A$_5$-C	2	30	0.365	0.004	0.01	0.85	1.3	0.06	0.65
A$_5$-D	2	60	0.345	0.021	0.062	0.58	10.7	3.9	5.4
A$_5$-E	5	10	0.346	0.012	0.035	0.84	4.1	1.9	0.82
A$_5$-G	5	20	0.340	0.017	0.050	0.93	5.4	2.6	1.08
A$_5$-H	5	30	0.484	0.035	0.072	1.10	6.6	3.4	1.3
A$_5$-I	5	40	0.518	0.045	0.086	1.05	8.3	4.2	1.7
A$_5$-A	7	0	0.321	0.031	0.097	0.86	11.3	5.2	1.6
A$_5$-B	7	10	0.320	0.037	0.115	1.01	11.4	5.7	1.6
A$_5$-C	7	20	0.365	0.067	0.183*	1.36	13.5	7.8	1.9
A$_5$-D	7	30	0.345	0.105	0.384*	2.02	13.7	10.1	2.0
A$_5$-E	7	40	0.346	0.102	0.294*	1.68	17.7	11.0	2.5
A$_5$-G	7	50	0.340	0.108	0.316*	1.41	22.4	13.1	3.2

* Maximum quaternary-sulfonate site capacity = 0.15 g. NaBr/ g. polysalt

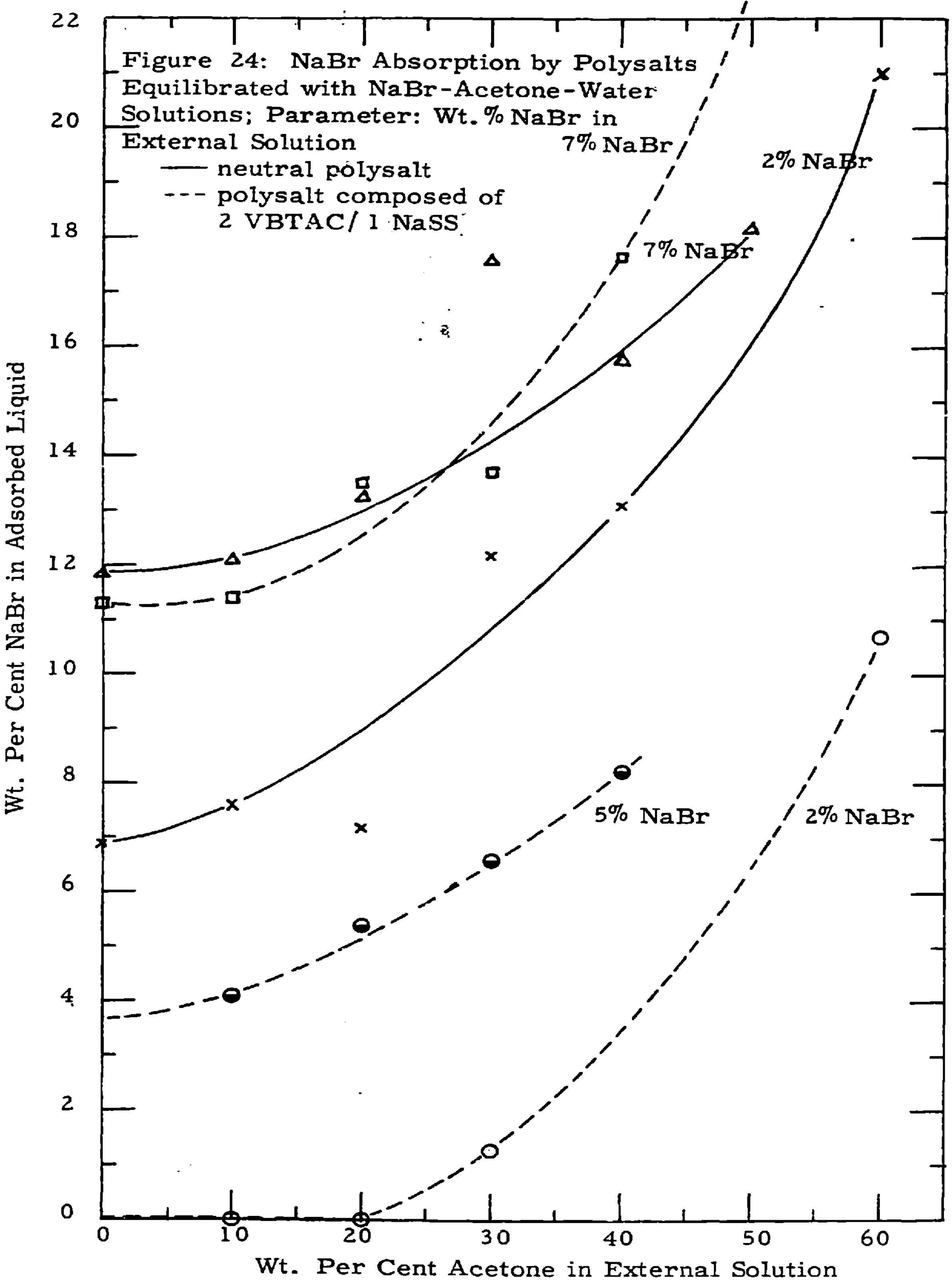


Figure 24: NaBr Absorption by Polysalts Equilibrated with NaBr-Acetone-Water Solutions; Parameter: Wt. % NaBr in External Solution

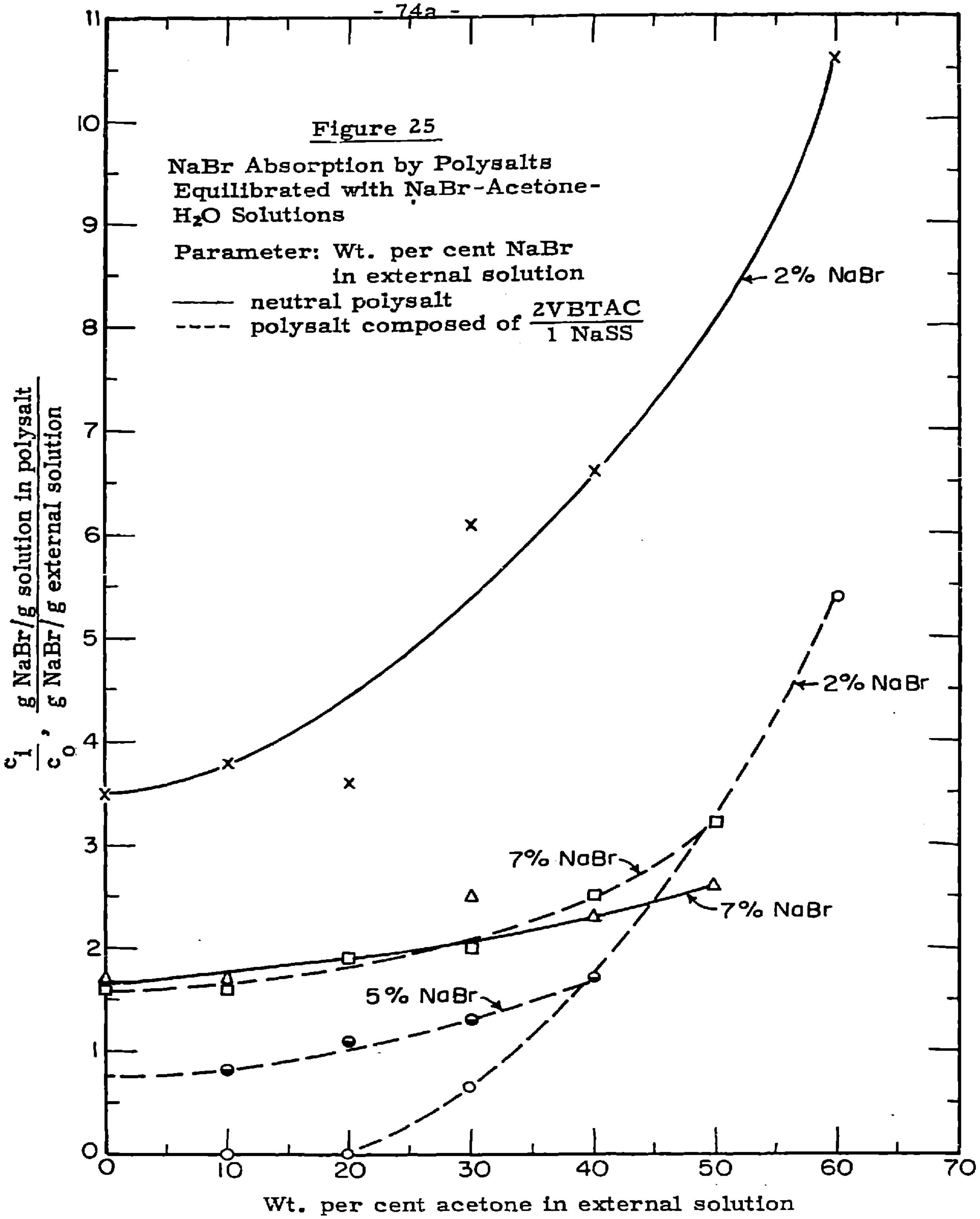


Figure 25

NaBr Absorption by Polysalts Equilibrated with NaBr-Acetone-H_2O Solutions

Parameter: Wt. per cent NaBr in external solution

Table XVI: K^+ / Na^+ sorption selectivity of neutral polysalt equilibrated with solution containing 0.1M NaCl, and 0.1 M KCl

Sample	Dry weight	MeqKCl absorbed	MeqNaCl absorbed	K^+/Na^+	Max. Capacity of polysalt, Meq	Fraction of total sites occupied
B-7	0.946g	0.170	0.135	1.26	2.3	0.13

Table XVII: Gelation behavior for mixtures containing various ratios and concentrations of VBTAC and NaSS dissolved in a solution containing 20% (by weight) acetone, 20% NaBr, and 60% water

Mixt.	VBTAC/NaSS in mixture	Wt. % VBTAC	Wt. % NaSS	Gellation induced by dilution with water	Gellation induced by acetone evaporation	Comment
1	10/1	4.55	.455	Yes	Yes	Fairly strong, continuous gel washed, dried gel swells about 30/1 in water, releases VBTAC
2	10/1	2.3	.23	Yes	Yes	Gels less rigid than mixture 1
3	10/1	1.5	0.15	No	No	Same gel fragments, but not continuous
4	20/1	4.76	0.248	Yes	Yes	Same as Mix. 2
5	30/1	4.84	0.16	Slight	No	Large gel fragments present, but not continuous gel
6	50/1	4.9	0.098	No	No	A few gel fragments
7	1/1	2.5	2.5	Yes	Yes	Gels are quite rigid
8	1/1	0.25	0.25	No	Slight	
9	1/1	0.17	0.17	No	No	
10	1/10	.455	4.55	Yes	Yes	Same as mix. 1, except NaSS released

V. DISCUSSION OF RESULTS

A. Determination of Polyelectrolyte Equivalent Weights

Table I gives the measured equivalent weights of batches of VBTAC and NaSS* purified at different times. The measured VBTAC equivalent weights are subject to estimated errors of ± 4%, corresponding to the range of equivalent weights obtained in measurements made on different solutions of Batch A over a period of about one year. The equivalent weight variations were due partly to inaccuracies in measuring the equivalent weights (± 3%), and partly to changes in the equivalent weight of the polymer while in solution even for short periods of time (apparently caused by bacterial attack of the polymer).

The measured NaSS equivalent weights, especially of Batch A, are subject to estimated errors higher than those inherent in the titration measurements for the following reason: Although NaSS is apparently quite stable both dry and in solution, the hydrogen form (HSS) is not. Upon standing for several months a 2% solution of HSS, originally colorless and quite viscous, had decomposed to a very low viscosity amber solution. The titrations made on NaSS Batch A are subject to errors caused by this degradation and may not be truly representative of the batch, since the samples titrated were maintained in the hydrogen form for longer times than the major part of the batch. The entire batch was partially in the hydrogen form for from two to ten days after being contacted with demineralizing resin and before

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* Reexamination of the data have indicated that a value of 230 would be more appropriate than 234 for the equivalent weight of NaSS Batch A, but since the small correction involved is well within the estimated experimental error, the orinally assumed value of 234 has been used throughout this report.

being ion exchanged back into the sodium form. The value of 224 for Batch B was determined for samples kept in the hydrogen form for less than 30 hours, and are surely more representative of the polymer equivalent weight before purification. The value of 224 agrees quite well with the value of 226 calculated for the theoretical mer unit of the polymer ($CH_2CHC_6H_4SO_3Na$) assuming one water of hydration per mer unit.

For uncertainties of ± 4% (ca. ± 10) in the measured equivalent weight of VBTAC Batches A and B, and ± 3% (ca. ± 8) in the equivalent weight of NaSS Batch A, the estimated (rms) errors in the VBTAC/ NaSS equivalent weight ratios for these batches are ± 5%.

B. VBTAC-NaSS Dilute Solution Interaction Stoichiometry

1. Mixtures Without Added Salt

The measured specific viscosities of the supernatant liquids of VBTAC-NaSS mixtures passed through their isoionic (precipitate flocculation) points are shown in Column 7 of Table II. These are compared in Columns 8, 9, and 10 to the measured specific viscosities of control samples made up to contain the excess over stoichiometric of the more concentrated polymer in the mixtures, plus the amounts of NaCl which would have been released into the supernatant liquids upon complete interpolymer ionic reactions. Thus, the control sample viscosities represent the values to be expected for the supernatant liquids of the corresponding mixtures upon stoichiometric and ionically complete reactions between the polymers. The data are shown graphically in Figure 7. Although Columns 9 and 10 of Table II show the agreement between mixture supernatant and control sample specific viscosities to be remarkably good, it would be premature to accept this evidence as proof of complete and stoichiometric interpolymer reaction, because a decrease in the amount of excess polymer in solution might be fortuitously compensated viscometrically by a corresponding decrease in the amount of salt released into solution (the solution viscosities are quite sensitive to both polymer and salt concentrations).

Table III compares the measured supernatant liquid chloride contents per gram of VBTAC in some of the mixtures to the measured chloride ion contents per gram of unreacted VBTAC. The data show that within the limits of experimental accuracy (± 4%), all of the chloride counterions of the precipitated VBTAC were released into solution. These results corroborate the evidence of the viscosity measurements; namely, that within narrow limits, the interactions between VBTAC and NaSS in sufficiently dilute, salt free solutions are both stoichiometric and complete, regardless of the ratio of the two polymers present in the mixtures.

Table IV shows the deviations from stoichiometric interpolymer reactions corresponding to the measured differences between the mixture supernatant liquid and control sample viscosities, plus the additional deviations to be expected if 3% of the total NaCl were retained in the precipitates. The changes in specific viscosity with polymer concentrations ($\partial\eta_{sp} / \partial c_p$) were determined from the slopes of the lines in Figure 7, and the changes in specific viscosity with NaCl concentration were calculated from the individual polymer viscosity data of Smith (34), assuming the effects of NaCl and NaBr to be the same in the concentration ranges used (see Appendix B, Section A). Column 8 of Table IV shows that the combined errors give a maximum deviation of 4% from stoichiometric interpolymer reaction. This is within the estimated error of ± 5% in the measured equivalent weight ratio of the polyelectrolytes (see Section V-A).

Table V gives viscosity data obtained for mixtures deliberately kept from being passed through their ionic equivalence points. The supernatant liquids of these mixtures were all somewhat turbid because some of the precipitate particles were too small to be removed from solution by the centrifuge used. These suspended particles probably caused the 5-7% elevation in the supernatant specific viscosities over the control sample specific viscosities of Mixtures 11, 12, and 13. One would expect that if deviations from stoichiometric reaction occurred at polymer ratios away from the equivalence points, they would be in a direction such that the polyelectrolyte being added (the one in lesser concentration) would react with more than a stoichiometric amount of the polymer in excess, with a corresponding decrease in the amount of residual unreacted polymer in solution. This must be the case to some extent, since the small suspended particles undoubtedly contain some residual ionic charge. The ionic interactions must be substantially complete for these mixtures, since complete reaction occurs even in mixtures containing equal amounts of both polymers (i.e., where all of the ions of both species must be mutually reacted). It should be pointed out that these mixtures were made by mixing together solutions with (initial) polyelectrolyte concentrations which were sufficiently high--0.1 to 0.15 g/dl--so that about 50% of the total precipitates formed were flocculated, and easily centrifuged from the solutions. Completely dispersed precipitates were formed only when the polymers were mixed at concentrations below about 0.05 g/dl. The reasons for flocculent precipitate formation at non-stoichiometric polymer ratios are discussed in Appendix A, Section B.

The data for Mixture No. 14 were included in Table V primarily to show the deviations from stoichiometric reactions which occurred when more concentrated polymer solutions were mixed. Substantial deviations from stoichiometric reactions began to occur in the NaBr-free mixtures when VBTAC more concentrated than 0.15 g/dl was mixed with 0.2 g/dl NaSS, or when NaSS more concentrated than 0.1 g/dl was mixed with 0.2 g/dl VBTAC. Apparently, when these more concentrated solutions were mixed, portions of the solution being added became surrounded by an impermeable precipitate layer which prevented further interpolymer reaction, representing the beginnings of interfacial film formation (see Section III-E). It is doubtful that the elevated viscosity of Mixture 14 was due to suspended precipitate, since the supernatant liquid was almost completely clear.

Thus, the data show that within the limits of experimental accuracy (± 5%), the reactions occurring between VBTAC and NaSS in sufficiently dilute, salt-free, aqueous solutions are ionically complete regardless of the ratio in which the two polymers are mixed. If the mixtures are passed through their ionic equivalence points, the reactions are stoichiometric as well as complete. These rather surprising results indicate that the polymers combine in some fashion other than by random interaction between the polyions, for if this were the case, a tangled, highly matted network would be formed, and one would expect that a considerable fraction of the ions of each polymer would be sterically prevented from reacting. The conclusion is that molecular pairing occurs between relatively long segments of the reacting molecules. Since the polymers used here have equal ionic spacings, pairing allows virtually complete reaction of the ions. The probable mechanism of pair formation is as follows: Initial contact between two molecules occurs at some point along the polymer chains (this will not be completely random because the oppositely-charged molecules are drawn toward each others' centers of charge). Once an initial reaction has occurred, however, the most probable points for further interaction are between ions adjacent to the reacted site, since they are of necessity very close to each other. If reactions continue to occur at sites immediately adjacent to those already reacted, the result will be a "zippering" reaction which will propagate until the end of a molecule is reached, or until terminated by a reaction propagating from some other point on one of the molecules.

It would seem that the lack of rotational freedom of the benzene rings around the hydrocarbon chains might make it difficult for all of the polyions on a pair of actactic molecules to associate with one another. However, dielectric polarization measurements made on dilute solutions of poly (p-chlorostyrene) by deBye and Buche (12, 6) have indicated that adjacent phenyl groups on that polymer tend to occur on alternate sides of the backbone chain. This tendency toward syndiotacticity may be enhanced for the polyelectrolytes used here, because the bulky, mutually repelled ionic groups (which were already present on the monomers at the time of polymerization) might have made it difficult for the materials to polymerize with adjacent phenyl groups lying on the same side of the backbone chains. Also, the oppositely-charged polyions need not approach indefinitely close to one another in order to react, but need only be in sufficient mutual proximity to allow the escape of their counterions into solution. The polymers most probably associate as randomly twisted pairs.

2. Mixtures with Added Sodium Bromide

Table VI gives the mixture compositions, flocculation points, and supernatant specific viscosities of polyelectrolyte mixtures made in the presence of 0.1 M NaBr. The flocculation points, which were fairly reproducible, occurred before the equivalence points were reached, regardless of the order of addition of the two polymers. At the flocculation points (mixtures 0.1-13 and 0.1-14), the clear supernatant liquids were essentially free from excess polymer, having almost the same viscosity as the solvent. If polymer solution addition was continued beyond the flocculation points, some of the additional polymer entered the precipitates. When VBTAC was added in excess, more than an equivalent amount entered the precipitate within 3 hours from the time of mixing, and continued to enter the precipitate over longer periods of time (10 days), apparently approaching the precipitate composition at the flocculation point obtained when

VBTAC was titrated by NaSS. Conversely, when NaSS was added to VBTAC, initial flocculation occurred at a ratio of about 0.654 equivalents of NaSS per equivalent of VBTAC, but when additional NaSS was added, some of it entered the precipitate, reducing the ratio to 0.86 to 0.99 equivalents of NaSS per equivalent of VBTAC within three hours from the time of mixing. After 10 days the NaSS/ VBTAC combining ratios had increased to 1.01 to 1.14, apparently approaching the ratio at the flocculation point obtained when VBTAC was added to NaSS. Figure 8 illustrated graphically the supernatant liquid specific viscosities and their relations to the stoichiometric (solid line) and flocculation point (dotted lines) combining ratios.

These same effects were noted for polyelectrolyte mixtures containing 1.0 molar NaBr, as shown in Table VIII, and illustrated in Figure 10. The flocculation points of these mixtures were not recorded, and the dotted lines in Figure 10 represent the supernatant viscosities for polymer concentrations corresponding to the excesses over the precipitate compositions obtained at the flocculation points of the 0.1 M NaBr mixtures. The data indicate that the combining ratios of the polymers are the same in the presence of 1.0 molar NaBr as in the presence of 0.1 molar NaBr, and that the precipitates achieve their final compositions much more rapidly in the more concentrated salt solutions (the viscosities of the 1.0 molar NaBr mixtures were measured within 24 hours after the initial mixing). The fact that one equivalent of NaSS is able to combine with 1.5 equivalents of VBTAC when VBTAC is in excess, but one equivalent of VBTAC is able to combine only with 1.2 equivalents of NaSS when NaSS is in excess, probably reflects the greater ion suppressing effect of Br^- on VBTAC than of Na^+ on NaSS.

In the presence of 0.01 M NaBr (see Table VII and Figure 9), the combining ratios of the polymers do not deviate from stoichiometric as much as they do at the higher salt concentrations, although the NaSS is able to precipitate an appreciable excess of VBTAC (ca. 1.1-

1.2 Meq VBTAC/ Meq NaSS) when VBTAC is present in more than stoichiometric amounts. Since the viscosities of these mixtures were measured only once, it is not known whether greater deviations from stoichiometric reaction would have occurred after longer periods of time.

In summary, the ionic reactions between dilute solutions of VBTAC and NaSS are such that complete precipitation of both polymers occurs for mixtures in the approximate composition range 1.2:1 to 1:1 Meq VBTAC: Meq NaSS in the presence of 0.01 M NaBr, and for mixtures in the approximate composition range 1.5:1 to 0.82:1 Meq VBTAC:Meq NaSS in the presence of 0.1 - 1.0 M NaBr.

Complete coprecipitation of both polyelectrolytes throughout a rather broad range of equivalent ratios is, qualitatively, at least, consistent with the formation of a randomly cross-linked, polyion network. In the presence of 0.1 M NaBr, the viscometric measurements on the individual polymers also indicate that both exist in solution in more or less highly coiled conformations. It is thus suggested that, in the presence of extraneous electrolytes, the coiled polymer molecules may bond together as semirigid, oppositely charged particles, forming initially a coagulum in which only a small fraction of the available polyion pairs have coreacted. Slow structural rearrangements within the precipitate may allow gradual increase in polyion bridging, with concurrent microion release. The capacity of these non-stoichiometric, incompletely ion-bridged structures to absorb and retain excess polycation or polyanion is readily explained by their necessarily high concentration of "unbound" segments of both positive and negative polyion charge.

The observation that the limiting sorptive capacities of these precipitates for polyanion and polycation appear to be related to the flocculation ratios for the reverse orders of addition is provocative, in that it suggests the existence of some special kind of polymer-ordering in the precipitate.

C. VBTAC-NaSS Mutual Titrations

Table IX shows that the VBTAC:NaSS weight ratios at the endpoints of the mutual titrations agree very well with the equivalent weight ratios determined by counterion titrations. Because the mutual titrations could be made rapidly and easily, they were used in lieu of counter ion titrations for determining the equivalent weight ratios of the unpurified polyelectrolyte samples used in the salt-shielded mixtures (see Section III-G). The consistent 1-2% difference in the endpoints of titrations made in opposite directions (VBTAC titrated by NaSS vs. NaSS titrated by VBTAC), although within the estimated accuracy of the measurements (± 3%), is undoubtedly real, and represents the ability of polymer present in sub-stoichiometric amounts to react with slightly more than an equivalent amount of the polymer in excess. As discussed in Section V-B, this ability becomes much greater in the presence of 0.1 - 1.0 molar added salt (NaBr). In all of the mutual titrations the mixtures began to flocculate slightly before the indicated endpoints were reached, becoming completely flocculated at the endpoints.

Table X and Figure 11 show that small amounts of polyvalent metal ions (Ca^{++}, Fe^{+++}) strongly affect the endpoints when NaSS is titrated by VBTAC, but do not measureably change the endpoints when VBTAC is titrated by NaSS. Although there are linear relations between the amounts of $FeCl_3$ or $CaCl_2$ added to the mixtures and the apparent amounts of NaSS which they titrate (decreases in amounts of VBTAC required), there is no logical correspondence between the ionic equivalents of NaSS and the equivalents (or moles) of either $FeCl_3$ or $CaCl_2$. This observation, coupled with the fact that the reverse titrations--VBTAC plus salt titrated by NaSS--are unaffected by iron or calcium ions in the concentration ranges used, indicates that the function of the cations is not merely to titrate the NaSS in competition with VBTAC. Probably, the cations hinder molecular pairing between the polymers by ionically bridging portions of the

NaSS molecules, leaving segments isolated sterically from the VBTAC. The reverse titrations are unaffected because the polymers react so rapidly that cation bridging of the NaSS molecules does not have time to occur. The linear relations between the amounts of NaSS and $CaCl_2$ or $FeCl_3$ do not continue to indefinitely high salt concentrations, for it has been observed that VBTAC is able to precipitate NaSS even from nearly saturated solutions of $FeCl_3$.

Other experiments showed that up to 0.004 molar NaBr had no effect on mutual titrations made in either direction. The studies were not carried to higher salt concentrations because the indicator's efficacy was destroyed in the presence of 0.003 - 0.005 molar or more of any of the salts.

The mechanism of indicator action is probably as follows: In the presence of a very slight excess of VBTAC, comparable ionically to the amount of dichlorofluorescein present, the dye reacts ionically with the VBTAC and precipitates it into lyophobic colloidal particles, losing its green fluorescent color, just as when adsorbed on a silver chloride surface. When further excess VBTAC is added, the dye redistributes itself over all of the quaternary polymer molecules, but does not precipitate them, and therefore loses its indicating ability. The methylene blue chloride, although it adsorbs on the complex precipitate in the presence of excess VBTAC, serves mainly to accentuate the color change upon adsorption of the dichlorofluorescein.

D. Polysalt Interfacial Films

1. Unsupported Films

a. General Observations of Film Characteristics

Because of their extreme fragility, about half of the unsupported interfacial films broke while being removed from the wash solutions, even though considerable care was used in removing them. Wet films which were successfully removed from the wash solutions could be laminated to convex solid surfaces with good success, very few of them breaking before the laminations were completed. About half of the unsupported films placed in the dessicator to dry at 50% relative humidity survived until dry over about 70-90% of their surface areas. However, all but about 2% of the unplasticized films broke from shrinkage stress before they were completely dry. Films plasticized by the addition of 0.25-0.5% glycerin or dextrose to the wash water were much more stable during the final stages of drying, about 10% of them surviving for over a week when undisturbed. While a film was drying, a sharp gradation in thickness existed between the dry and wet portions of the films, indicating the tendency of the dry surfaces to become hydrophobic. Figure 26 is a sketch of the appearance of a typical film while drying.

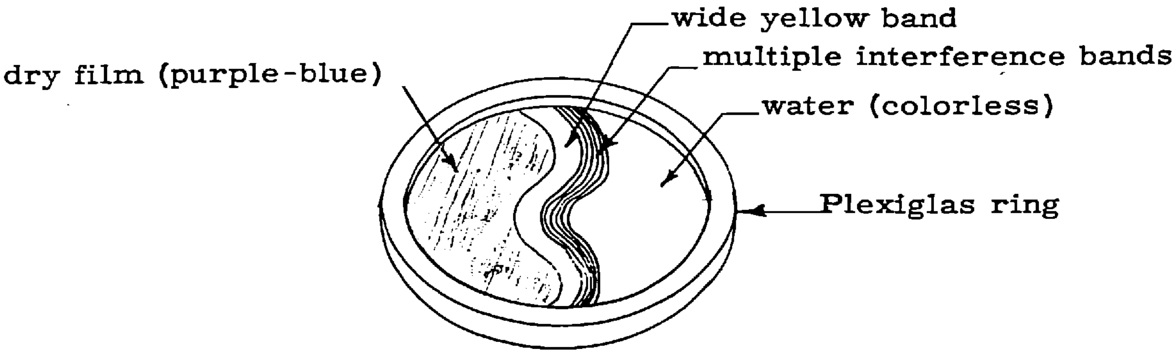

Figure 26. Appearance of Interfacial Films While Drying

The dry films were transparent, but in reflected light resembled "black" soap films. Films plasticized by the addition of more than 0.5-1.0% glycerin or dextrose to the wash water were thick enough, at least in places, to show interference patterns in reflected light, indicating that they were considerably thicker than the unplasticized films. The dried films adhered spontaneously and quite tenaciously to any solid surface with which they came in contact, a characteristic also observed for other polymer films below 0.22 microns in thickness (3). When the films broke, they contracted into fine white threads which were very weak and rather brittle.

Single films laminated to solid surfaces were invisible even by reflected light, but as multiple layers were built up, the reflected light color first became blue, then progressed through green to a light pink as further layers were added. The thickness of the films was evidently rather sensitive to humidity, because an 11-film laminate (the one used for thickness measurements) was green in color on a day when the relative humidity was about 40%, but pink on the following day when the humidity was 90%.

b. Electron Photomicrographs of Unsupported Interfacial Films

Figures 12 and 13 are electron photomicrographs of dry interfacial film surfaces. The films were chrome shadowed at an angle of approximately 18° from the film surfaces, so the shadow lengths (white areas) are three times the heights of the surface irregularities. The uniform texture of the surfaces is typical of amorphous polymers. Note that some holes or tears of about 1000-3000 Å diameter are present in the film surfaces. These tears probably initiate breakage of the larger film samples. The foreign material present in the lower middle of Figure 12 and the upper right hand corner of Figure 13 is probably some precipitate formed by reaction between the diluted excess polyelectrolyte solutions during the wash process. The rather uniform beaded structure certainly does not contradict the theory that in very dilute solutions the polyelectrolytes react principally by molecular pairing. The diameter of the beads in the "string" marked by the letter A in Figure 12 is about 150 Å, corresponding roughly to a pair of molecules of molecular weight 650,000 each (density 1.26 g/cc).

c. Film Thickness Measurements

Figure 14 is a plot of per cent reflectance vs. wavelength of monochromatic light incident on an 11 film laminate of interfacial films supported on a silvered, 1/2 inch diameter convex glass lens surface. The minimum in the reflectance curve and fairly steady rise thereafter are interpreted as follows: When monochromatic light strikes a thin, transparent film of material which is surrounded by media of lower refractive index, the light reflected from the upper surface of the film undergoes a 180° phase shift, destructively interfering with light reflected from the lower surface (at which no phase shift occurs), causing a reflectance minimum when the film thickness is a multiple of 1/2 the wave length of the light in the film (wave length of the light in air divided by the refractive index of the film). Similarly, the light reflected from the upper surface will be reinforced by the emergent light reflected from the lower surface when the thickness of the film is an odd multiple of 1/4 of the wave lnegth of the light in the film. The data indicate that the reflectance minimum is first order (i.e., 1/2 the light wavelength rather than a multiple of it), since there are no other peaks or valleys in the range of wavelengths used. The reflectance appears to be rising toward a peak at about 960 millimicrons where the film thickness would be 1/4 the light wavelength. Assuming the minimum at 480 millimicrons to be a true first order reflectance minimum, then the thickness of the 11-film laminate is 240 millimicrons divided by the refractive index of the films. Assuming a reasonable value of 1.5 for the refractive index (most polymers and ionic salts have refractive indices in the range 1.45-1.55), the thickness is about 160 millimicrons for the 11-film laminate, or 14.5 millimicrons (145 Å) per film. A more complete discussion of reflectance phenomena is given in Section B of Appendix B.

d. Interfacial Film Surface Anisotropy

Since the relative degrees of adhesion of methylene blue chloride (cationic) and kaolin (anionic) to the NaSS and VBTAC sides of the interfacial films were determined only qualitatively by visual inspection, no exact values of adhesion differences can be given. It is estimated that the adhesion of kaolin to the VBTAC sides of the films was about twice as great as its adhesion to the NaSS sides, and that the coloration of the NaSS sides of the films by methylene blue chloride was about twice as intense as the coloration of the VBTAC sides of the films. None of the surfaces were strongly colored by the dye or heavily coated by the kaolin particles. The coloration of dye-rinsed films, and the milkiness of kaolin-rinsed films were not very uniform, particularly on the surfaces originally in contact with polymer of the same charge as the rinse solution being used (kaolin on the "NaSS" surfaces or methylene blue chloride on the "VBTAC" sides), suggesting that the film surfaces may not have been sufficiently water-washed to remove all of the adhering polyelectrolyte. The film surfaces were all quite hydrophobic, indicating that if there was appreciable unreacted polymer on them, it was probably oriented with the ionic groups directed inward.

2. Diffusivities of Supported Interfacial Films Toward Microionic Salts

Table XI gives the values of diffusion rates of NaCl through filter papers and a millipore filter both before and after being treated to contain imbedded polysalt interfacial membranes. Within the limits of measurement accuracy (± 5%), there was no difference in the observed diffusion rates through the treated and untreated filters. This very high diffusivity toward NaCl indicates that very little, if any, cation/ anion barrier selectivity existed in the films because of residual surface polymer. The complete data for the measurements are given in Appendix B, Section C.

To determine whether greater barrier characteristics would be exhibited toward bulkier ionic species, some qualitative measurements were made using methylene blue chloride dye as the permeating species. It was found that about 1 1/ 2 hours were required before any dye could be seen entering pure water placed opposite a 1/ 2% solution of the dye when a treated filter paper was used, while only 30 minutes were required for visible dye permeation of the untreated filter paper. After the dye began to permeate the filter paper containing the imbedded interfacial film, however, it came through quite rapidly. Subsequent measurements showed that the film was no longer impervious to the flow of pure water, indicating that it was attacked and at least partially destroyed by the dye. Qualitative observations also indicated that the films were reasonably permeable to both dextrose and sucrose (5% solutions).

E. Polysalt Solubilities in NaBr-Acetone-Water Solutions

Figure 15 shows the range of sodium bromide, acetone, and water concentrations in which both VBTAC and NaSS could be dissolved without coreacting. The solubility limits shown apply to polyelectrolyte concentrations totalling 1% or less. At concentrations exceeding about 0.5% by weight of each polymer in the mixtures, gelation rather than precipitation occurred at the boundaries of the solution region, making it difficult to determine the exact limits of the region. Within minor limits, however, the boundaries do not change until the polyelectrolytes become sufficiently concentrated so that their counterions add significantly to the total salt concentration, thus shifting the solubility region toward lower salt concentrations. The same solubility limits apply to mixtures containing VBTAC and NaSS in the ionic ratios 2 VBTAC/ 1 NaSS and 1 VBTAC/ 2 NaSS as well as to mixtures containing equiequivalent amounts of the two polymers.

The solubilities are limited at high NaBr and acetone concentrations by salt-out of NaSS, as shown in Figure 15. The salt-out curve has been extended (dotted line) to show its position in the region where the polymers coreact ionically.

At salt concentrations above those marked by the dotted-line extension of the "complete shielding" curve, no interpolymer ionic reactions occurred, so VBTAC was leached out of (previously formed) polysalts and dissolved, leaving behind a skeleton of solid NaSS. The position of this dotted line was determined by observing polysalt fractionation during polysalt swelling measurements (see Section V-F).

The supper solid line on the diagram represents the mutual solubility limits of the three solvent components. At these compositions, the solutions separated into two liquid phases, one acetone-rich, the other water-rich.

The increase in NaSS solubility in the presence of small amounts of acetone (see NaSS salt-out curve) reflects the dualistic organo-ionic nature of the polyelectrolytes. The "complete shielding" curve shows clearly that the addition of acetone, even in small amounts, greatly enhances the ability of NaBr to suppress interpolymer reactions (polymer ionization), probably because of increased salt activity. From this latter observation alone, a decrease in the NaBr concentration required for NaSS salt-out would be anticipated even at very low acetone concentrations. Apparently, however, the addition of a limited amount of acetone sufficiently increases the solvent compatibility of the hydrocarbon portions of the molecules to more than compensate for the additional desolvation of the ionic groups. At higher acetone concentrations, the solubility of the NaSS decreases rapidly, and at about 50% acetone it is insoluble even in the absence of salt. The latter behavior is to be expected, since the hydrophil-lipophil balance of the polymers is such that they are very soluble in pure water, but almost completely insoluble in low-polarity organic liquids.

F. Properties of Polysalts Formed by Precipitation from NaBr-Acetone-Water Solutions

1. General Polysalt Characteristics

After final washing, the dried polysalts were amber, transparent solids. Flame tests made on the polysalts indicated that the VBTAC-rich and neutral polysalts were almost completely free from residual sodium ions, while the NaSS-rich samples gave brilliant, long-lasting sodium flames. No visible precipitate formed upon the addition of silver nitrate to tenth molar sodium nitrate solutions equilibrated with samples of the NaSS-rich and neutral polysalts, but dense AgBr precipitation was obtained from sodium nitrate solutions equilibrated with VBTAC-rich polysalts. The surprising lack of residual sodium or halide ions in the neutral polysalts indicates that the polymers were able to rearrange during the washing and drying processes to allow almost complete ionic reaction to occur. The silver nitrate tests were not as sensitive as the sodium flame tests, and it is estimated that 1-2% residual halide could have remained undetected in the samples. Also, small amounts of residual sodium and bromide ions may have been removed from the polysalts by ion-exchange with dissolved carbonic acid rather than by interpolymer reactions, since no attempts were made to prevent CO_2 absorption by the (demineralized) wash water.

The polysalts were very moisture sensitive, and shattered into small fragments if suddenly exposed to normal room air after being dried over phosphorous pentoxide. For this reason, most of the physical property measurements were made on polysalt samples dried only to 50% relative humidity.

The densities of the dried polysalts were measured to be 1.26 g/cc (neutral polysalt) to 1.28 g/cc (polysalt composed of 2VBTAC/1 NaSS).

When immersed in various NaBr-acetone-water solutions, the polysalts became opaque whenever they absorbed their own (dry) weight or more of solution (see Section V-F-4), but became transparent again when dried. A VBTAC-rich polysalt, rendered opaque by equilibration with water, remained opaque when subsequently equilibrated with acetone, and did not become transparent when dried. When dried after being re-equilibrated with water, however, the sample returned to its original transparency. The experiment illustrates that the opacity was due to porosity or other heterogeneities in the polysalt which usually disappeared upon drying because of structural rearrangement, probably ionic bond transfer by internal ion exchange between the VBTAC ion-bonded to the NaSS and the unreacted (excess) VBTAC. The acetone prevented this structural rearrangement because it desolvated the ions to the extent that bond transfer could not occur. A further discussion of polysalt structural rearrangement is given in connection with polysalt swelling hysteresis in Section V-F- 4.

2. Oriented Polysalt Fibers and Films

The oriented polysalt films obtained by 2-5X unidirectional stretching of partially precipitated polysalt gels were transparent, noncontractile solids after being washed with water and dried. The film structures were quite highly oriented as evidenced by the high degree of birefringence which they exhibited in polarized light. However, no crystallinity could be detected by X-ray scattering measurements. The most striking characteristic of the films was their highly fibrous structure, reminiscent of the asbestos minerals. Figure 16 is a photomicrograph of a segment of a neutral polysalt film, showing fibers pulled loose from the film at a tear. The smaller fibers have diameters of 0.5-1.0 microns, but it is possible that the strands were further divisible. This fibrous character may be a macroscopic manifestation of molecular pairing which, after film orientation, could result in bundles of paired molecules attached to the surrounding structure by only a few bridging molecules. Another possibility is that there were many small, undetected pores in the gels which became elongated during the orientation, giving apparent fibrous structures to the films.

The filaments drawn from solvated VBTAC-NaSS liquid mixtures and gelled by acetone evaporation had characteristics somewhat different from those of the oriented films. After being washed briefly with water, dried, and rewetted, the filaments could be oriented by stretching a maximum of about 1.5 to 2 X. While being stretched, the filaments tended to "neck down" to somewhat smaller but still uniform diameters, and had no tendency to return to their original lengths. They were flexible and transparent, but did not exhibit any of the fibrous character of the oriented films. The filaments were also birefringent but noncrystalline. A filament with a diameter of 0.14 mm supported a load of 60 grams before breaking, corresponding to a breaking stress of about 6,000 psi. Although this is not a high strength for a filament, it represents an estimated 2- to 3-fold increase in strength over the unstretched filaments.

3. Electrical Properties of Polysalts

The measured dielectric constants, volume resistivities, and loss factors of polysalts composed of VBTAC:NaSS in the ionic ratios 2/1, 1/1, and 1/2 at both 50% and 0.0% relative humidity, and room temperature are tabulated in Table XII. The high dielectric constants at low frequencies of the sulfonate-rich polysalt at 50% humidity (13% moisture content), and of the quaternary-rich polysalt at both 50% humidity and 0.0% humidity indicate that interfacial polarization was taking place. This type of polarization occurs in heterogeneous materials where the components of the structures have different dielectric constants and conductivities. The effect is brought about when ions or electrons pile up at the interfaces of the components during each alternation of the applied electric field. If the frequencies had been reduced to sufficiently low values, the dielectric constants would have eventually leveled off and become constant. The relative absence of interfacial polarization in the neutral polysalt indicates that the structural heterogeneity is due primarily to the presence of excess unreacted polymer in the non-neutral polysalts. Apparently, the non-neutral polysalts are quite highly segregated into regions of neutral polysalt and excess unreacted polyelectrolyte. The dimensions of the regions cannot be determined from the measurements made, but comparison with literature values given by Von Hippel (38) shows that the dielectric constant-frequency behavior of the quaternary-rich polysalt at 50% humidity is similar to the behaviors of such heterogeneous materials as beefsteak, and rubbers compounded with carbon black (both measured at 0.0% humidity).

Since orientation of the components in the electrical field lags the applied voltage in regions of changing dielectric constant, electrical energy is absorbed during each alteration, and dissipated as heat (33). The loss factor, ϵ'', is a measure of this anomalous dispersion, and is proportional to the conductance G" of a resistor that would dissipate the energy lost in the anomalous dispersion;

$$\epsilon'' = G''/(2\pi f C_o)$$

where f is the applied a-c frequency (cps) and C_o is the geometric capacitance of the material (i.e., the capacitance of a condenser using as its dielectric a volume of air or vacuum of the same dimensions as the sample of material in question). The loss factors are related to the dielectric constants, rising to maxima at the points of maximum rate of change of dielectric constant with frequency. Examination of Table XIII shows that, except for the neutral polysalt at 0.0% humidity, the ϵ'' values are decreasing with increasing a-c frequency, indicating that the maximum rates of change of dielectric constant occur at frequencies below the ranges measured, so the ultimate low-frequency dielectric constants are probably at least twice as great as the highest values measured. The rising loss factor of the neutral polysalt at somewhat higher frequencies probably represents the beginnings of dipole polarization of the quaternary-sulfonate ion pairs.

The rather low volume resistivities of the NaSS-rich and VBTAC-rich polysalts reflect the current carrying capacities of the unpaired polyions, especially when hydrated. The volume resistivities of the neutral polysalt at 0.0% humidity are quite high, being comparable to those of bakelite, which has a volume resistivity of 2×10^{11} ohm-cm at 100 cps (38).

4. Swelling of Polysalts in NaBr-Acetone-Water Solutions

Figures 17, 18 and 19 are triangular diagrams which show the amounts of NaBr-acetone-water solutions absorbed by the polysalts in grams of solution absorbed per gram of dry polysalt. The lines labeled "complete shielding" (see Figure 15) represent the limiting NaBr concentrations above which complete suppression of polyelectrolyte ionic interactions occurred. The data are replotted in Figures 20, 21, and 22 to show the amounts of polysalt swelling at constant external solution NaBr concentrations. The curves apply to samples dried at 50% humidity before swelling (although swelling values are relative to bone dry weights), and were reproducible to about ± 5% below about 0.7 g. solvent absorbed per g. dry polysalt, and to about ± 20% above 1.0 g. solution absorbed per g. dry polysalt. The amounts of swelling of the neutral polysalts in water-acetone solutions were independent of the degree to which the samples were dried (0.0 or 50% humidity) before being immersed in the solutions, but swelling of the non-neutral polysalts was as much as 65% lower* after the samples

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* After being repeatedly swelled in water and water-acetone solutions with intermediate drying to 50% humidity, a sample of VBTAC-rich polysalt originally dried over P_2O_5 approached the same degrees of swelling as samples never dried below 50% humidity (see Table XIII and Figure 23).

were dried over P_2O_5.

It is interesting to note (Figures 20, 21 and 22) that although acetone alone was incapable of swelling the polysalts at all, solutions containing up to 40% acetone in water induced greater swelling of the polysalts than water alone. In separate experiments--the results of which are given in Table XIII and Figure 23--VBTAC-rich polysalt samples which had been immersed in 20% aqueous acetone solutions were placed in pure water without intermediate drying. The swelling of the samples increased slightly* rather than decreasing to the values obtained when the dried polysalts were equilibrated with water(see Figure 23, steps 3-4-5, and 7-8-9). After the samples were dried to 50% humidity, however, their water swellability decreased again. These results show that the enhanced swelling in the presence of acetone was definitely due to rearrangements in the polysalt structures into more expandable forms. The following mechanism is probably responsible.

When the polysalts are precipitated from the ternary solvent, the initial gelation is presumably due to random interactions between marginally unshielded molecules. As the hardening process proceeds, the molecules rearrange by ion transfer and molecular uncoiling into a structure thermodynamically more compatible with the less saline environment. By the time final drying has taken place, the polymers have achieved maximum ionic interaction. The non-stoichiometric polysalts are apparently segregated into regions of essentially neutral polysalt plus regions of unreacted excess polyelectrolyte (see Section V-F, 3). This heterogeneity of structure is produced by the same

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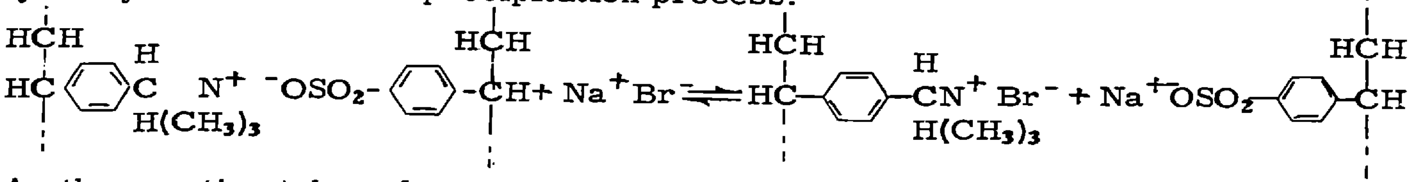
* These slight increases in swollen weights could be accounted for by replacement of internally absorbed acetone by water (which is denser), so the swollen volumes of the samples probably did not increase.

thermodynamic forces which induce micelle formation in surfactants: The interacted portions of the molecules, being relatively hydrophobic, are drawn together and tend to exclude water, whereas the molecular segments containing unreacted polyions are drawn into the more hydrous regions of the mixture. This tendency becomes strongest as the total water content becomes low, since at this time the repulsive forces between polyions of like charge are diminished due to the high counterion concentration, and the counterions compete strongly for the available water of hydration. Rearrangement ceases when the water content becomes sufficiently low so that the molecules are immobilized sterically. When the dried polysalts are equilibrated with water they swell, and at least some reverse structural rearrangement into a more homogeneous, expanded configuration takes place by ionic bond transfer between the unreacted and (previously) reacted polyions. At sufficiently high degrees of swelling, the osmotic expansion forces become low enough relative to the homopolar associations between the organic portions of the molecules in the neutral regions so that the latter are able to prevent further bond rearrangements. In the presence of acetone, however, the nonionic association forces are reduced because of increased solvent compatibility of the organic portions of the molecules. This increases the lability of the neutral regions and allows further bond transfer and structural rearrangement to occur. If the acetone is replaced by water, the homopolar association forces will again increase, making further swelling virtually impossible.

Figures 21 and 22 show that the swelling of polysalts containing excess amounts of NaSS or VBTAC is greatly suppressed by the addition of small amounts of NaBr to the acetone-water solutions, the swelling reaching a minimum at about 2% by weight of NaBr in the external solutions. This is due to the ion exclusion or Donnan equilibrium effect which requires that the activity of an ionic species be the same within the polymer phase as in the equilibrium external liquid. Since the non-neutral polysalts already contain high internal concentrations of sodium or bromide ions present as counterions to the excess polymer molecules, the salt in the external solution is prevented from entering the polysalts, but competes with them for water, thus reducing their swelling.

The neutral polysalt contains no excess polymer so it does not exhibit an ion-exclusion effect. On the contrary, it absorbs enough salt so that the internal salt concentration is greater than the external salt concentration (see Figure 24). This absorption takes place primarily at the points of mutual ionic interaction of the polyelectrolytes by reversal of the precipitation process:



As the reaction takes place, the degree of ionic cross-linking is automatically reduced, allowing polysalt swelling to increase. This reaction must also take place at the quaternary-sulfonate sites in the non-neutral polysalts and, at NaBr concentrations above 2% in the external solutions, the resultant decrease in ionic crosslinking allow increased polysalt swelling to occur in spite of the ion exclusion effects of the excess polyelectrolytes.

At most of the added salt concentrations the data show that polysalt swelling drops off at sufficiently high acetone concentrations. This is probably due to exclusion of acetone from the polysalt phase, which produces a dehydration effect analogous to the dehydrating effects arising from ion exclusion by the non-stoichiometric polysalts (polysalt acetone-exclusion is discussed in more detail in the next section). Dotted line extensions have been added to some of the data curves to show the estimated acetone concentrations at which decreases in swelling will begin to occur.

5. Sodium Bromide Absorption by Polysalts Equilibrated with NaBr-Acetone-Water Solutions

In addition to the swelling measurements, the amounts of salt absorbed by the polysalt samples from some of the NaBr-acetone-water solutions were measured. The results of these measurements are tabulated in Tables XIV and XV and shown graphically in Figure 24. The data are replotted in Figure 25 as the ratio of internal to external salt concentrations vs. per cent acetone in the external solution. In this plot the internal salt concentration c_i is the weight fraction of salt in the liquid absorbed by the polysalt samples, and the external salt concentration c_o is the weight fraction of NaBr in the external solution, and is the parameter.

At low salt concentrations (2% NaBr = 0.2 M NaBr), the internal salt concentrations in the neutral polysalt are much higher than the external salt concentrations, even in the absence of acetone. At least some of the salt is absorbed at the double polyion sites by reversal of the precipitation reaction. This absorption is undoubtedly promoted most strongly at the double polyion sites which are strained because of steric hindrances in the structure. In the absence of acetone, the drive for this internal stress relief may be the primary reason that the internal salt concentrations are greater than the external salt concentrations (the ion exchange selectivities are more favorable for the formation of quaternary-sulfonate than quaternary-bromide and sodium-sulfonate ion pairs). The data are compared below in Figure 27 to the NaCl absorptions by a snake-cage polyelectrolyte resin reported by Hatch, et. al (21).

The ion exclusion effect of the excess polyelectrolyte in the VBTAC-rich polysalt greatly reduces its salt absorption capacities at low salt concentrations. The markedly increased salt absorption at higher salt concentrations is due partly to decreased ion exclusion upon dilution of the excess quaternary polymer with increased polysalt swelling, and probably also partly to increasing ability of neutral

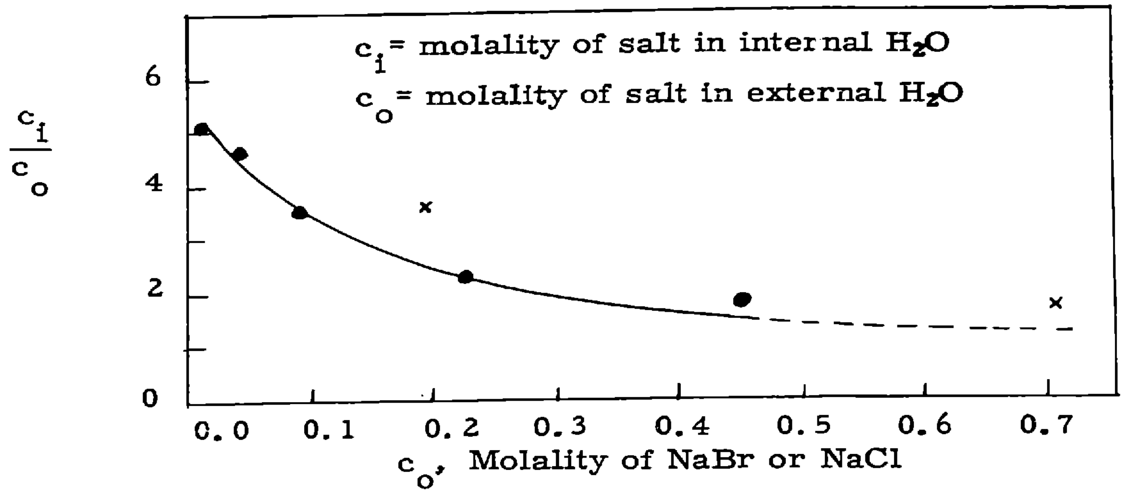


Figure 27. Comparison of NaBr Absorptions by a Neutral Polysalt with NaCl Absorptions by a Polyacrylate-Dowex 2 (Polyquaternary Ammonium) Snake-Cage Resin (21). (o), NaCl Absorption by Snake-Cage Resin; (x), NaBr Absorption by Neutral Polysalt

regions in the polysalt to absorb NaBr independently of the adjacent ion-excluding regions.

The greatly enhanced salt absorptions by both polysalts in the presence of added acetone can be explained as follows: The activity coefficient of NaBr in aqueous acetone solutions is higher than its activity coefficient in pure water. That this is so can be seen from the fact that NaBr is less soluble in acetone-water solutions than in pure water. If the polyelectrolytes behave at all similarly to the corresponding ion exchange resins (see Figure 28 below), then acetone is excluded from the resin phase. If this is the case, then as acetone is added to the external phase, the equilibrium internal salt concentrations will increase relative to the external salt concentrations until the activity of the salt is the same in both phases. The increased internal salt concentrations cannot be due entirely to increased salt absorption tendencies of the double polyion sites in the presence of acetone, since the amounts of internal NaBr exceed the maximum possible absorption capacities of the polysalt ionic sites in some cases (see Tables XIV and XV).

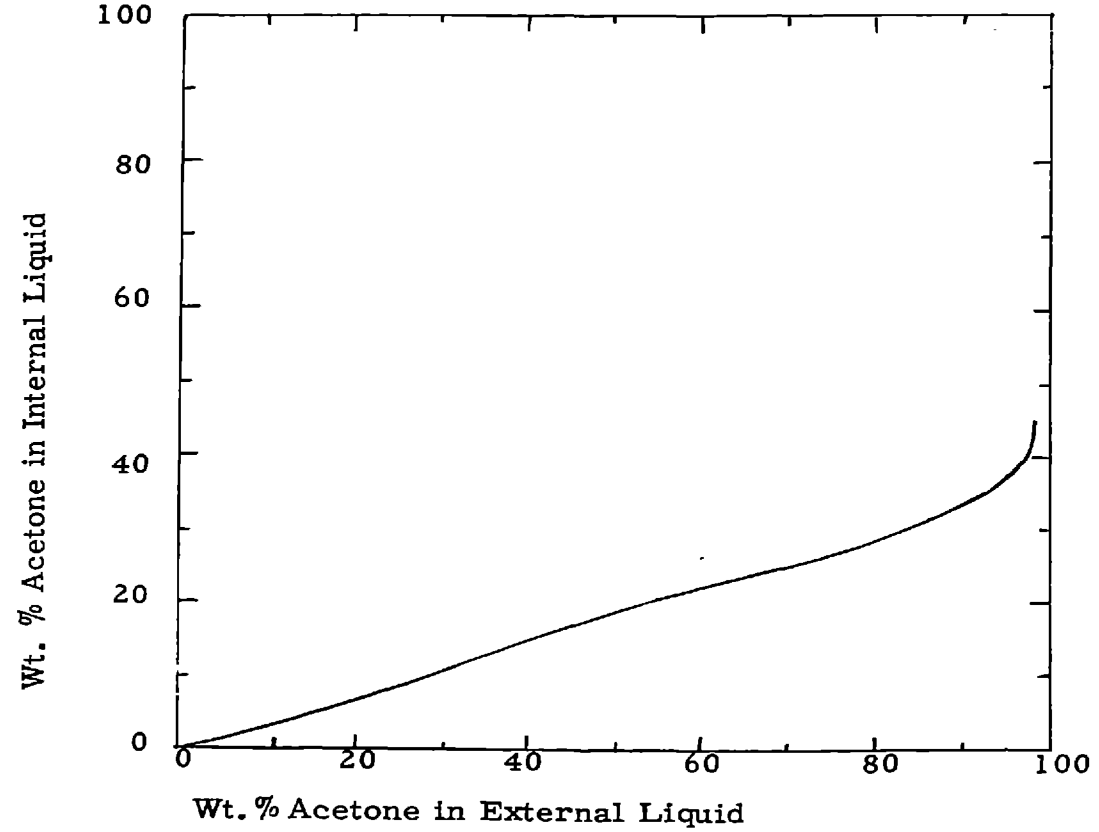


Figure 28. Exclusion of Acetone from Sulfonated Polystyrene (10% cross-linked) in Contact with Aqueous Acetone Solutions (22, 5)

6. Potassium/ Sodium Absorption Selectivity of Neutral Polysalt

Table XVI shows the relative amounts of NaCl and KCl absorbed from an N/ 10 equimolal aqueous solution of the two salts, and the fraction of the polysalt ionic sites occupied. The K/ Na selectivity ratio of 1.26/ 1 is in good agreement with a similar measurement performed by Sujata (35) on Dowex 50 ion exchange resin (essentially NaSS except in the hydrogen form). He found the selectivity for potassium over sodium to be 1.52/ 1. The agreement is probably better than the numbers indicate, since selectivity decreases with decreasing resin-phase ion concentration. Thus, the double polyelectrolyte environment does not markedly affect the cation absorption selectivity of NaSS, at least in the case of the two cations investigated.

7. Minimum NaSS and VBTAC Concentrations for Gelation of Shielded Mixtures

Table XVII shows that the ability of shielded VBTAC-NaSS solutions to gel was not dependent on the relative amounts of the two polymers in solution, at least up to a ratio of 30/ 1 of one polyelectrolyte over the other. The important variable was the concentration of the more dilute polymer. Gelation could not be induced at VBTAC concentrations below about 0. 5% by weight of the mixtures, or at NaSS concentrations below about 0. 2% by weight of the mixtures. Polysalts formed from mixtures containing VBTAC/ NaSS in ionic ratios 10/ 1 and 1/ 10 released excess polyelectrolyte into solution quite rapidly when contacted by water. These polysalts, after drying, absorbed 20-50 time their weight of water to yield transparent, rather weak gels. Although no experiments were made on polysalts containing the two polymers in ionic ratios between 2/ 1 and 10/ 1, it is probable that the polysalts are not compositionally stable in water at VBTAC/ NaSS ratios much above 2/ 1 or below 1/ 2.

Assuming that the polyelectrolytes in highly saline solutions behave as charged spheres of the approximate dimensions of random coils, the minimum gelation concentrations can be predicted. It has already been calculated (see footnote, Section III-B) that the randomly coiled end-to-end extension, $\sqrt{\overline{r_o^2}}$, of a VBTAC or NaSS molecule of molecular weight 500, 000 is approximately 354 Å. Flory (11) has shown that the root-mean-square distance, $\sqrt{\overline{s^2}}$, of a chain element from the center of gravity of a randomly coiled molecule is

$$\sqrt{\overline{s^2}} = \sqrt{\overline{r_o^2}/6} = 0.425\sqrt{\overline{r_o^2}}$$

It can also be readily shown that for a sphere, the root-mean-square distance of a volume element from the center of gravity is 0.775 r, where r is the radius of the sphere. Thus, the outside diameter, D, of a randomly coiled, spherical VBTAC or NaSS molecule of Mw 500,000, is given by

$$D = \frac{2}{0.775}\sqrt{\overline{s^2}} = \frac{2}{0.775}\left(0.425\sqrt{\overline{r_o^2}}\right)$$

$$= 390\ \text{Å} \text{ for } \sqrt{\overline{r_o^2}} \text{ of } 354\ \text{Å}$$

For gelation, the average spacing between the molecules of the more dilute polyelectrolyte species must be such that the molecules of the oppositely-charged species are able to bridge between them. The limiting concentration will thus be such that the solution volume per molecule of the more dilute species will be a sphere of twice the diameter of the randomly coiled molecule, or about 800 Å:

$$\text{Volume per molecule} = \frac{1}{6}\pi(2D)^3 = \frac{\pi}{6}(8\text{x}10^{-6})^3 = 268\text{x}10^{-18}\ \text{cm}^3/\text{molecule}$$

$$\text{Limiting polymer conc.} = \frac{5\text{x}10^5}{6.02\text{x}10^{23}}\ \frac{\text{g}}{\text{molec}}\ \text{x}\ \frac{1}{268\text{x}10^{-18}}\ \frac{\text{molec}}{\text{cm}^3}$$

$$= 3.1 \text{ x } 10^{-3}\ \text{g/cc} = 0.31\ \text{g/dl}$$

The calculated minimum gelation concentration of 0.31 g/dl is in good agreement with the measured minimum gelation concentrations of 0.5 g/dl for VBTAC, and 0.2 g/dl for NaSS.

VI. CONCLUSIONS

1. In dilute (<0.2 g/dl), salt free aqueous mixtures, the interactions between poly(vinylbenzyltrimethyl ammonium chloride) and poly(sodium styrene sulfonate) are ionically complete within ± 3% and, if the mixtures are passed through their ionic equivalence points, the reactions are stoichiometric within ± 5% regardless of the ratio of the polyelectrolytes being mixed. These rather surprising stoichiometric relations lead to the conclusion that molecular pairing occurs between NaSS and VBTAC, which have similar structures and identical ionic spacings.

2. In the presence of added sodium bromide (≥ 0.01 M), the interactions are no longer soichiometric, but instead complete mutual precipitation of both polyelectrolytes occurs over a considerable range of relative concentrations of the two polymers (VBTAC/ NaSS ionic equivalence ratios in the approximate range 0.82-1.54). It is presumed that under these conditions, molecular pairing is inhibited or substantially decreased because the salt-induced suppression of polymer ionization results in sufficient molecular coiling to sterically prevent many of the polyions from reacting.

3. The polysalt interfacial films which form between more concentrated (>0.6 g/dl) aqueous solutions of VBTAC and NaSS can be isolated from their polyelectrolyte environments. They are approximately 150 Å in thickness when dry, exhibit the microadhesive properties of other polymer films below 0.22 microns in thickness, and have very high diffusivity toward low molecular weight electrolytes (NaCl), but lower diffusivity toward larger ionic species (methylene blue chloride). The dry films are rather hydrophobic, but tend to retain small amounts of excess unreacted VBTAC or NaSS on the surfaces in contact with VBTAC and NaSS solutions, respectively, at the time of formation.

4. Fairly large quantities (10 g/ dl) of both VBTAC and NaSS can be dissolved in a ternary solvent comprised of ca. 20% by weight acetone, 20% NaBr, and 60% water. By suitable washing and drying techniques, these mixed-polyelectrolyte solutions can be gelled, and hardened into continuous, transparent polysalts free of extraneous electrolyte. Stable polysalts containing fairly large excesses of either polyelectrolyte (2VBTAC/ 1NaSS to 2 NaSS/ 1 VBTAC) can be obtained by this route.

5. Polysalts composed of equiequivalent quantities of VBTAC and NaSS exhibit the following properties:

a.) When thoroughly washed with water they are almost completely free from extraneous microions, and interpolymer reaction is sufficiently complete so that less than 1% of the Na^+ or Cl^- ions originally associated with the polyions remain in the washed polysalts.

b.) They are structurally quite homogeneous, exhibiting only small amounts of interfacial polarization in low frequency a-c fields. When dried over P_2O_5, they have sufficiently high volume resistivities (2.3×10^{11} ohm-cm at 100 cps) to make them potentially useful as electrical insulators.

c.) Their equilibrium swelling in acetone-water mixtures varies from 0.38 g. solution absorbed per gram dry polysalt in pure water to a maximum swelling of 0.42 g. solution/ g. polysalt in 20-30% aqueous acetone, diminishing to 0.0 g. solution/ g. polysalt in 100% acetone. The slightly increased swelling at low acetone concentrations is attributed to enhanced solvent affinity for (and hence decreased homopolar associations between) the nonionic portions of the polymer molecules. Their swelling is independent of previous swelling or drying history.

d.) Polysalt swelling is increased at all acetone concentrations by the addition of even small amounts of NaBr to the solutions. The increased swelling is due to decreased ionic cross-linking caused by absorption of the sodium and bromide ions as counterions at the double polyion sites (reversal of the precipitation process). By this mechanism of "internal ion exchange" the neutral polysalts are able to selectively sorb microionic salts (NaBr, KCl, NaCl) from aqueous solutions, the salt concentrations in the internally absorbed water being over three times the external salt concentrations at low (ca. 0.2 molar) external salt concentrations. Salt absorption is markedly increased by the addition of acetone to the external solutions. This is attributed to increased external solution salt activity coupled with exclusion of acetone from the polymer phase.

6. Polysalts composed of VBTAC and NaSS in the ionic ratios 2VBTAC/ 1 NaSS and 2 NaSS/ 1 VBTAC exhibit the following characteristics:

a.) After thorough washing with water, no detectable residual halide ion remains in the NaSS-rich polysalts, and no residual sodium ion remains in the VBTAC-rich polysalts, indicating that interpolymer ionic reactions are complete.

b.) They are structurally inhomogeneous, exhibiting high dielectric constants and loss factors (interfacial polarization at low a-c frequencies. The structures are apparently segregated into zones of essentially neutral polysalt and zones of unreacted polyelectrolyte. When dried over P_2O_5 their volume resistivities are only 1/ 10 (NaSS-rich) to 1/ 1000 (VBTAC-rich) as high as that of the neutral polysalt.

c.) Their steady-state swelling in acetone-water mixtures after being dried at 50% relative humidity varies from about 3 (VBTAC-rich) or 6 (NaSS-rich) g. solution absorbed per g. dry polysalt in pure water, to maxima of 5(VBTAC-rich) or 9 (NaSS-rich) g. solution per g. polysalt in 20-30% aqueous acetone solutions, and to minima of 0.0 g. solution per g. polysalt in pure acetone. The amount of swelling in a given solution is strongly dependent on the previous swelling and drying history of the polysalt. The latter behavior, and the markedly enhanced swelling in 20-30% acetone solutions are attributed to structural rearrangements by a mechanism of ionic bond transfer between the reacted and unreacted polyelectrolyte molecules (or molecular segments) in the polysalts.

d.) Their swelling is greatly decreased by the addition of small amounts (2%) of NaBr to the external solutions, because of the ion exclusion effect of the excess polyions. At higher salt concentrations swelling again increases as the degree of ionic cross-linking is reduced by absorption of salt at the double polyion sites. Salt absorption from dilute aqueous NaBr solutions is markedly less than that of the neutral polysalt, again because of the ion exclusion effect. If acetone is added to the external solutions at constant NaBr concentrations, salt absorption is increased, approaching or exceeding that of the neutral polysalt.

7. Before final washing and drying of the polysalts being precipitated from the mixed-solvent system, the polysalts are elastic gels which can be oriented by unidirectional stretching 3-5X or more. After being hardened by washing (with water) and drying, the oriented polysalts are birefringent but non-crystalline, flexible, transparent solids which have highly fibrous structures. The fibrosity suggests the possibility that molecular pairing can occur even in polysalts precipitated from highly saline solutions.

VII. RECOMMENDATIONS FOR FURTHER WORK

Since the present work has been of an exploratory nature, all of the areas studied lend themselves to further investigation. The recommendations below are divided into four categories: 1), general recommendations concerning treatment and handling of polyelectrolytes; 2), further studies of dilute solution interactions; 3), further studies of interfacial film properties; and 4) further studies of the properties of polysalts precipitated from ion-shielded solutions.

1) General Recommendations Concerning Treatment and Handling of Polyelectrolytes

a. Purifications

The demineralizing resin purification method offers a rapid, convenient, and powerful method for removing microionic impurities from aqueous polyelectrolyte solutions. However, the hydrogen form of NaSS, and no doubt also the hydroxide form of VBTAC (which are produced by ion-exchange with the demineralizing resin) are not compositionally stable, especially at high polymer concentrations or elevated temperatures. It is therefore recommended that the polyelectrolytes be returned to the more stable forms as rapidly as possible after contact with the resin. This could be accomplished by titrating the demineralized solutions with NaOH (NaSS) or HCl (VBTAC) to neutral endpoints, using a pH meter as an endpoint indicator. Another method would be to contact the solutions repeatedly with small batches of fresh ion exchange resins of the desired ionic forms until all of the hydrogen or hydroxide counterions were removed from the polyelectrolytes.

Isolation of the purified samples as dry powders could be accomplished by precipitating them from solution with adverse solvents such as acetone or other low-polarity organic liquids. Evaporation of aqueous solutions to dryness should be done in vacuo at reduced temperatures to avoid thermal or bacterial degradation of the polymers.

b. Equivalent Weight Determinations

The equivalent weight of NaSS might better be determined by a sulfur ignition gravimetric method than by hydrogen counterion titrations. Flame photometric sodium determination is also to be recommended, but requires a flame photometer with a constant volumetric feed rate apparatus for viscous liquids.

c. Viscosity Measurements

The measured viscosities of the polyelectrolyte solutions used in this study, particularly the NaSS, were found to be somewhat dependent on the previous dilution history of the samples and the age of the solutions. Care should be taken that any direct viscosity comparisons (e.g., between mixture supernatant liquid and control sample viscosities) be made on solutions with identical dilution histories and of equal ages. For very accurate measurements, the use of a Couette viscometer operated at very low shear rates would be advantageous, since polyelectrolyte solution viscosities are known to be quite shear dependent.

2) Further Studies of Dilute Solution Interaction Stoichiometry

The hypothesis that molecular pairing occurs between the two polyelectrolytes used in this investigation could be substantiated (or disproved) by types of measurements other than those made to date. Electron photomicrographs of precipitates prepared by combining the polymers at varying relative and absolute concentrations, both in the presence and absence of added microionic salts should help to establish the mechanism by which the polymers combine. More accurate measurement techniques are needed to determine the limits of approach to stoichiometric and complete VBTAC-NaSS ionic interaction in salt-free solutions, especially in mixtures not passed through their ionic equivalence points, and over long periods of time. More accurate viscosity measurements could be made with a Couette viscometer operated at very low shear rates. Polyelectrolyte interaction stoichiometry could also be studied by carefully controlled conductivity measurements made both on dilute solutions of individual polyelectrolytes and on polyelectrolyte mixtures. This method would utilize the fact that the activity coefficients of polymer counterions are generally much lower than the activity coefficients of the same ions present at comparable concentrations in solutions containing only microions. The method has the advantages of being rapid and convenient, and could be used to continuously monitor changes in solution properties with changes in mixture compositions. Studies of the interactions occurring between polyelectrolytes with different polyion spacings should also help to clarify the role of molecular pairing in dilute solution interactions.

It is also recommended that fractionated polymer samples be used in future work, to determine if low molecular weight fragments play a major role in producing stoichiometric and ionically complete interpolymer reactions.

3) Further Studies of Interfacial Film Properties

The study of polysalt film properties constitutes one of the most intriguing and least investigated areas of study. A more reliable method for isolating and washing the unsupported interfacial films should be developed. The mechanism of film formation, and the factors which control film composition, thickness, permeability and strength should be investigated. Individual film thickness measurements could probably be made most rapidly and easily by the use of a polarized light ellipsometry apparatus. The use of radioactive counterions on the polyelectrolytes could be used to establish both the presence and concentrations of residual unreacted polyions in the films. Electron photomicrographs of films made under varying conditions should help to establish the mechanism of film formation.

All of the film properties cited above--composition, thickness, permeability, strength--could probably be made to vary widely by varying the polyelectrolyte and added salt concentrations, and solvent compositions of the solutions between which the films are formed (i. e., by varying the molecular configurations, concentrations, and degrees of ionization of the polyelectrolytes at the time of reaction).

4) Further Studies of the Properties of Polysalts Precipitated From Ion-Shielded Solutions

Further studies of the properties of continuous macroscopic polysalts would probably be most profitably directed toward developing specific practical applications for the materials which would utilize their unique properties. The investigations made to date have indicated that the neutral polysalts are better salt absorbers under some conditions than are the corresponding ion-retarding resins. Further investigations are necessary to determine the ability of the polysalts to absorb a variety of salts, and to determine the ease with which the absorbed salts could be eluted by water-washing. Another interesting study would be to prepare strong, elastic polysalts (by plasticization and/or introduction of nonionic cross-linking, etc.) and then determine whether the polyion salt absorption could be markedly increased by stressing the polysalts, and if so, whether or not the salt so absorbed could be released by relaxation of the applied stress with the polysalt submerged in an environment of higher salinity. If the postulated behavior could be made to occur, the polysalts might be useful for water desalinization.

VIII. APPENDIX

APPENDIX A--Additional Results and Discussions

A. Additional Results

Some additional a-c and d-c electrical measurements made on polysalt samples are discussed below. Since film thickness, areas of electrical contacts, and sample purities were not measured or carefully maintained, the data are not amenable to quantitative, or even very meaningful qualitative interpretation at this time. For this reason the data were omitted from the main body of the report, but are included here with the thought that the information may be useful in the interpretation of results of future experiments.

1. Semiconductivity of a VBTAC-Rich Polysalt Film

The d-c electrical conductivity of a thin precipitated polysalt film containing VBTAC/ NaSS in the weight ratio 2/ 1 was measured at 50% humidity and 25°C. It was found that the film exhibited a 4-fold difference in conductivity upon polarity reversal of the applied potential.

The film was made by dipping a platinum wire into a solution containing approximately 2% by weight of VBTAC and 1% NaSS in a solvating mixture of NaBr, acetone, and water. The thin liquid coating was allowed to harden by drying and was then washed with water to remove the sodium bromide, and redried. A 0.01 in. diameter platinum wire was wrapped in spiral fashion around the polysalt film. This assembly was connected into an electrical circuit as shown in Figure 29.

With the negative terminal of the battery connected to the heavy (inside) platinum wire, and the positive terminal connected to the outside wire, a steady state current of 2.8 ma. was reached after one hour. With the polarity reversed, the steady state current was 0.65 ma. These currents correspond to resistances of 8000 ohms and 33,600 ohms, respectively, for the film.

Further measurements showed that the film was unable to rectify alternating currents of frequencies as low as 20 cycles per second, indicating that the resistance changed rather slowly after polarity reversal. This slow change in resistance suggests that the effect was due to some type of ion migration within the polymer film.

A second set of measurements was made to determine the effects of an applied d-c potential on the subsequent a-c resistance of the film. The results are given below in Table XVIII and Figure 30.

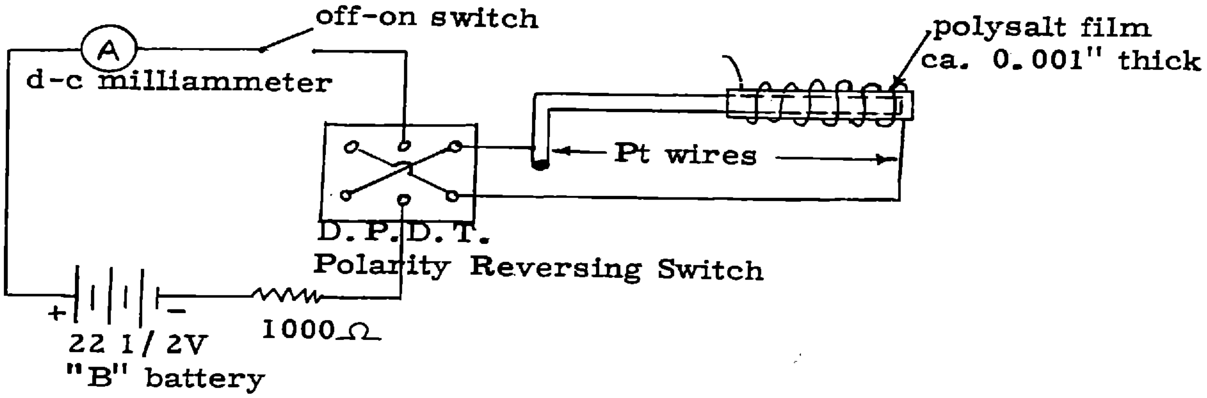


Figure 29

Table XVIII: a-c resistances (1000 cps, approx. 0.5V) of a VBTAC-rich polysalt film preconditioned by an applied d-c potential of 22.5 volts. Film was placed in dessicator maintained at 50% relative humidity and room temperature.

d-c treatment prior to a-c resistance measurement	Time from start of a-c resistance measurements, minutes	a-c resistance ohms x 10^{-2}
1. d-c pretreated with polarity applied for minimum film resistance (see text for polarity notation) for 10 min. d-c $\text{current}_{\text{max}} = 1.17$ ma	0	150
	0.25	280
	0.5	295
	1.0	255
	1.5	208
	2.0	190
	2.25	185 (minimum)
	3.0	195
	5.0	265
	10.0	495
2. d-c pretreated with polarity applied for maximum film resistance for 10 min. d-c $\text{current}_{\text{min}} = 0.6$ ma	0	<200
	0.5	435
	1.0	440
	1.5	425
	2.0	420
	3.0	480
	5.0	610
	10.0	940
No pretreatment, film left for 20 hours with no applied potential	"∞"	2000

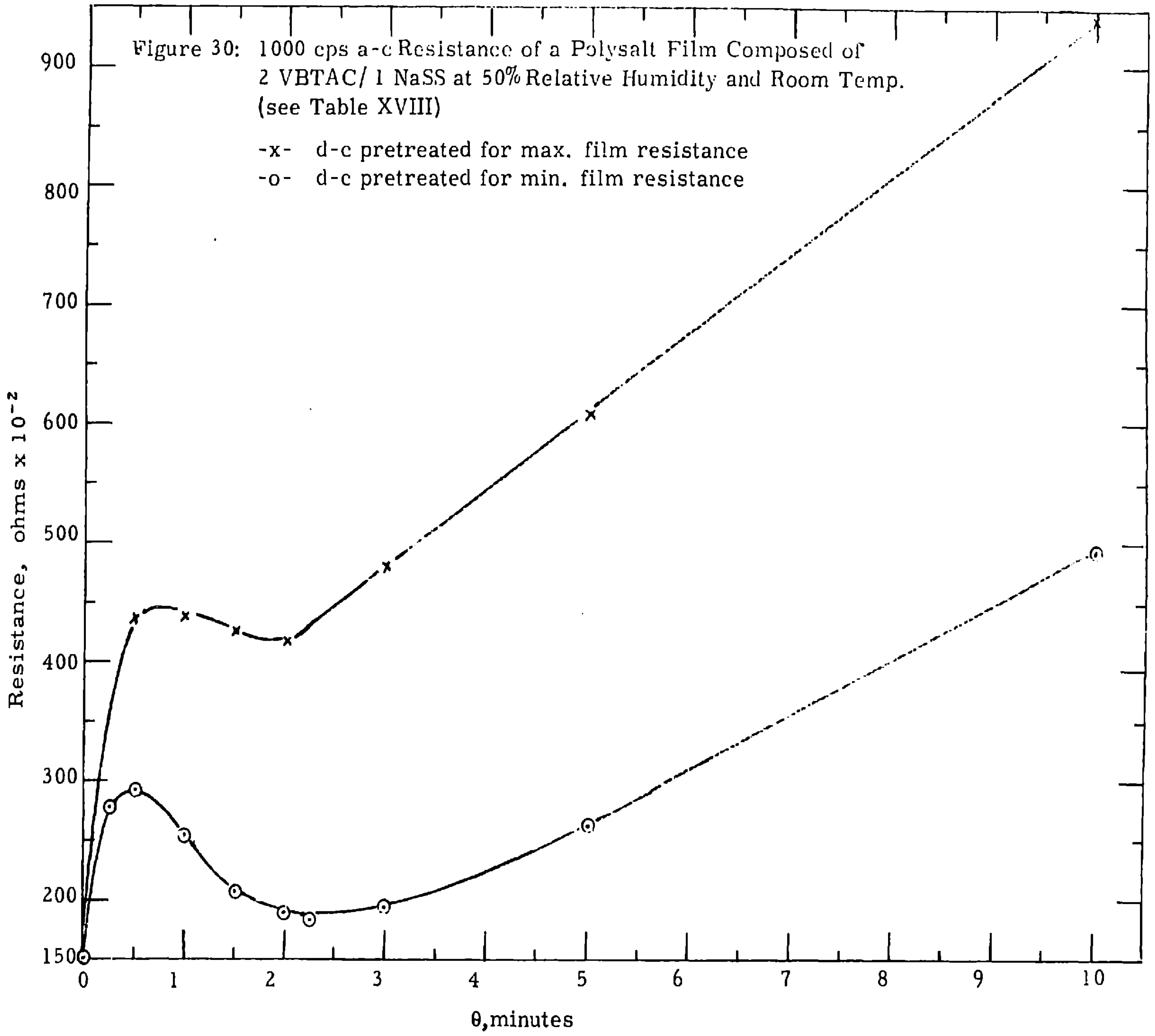


Figure 30: 1000 cps a-c Resistance of a Polysalt Film Composed of 2 VBTAC/ 1 NaSS at 50% Relative Humidity and Room Temp. (see Table XVIII)

2. Humidity Sensitivity of a Polysalt Interfacial Film

A washed polysalt interfacial film was laminated wet onto the head of an ordinary thumbtack, and allowed to dry. A nichrome wire was placed in contact with the upper surface of the membrane as shown below in Figure 31. Electrical leads from an ohmmeter were attached to the shaft of the thumbtack and to the nichrome wire so that the electrical resistance of the interfacial film could be measured.

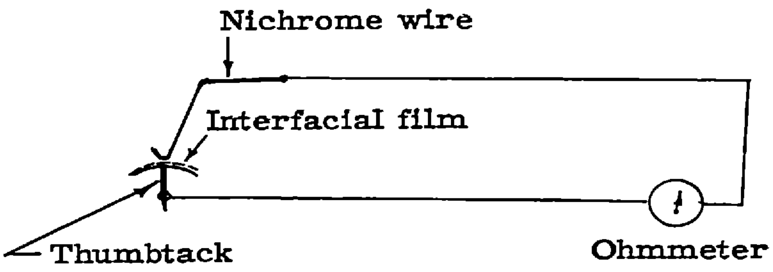


Figure 31

The resistance of the membrane in dry room air was measured to be approximately 100 megohms. If the film was "fogged" to increase its moisture content, its resistance dropped to about 100 kilohms in 10-15 seconds. If the membrane was allowed to dry again, its resistance returned to the original value of 100 megohms in approximately one minute. The magnitude of the measured resistance change with humidity for the interfacial film was similar to the resistance changes observed for the thicker polysalts (see Table XII). The rapidity of the resistance changes with moisture changes suggests that the films may be useful in rapid-response humidity sensing devices.

B. Further Discussion of Polysalt Pairing Phenomena

If perfect pairing is to occur between segments of oppositely-charged polyelectrolyte molecules, it is required a priori that a) the ionic spacings of the two polymers be identical; b) the molecular flexibilities and side group steric configurations be such that the molecules can come into intimate contact, at least under favorable conditions; and c) the molecular configurations in solution at the time of interaction be such that reasonably long segments of the molecules be exposed for reaction with the oppositely-charged species. Conditions a) and b) are determined by the structures and compositions of the polymer molecules, while condition c) is determined by the solution conditions (solvent polarity, polymer and added salt concentrations, temperature, etc.). For VBTAC and NaSS, condition a) is known to be fulfilled, and because of the structural similarity of the two polyelectrolytes it is not unreasonable to assume that condition b) is also fulfilled. The following discussion also assumes that condition c) is fulfilled for salt-free VBTAC-NaSS mixtures at reasonably low polymer concentrations.

Consider first the interaction between isolated VBTAC and NaSS molecules in infinitely dilute aqueous solution, the NaSS molecule being somewhat longer than the VBTAC molecule. Each molecule will be highly ionized and, because of repulsive forces between neighboring polyions, will assume an extended configuration in solution (end-to-end distances approximately 30-50% of the extended molecular lengths). Even if the molecules are separated by appreciable (but not infinite) distances, they will be electrostatically drawn toward each other's centers of charge as illustrated in Figure 32. As the molecules approach each other they will tend to align in much the same fashion as a pair of bar magnets, so that by the time initial contact is made, there may well be no portion, or only a very small portion,

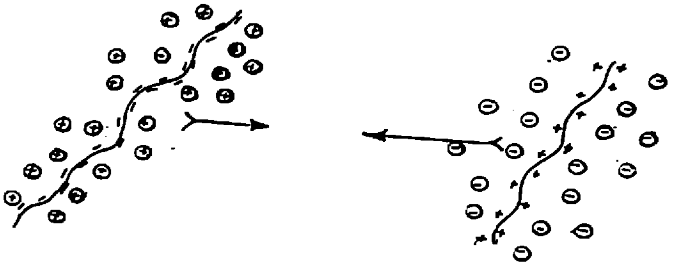


Figure 32

of the (shorter) VBTAC molecule which does not overlap the NaSS molecule as illustrated in Figure 33. The molecules will then proceed

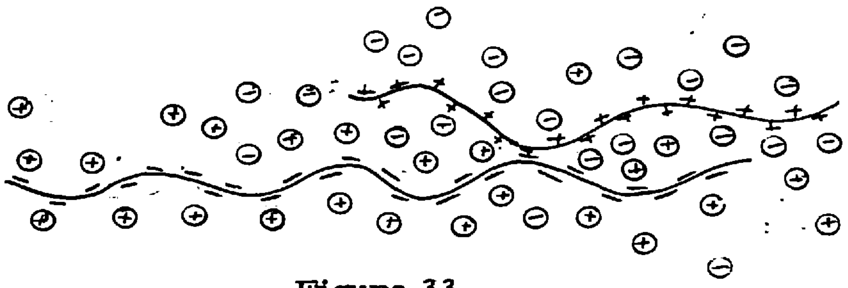


Figure 33

to pair along their entire overlapped length as illustrated in Figure 34.

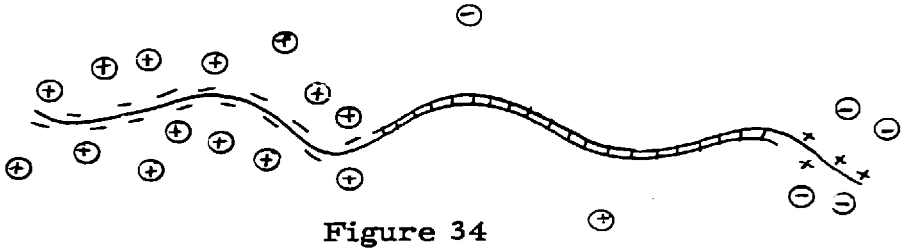


Figure 34

In the absence of any other molecules, and assuming that the paired segment is not a completely rigid rod, the unreacted VBTAC segment will eventually come in contact with a portion of the (longer) unreacted NaSS segment, and completion of the pairing reaction will take place (Figure 35).

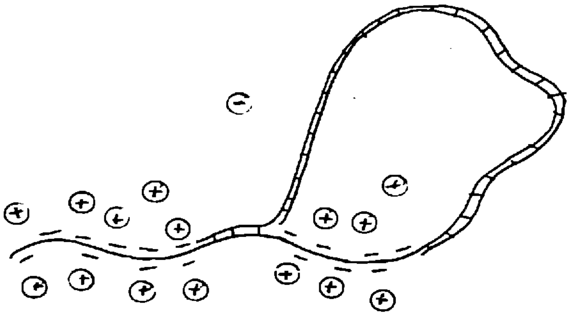


Figure 35

It is not altogether inconceivable, but seemingly unlikely, that the molecules would shift with respect to one another, displacing all of the previously formed bonds, so that complete pairing would occur along a single segment. One way that this might occur, however, would be by the formation and propagation of loops or kinks in one of the molecules as illustrated in Figure 36. The process would require

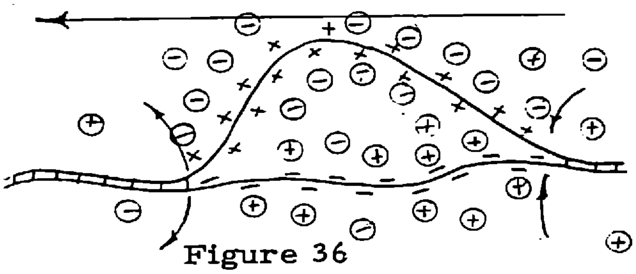


Figure 36

the availability of microions to act (at least momentarily) as counter-ions of the unreacted molecular segments and, given the existence of such a loop, one might justifiably question whether sufficient driving force would exist for its propagation.

At sufficiently high, finite concentrations of VBTAC and NaSS, occurrences of the type illustrated in Figure 35 would be quite rare, and instead one would expect (beginning with initial pair formation as illustrated in Figure 34) completion of pairing to take place as illustrated in Figure 37 (excess VBTAC) or 38 (excess NaSS). For clarity of illustration, the ends of the NaSS molecules have been marked by ⊖, and the ends of the VBTAC molecules by —⊕ .

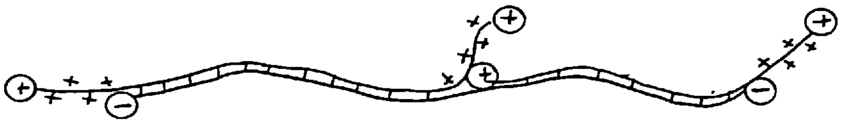


Figure 37. Pairing in Presence of Excess VBTAC

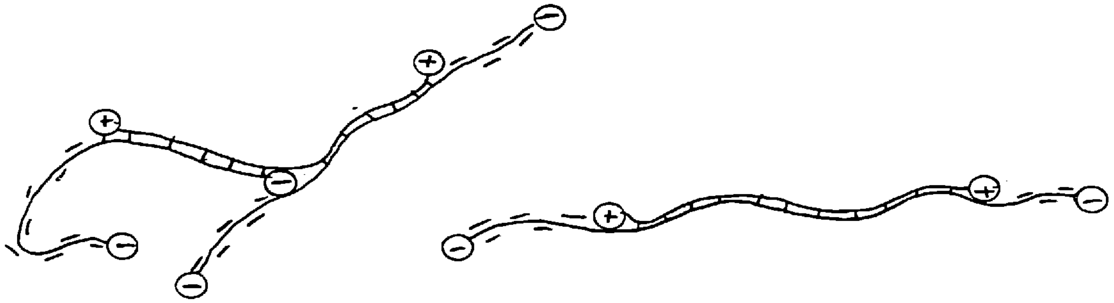


Figure 38. Pairing in the Presence of Excess NaSS

Upon further addition of the polyelectrolyte present in substoichiometric amounts, the molecular triad or doublet formation illustrated in Figures 37 and 38 will continue to occur until most or all of the (originally) more concentrated polyelectrolyte have been at least partially reacted, after which further addition of the second polyelectrolyte will result in bridging between the molecular doublets and triads to form larger molecular agglomerates as illustrated in Figure 39 (VBTAC being added, NaSS in excess). Gross flocculation occurs at or very near the equivalence point as the agglomerate size becomes very large.

With the pairing picture presented above, it is rather difficult to imagine how complete, or even nearly complete, pairing of the molecules can occur during the final stages of agglomeration (near the equivalence points) when the molecules being added must bridge

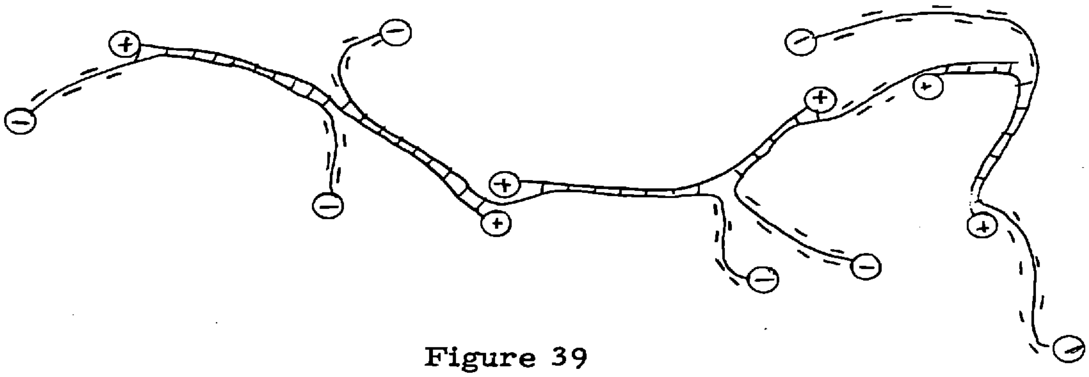


Figure 39

between molecular segments whose length and position with respect to the other segments are already fixed. Perhaps the initial pairing reactions between individual molecules are more nearly stoichiometric than implied by the pictorial representations given here, so that agglomeration involves only a very small fraction of the total polyions in the mixture. For this to be so, however, it seems likely that considerable shifting of the molecules from their original positions in the doublets and triads would have to occur. In addition to the "inch worm" or molecular loop propagations suggested earlier (see Figure 36), another type of molecular shifting and bond rearrangement is possible when a large number of molecules are present in solution. For the following analysis, we require that the molecules of each (or at least one) polyelectrolyte species vary considerably in degree of polymerization, which is normally the case for unfractionated polymers.

Suppose a molecular triad exists in a solution containing excess VBTAC as illustrated in Figure 40. VBTAC molecules 1 and 2

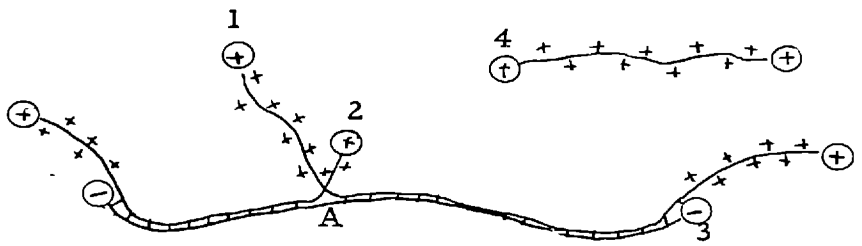


Figure 40

have intercepted each other in their propagation along NaSS molecule 3 at point A. Considerable stress is experienced by the double polyion bonds at point A as the unreacted ends of molecules 1 and 2 lash about in solution. The bonds between 1 and 3 are under greater tension than those between 2 and 3, because 1 has a longer unreacted segment than 2. Thus, there will be a driving force for replacement of 1-3 bonds by 2-3 bonds to give the configuration shown in Figure 41.

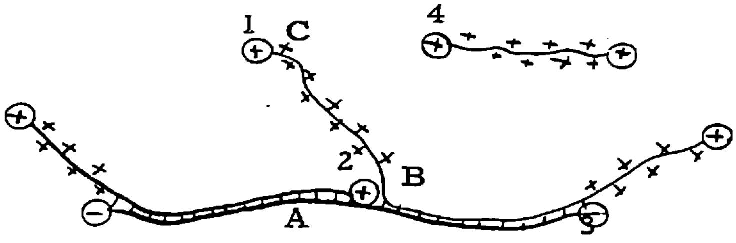


Figure 41

Now suppose molecule 4 (VBTAC), whose total length is less than the unreacted segment length (BC) of molecule 1, attaches by bond transfer to the point of strain between molecules 2 and 3. By the same process as just described for the transfer of 1-3 bonds to 2-3 bonds, it will completely displace molecule 1 as illustrated in Figure 42. The net result of this type of process will be a reduction in the number and length of unreacted ends of molecules in the agglomerates, and an approach to complete and stoichiometric interpolymer reaction.

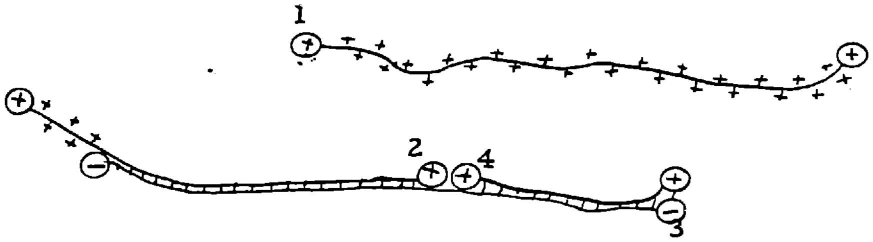


Figure 42

If the polymers are sufficiently concentrated at the time of initial interaction, the molecules of each species will tend to make simultaneous, or nearly simultaneous initial contacts with several molecules of the oppositely-charged species. When this happens, pairing will not result in the formation of molecular doublets or triads, but in the formation of polymolecular agglomerates in which the paired segment length between any two molecules will be relatively short. These agglomerates may initially contain many unpaired molecular segments (see Figure 39), and it may be difficult, if not impossible, for appreciable bond rearrangement to occur because the complexity the structure will make many regions sterically inaccessible to unreacted molecules.

It was actually observed that when VBTAC and NaSS solutions were mixed together at polymer concentrations above about 0.05 g/dl, some flocculent precipitate was formed even when a small amount of one polyelectrolyte was added to a large excess of the other. The average size of such flocculent precipitate particles became visibly larger as the polymer concentrations were increased. At concentrations of 0.2 g/dl or more of each polymer, the agglomerates formed away from the equivalence points were quite large and "stringy" in appearance, and appreciable deviations from stoichiometric interaction began to occur. The rather sudden onset of large deviations from stoichiometric reaction for small increases in polymer concentration strongly suggested that droplets of one of the polymer solutions became isolated from interaction by being surrounded by a layer of polymer-impermeable cross-linked polysalt precipitate.

Finally, at polyelectrolyte concentrations above about 0.6 g/dl the precipitates took the form of continuous interfacial films through which neither polymer species could permeate. The onset of interfacial film formation probably represents the condition at which, on the average, the molecules of each species react initially with more than two molecules of the oppositely-charged species. Very likely, the film thickness is related to the average length of segmental pairing between two molecules.

APPENDIX B: Supplementary Details and Calculations

A. Effects of NaCl and NaBr on the Viscosities of NaSS and VBTAC Solutions

1. Viscosity Changes Due to Incomplete NaCl Release From Precipitates of Dilute, NaBr-Free VBTAC-NaSS Mixtures

The supernatant liquid η_{sp} changes to be expected upon incomplete release of NaCl from dilute solution precipitates (see Table IV) are calculated below. It is assumed that in the concentration range of interest, a given change in NaCl concentration produces the same (or a lesser) fractional change in η_{sp} as the same change in NaBr concentration. This assumption allows the use of the individual polyelectrolyte viscosity data of Smith (34) for calculation of the NaCl effect on polyelectrolyte viscosities, although it should be recognized that Br^- probably produces a greater suppression of VBTAC viscosity than does Cl^-.

Table XIV below gives the supernatant liquid NaCl concentrations for 100%, 90%, 80%, and 70% of maximum salt release in mixtures 1-7 (see Table II), and the stoichiometric excess polyelectrolyte concentrations in both Meq/ dl and g/ dl. Smith's data are plotted in Figure 43 as $\log(\eta_{sp}/c_p)$ vs. log NaBr (assumed≈NaCl) concentration at the polyelectrolyte concentrations of interest. Table XX gives the ratios of $\dfrac{\eta_{sp} \text{ at } 90, 80, \text{ or } 70\% \text{ salt released}}{\eta_{sp} \text{ at maximum salt release}}$ calculated from values taken from Figure 43. Examination of this table shows that in the concentration ranges of interest, both VBTAC and NaSS are affected about equally by a given fractional change in salt concentration, so that a single plot of $\dfrac{\eta_{sp}}{\eta_{sp\ \text{max salt}}}$ vs. fractional salt release will adequately represent all of the values. Figure 44 is the desired plot, from which it can be seen that

$$\frac{\eta_{sp}\ 97\%\ \text{salt release}}{\eta_{sp}\ \text{maximum salt release}} = 1.02$$

for each of the mixtures. This ratio has been used to calculate the η_{sp} deviations for 97% of maximum salt release given in Column 3 of Table IV.

Table XIX: Supernatant liquid NaCl concentrations for incomplete ionic interactions between VBTAC and NaSS in dilute, NaBr-free mixtures (see Table II)

	Ionic excess of NaSS in mixture		Ionic excess of VBTAC in mixture		Mixture supernatant liquid NaCl conc. (M/1 x 10^2) for various degrees of VBTAC-NaSS ionic reaction			
Mixture	Meq/dl	g/dl	Meq/dl	g/dl	Max(100%) interaction	90% of max interaction	80% of max interaction	70% of max interaction
1	0.342	0.08	--	--	0.086	0.077	0.069	0.060
2	0.256	0.06	--	--	0.177	0.160	0.142	0.124
3	0.171	0.04	--	--	0.256	0.230	0.205	0.180
4	0.0	0.0	0.0	0.0	(0.342)	--	--	--
5	--	--	0.135	0.036	0.249	0.224	0.199	0.174
6	--	--	0.218	0.058	0.166	0.149	0.133	0.166
7	--	--	0.301	0.080	0.083	0.075	0.066	0.058

Table XX: Ratios of $\dfrac{\eta_{sp} \text{ for incomplete VBTAC-NaSS ionic reaction}}{\eta_{sp} \text{ for complete VBTAC-NaSS ionic reaction}}$ for supernatant liquids of NaBr-free dilute solution mixtures 1-7 (see Tables II and XIX), determined from values in Figure 43

Mix- ture	NaSS in supern. g/dl	VBTAC supern. g/dl	Max NaCl supern. $M/1x10^2$	η_{sp}/η^*_{sp} max salt in supernat.		
				90% max NaCl in supern.	80% max NaCl in supern.	70% max NaCl in supern.
1	0.08	--	0.086	1.08	1.11	1.18
2	0.06	--	0.177	1.06	1.12	1.20
3	0.04	--	0.256	1.06	1.13	1.21
4	0.0	0.0	(0.342)	--	--	--
5	--	0.04	0.249	1.06	1.12	1.19
6	--	0.06	0.166	1.06	1.12	1.19
7	--	0.08	0.083	1.06	1.13	1.19

*Example calculation of $\eta_{sp}/\eta_{sp \text{ max salt}}$

For mixture 1, 90% of maximum NaCl in supernatant is 0.00077 molar. From Figure 43, η_{sp}/c_p of 0.08 g/dl NaSS at maximum (0.00086 M) NaBr ($\approx$NaCl) is 24, and at 0.00077 M NaBr is 26.

$$\frac{\eta_{sp \text{ } 90\% \text{ NaCl}}}{\eta_{sp \text{ max NaCl}}} = \left(\frac{\eta_{sp}/c_{p \text{ } 90\%}}{\eta_{sp}/c_{p \text{ max NaCl}}} \right)_{c_p = \text{const}} = \frac{26}{24} = 1.08$$

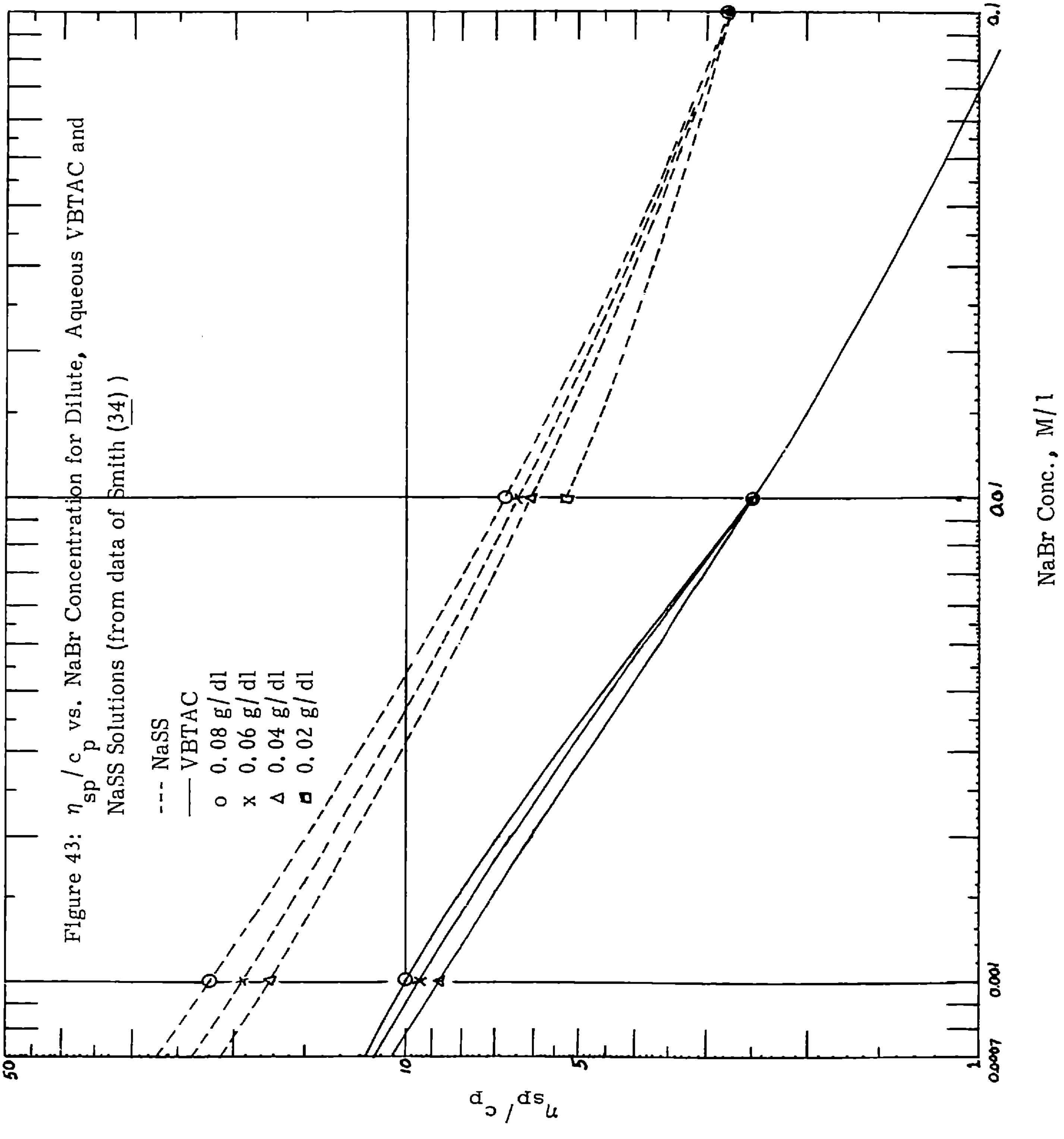
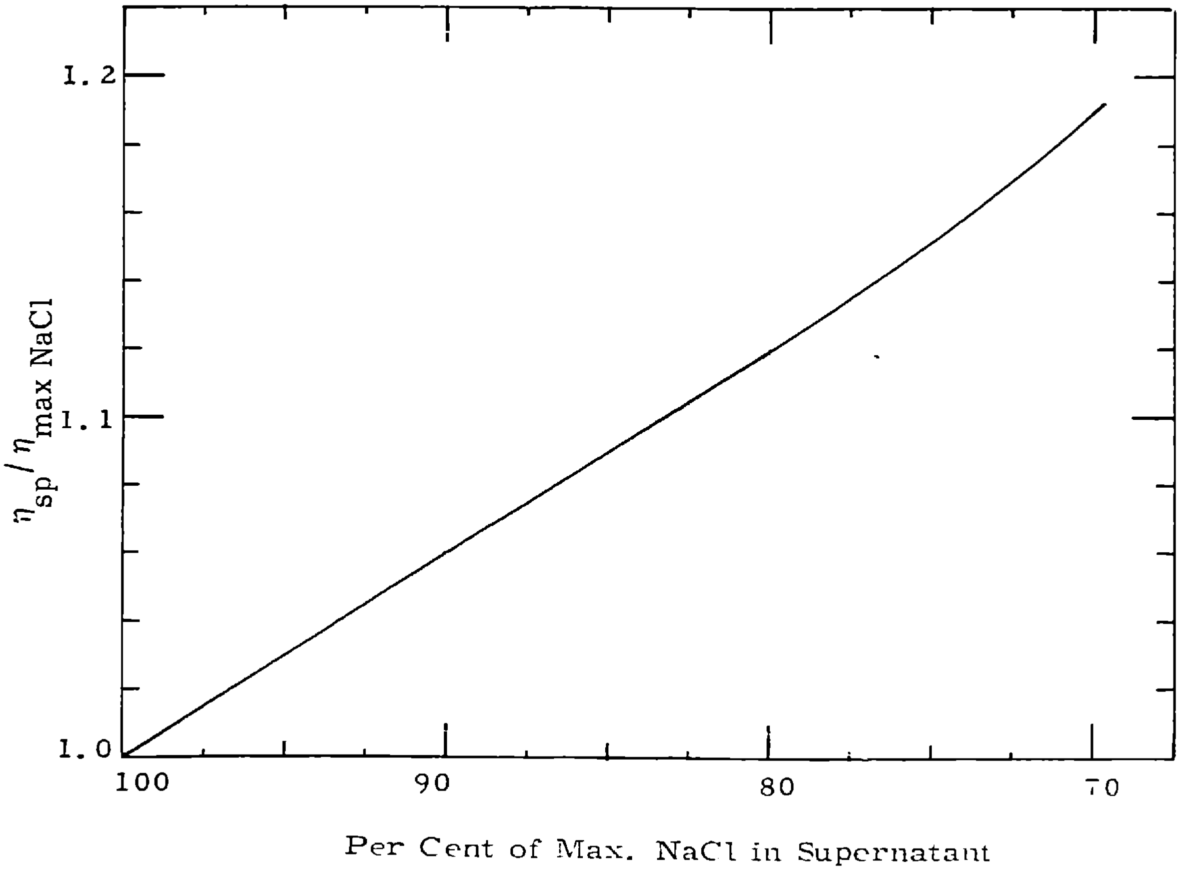


Figure 43: η_{sp}/c_p vs. NaBr Concentration for Dilute, Aqueous VBTAC and NaSS Solutions (from data of Smith (34))

Figure 44: $\eta_{sp}/\eta_{max\ NaCl}$ for Incomplete Ionic Reaction in VBTAC-NaSS Mixtures 1 - 7 (see Tables IV, XIX, and XX)



2. Theoretical Specific Viscosities of VBTAC-NaSS Mixtures Containing 0.01 M NaBr

The theoretical (for stoichiometric and complete interpolymer reactions) η_{sp} values for VBTAC-NaSS mixture supernatants containing 0.01 M NaBr are calculated below using the data of Smith plotted in Figure 43. For the calculations it is assumed that the NaCl released upon VBTAC-NaSS interaction has the same effect on supernatant viscosity as an equal amount of NaBr.

Table XXI gives the supernatant liquid compositions of mixtures 0.01-1 to 0.01-11 (see Table VII) to be expected if interpolymer reactions were both stoichiometric and complete. Columns 5 and 6 of Table XXII give the η_{sp}/c_p and η_{sp} values corresponding to these polymer and added salt concentrations, taken from the data of Smith (Figure 43). Since the viscosity of a solution containing a given polyelectrolyte and added salt concentration varies somewhat depending on the batch of polymer used, these values cannot be used directly as the theoretical η_{sp} values for the mixture supernatants. It is reasonable to assume, however, that the rates of change of η_{sp} with changing polymer and salt concentrations are about the same for any VBTAC or NaSS batch, provided that the concentration ranges involved are not too great. The η_{sp} values of 0.10 g/dl VBTAC and NaSS in 0.01 M NaBr were measured (mixtures 0.01-1 and 0.01-11) for the polymer stock solutions used to make up the mixtures. The ratio of the theoretical mixture η_{sp} values to the 0.1g/dl polyelectrolyte solution η_{sp} values are assumed to be the same as the corresponding ratios obtained from Smith's data. Column 7 of Table XXII gives Smith's $\eta_{sp}/\eta_{sp0.1g/dl}$ ratios, and Column 8 gives the corrected theoretical supernatant specific viscosities for the mixtures, obtained by multiplying the ratios in Colmn 7 by the 0.1 g/dl VBTAC or NaSS η_{sp} values of the mixture stock solutions.

Table XXI: Supernatant liquid salt and polyelectrolyte concentrations for stoichiometric and complete interpolymer reactions in aqueous VBTAC-NaSS mixtures containing 0.01 M NaBr (see Table VII)

Mixture	VBTAC Meq/dl	NaSS Meq/dl	Ionic excess of VBTAC or NaSS Meq/dl	Ionic excess of VBTAC or NaSS g/dl	Maximum supernatant NaCl conc. M/1	Super-natant NaBr conc. M/1	Max. total supernatant salt conc. M/1
0.01 - 1	0.427	0.00	0.427	0.10	0.00	0.01	0.010
0.01 - 2	0.427	0.0855	0.342	0.08	0.00086	0.01	0.0109
0.01 - 3	0.427	0.171	0.256	0.06	0.00171	0.01	0.0117
0.01 - 4	0.427	0.256	0.171	0.04	0.00256	0.01	0.0126
0.01 - 5	0.427	0.342	0.086	0.02	0.00342	0.01	0.0134
0.01 - 6	0.427	0.427	--	--	--	0.01	--
0.01 - 7	0.342	0.427	0.086	0.02	0.00342	0.01	0.0134
0.01 - 8	0.256	0.427	0.171	0.04	0.00256	0.01	0.0126
0.01 - 9	0.171	0.427	0.25	0.06	0.00171	0.01	0.0117
0.01 - 10	0.0855	0.427	0.342	0.08	0.00086	0.01	0.0109
0.01 - 11	0.00	0.427	0.427	0.10	0.00	0.01	0.010

Table XXII: Theoretical (stoichiometric) η_{sp} values for supernatant liquids of VBTAC-NaSS mixtures containing 0.01 M NaBr (see Tables VII and XXI, and Figure 43)

Mixture	Theoret. supern. VBTAC conc. g/dl	Theoret. supern. NaSS conc. g/dl	Maximum super. salt (NaBr+ NaCl) conc. M/1	Data of Smith, from Figure 43			η_{sp}* stoichio-metric
				η_{sp}/c_p (g/dl)$^{-1}$	η_{sp} $(=c_p \cdot \frac{\eta_{sp}}{c_p})$	$\frac{\eta_{sp}}{\eta_{sp_{0.1g/dl}}}$	
0.01 - 1	0.10	--	0.0100	2.50	0.250	1.00	0.294
0.01 - 2	0.08	--	0.0109	2.36	0.189	0.755	0.222
0.01 - 3	0.06	--	0.0117	2.26	0.136	0.545	0.160
0.01 - 4	0.04	--	0.0126	2.20	0.088	0.352	0.103
0.01 - 5	0.02	--	0.0134	2.12	0.0425	0.170	0.050
0.01 - 6	0.00	0.00	--	--	--	--	0.00
0.01 - 7	--	0.02	0.0134	4.8	0.096	0.134	0.104
0.01 - 8	--	0.04	0.0126	5.55	0.222	0.310	0.241
0.01 - 9	--	0.06	0.0117	6.00	0.360	0.503	0.390
0.01 - 10	--	0.08	0.0109	6.45	0.517	0.722	0.560
0.01-11	--	0.10	0.0100	7.15	0.715	1.00	0.776

* Values obtained by multiplying $\eta_{sp}/\eta_{sp_{0.1g/dl}}$ values of Column 7 by η_{sp} of 0.1 g/dl VBTAC (mixt. 0.01-1) or 0.1 g/dl NaSS (mixt. 0.01-11) solutions made from same stock solutions as used to prepare mixtures 0.01 - 2 to 0.01 - 10.

B. Details of Reflectance Measurement of Interfacial Film Thickness

1. Theory

Suppose a beam of monochromatic light traveling in air (refractive index = 1) is incident at an angle i from perpendicular on the surface of a thin film (refractive index $n_f > 1$) at point o as shown in Figure 45.

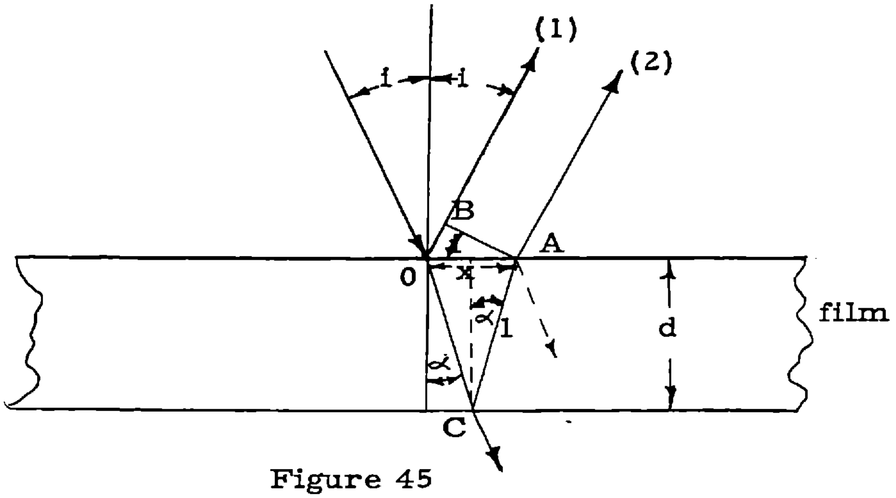


Figure 45

At the first interface, part of the beam will be reflected (beam (1)), and will be 180° out of phase with the incident beam, since it is reflected from the surface of an optically denser medium. The remainder of the beam will be transmitted (DC), and at the second interface, part will be transmitted and part reflected (CA). The light reflected at C will not undergo a phase shift, since it is reflected at the surface of an optically rarer medium. Part of beam CA will be reflected at the first surface, and the remainder will be transmitted (beam (2)). Parallel beams (1) and (2) will reinforce each other if they are in phase, but will destructively cancel each other if they are out of phase.

The phase difference between (1) and (2) may be determined by the phase difference between points A and B (AB is perpendicular to beams (1) and (2)).

Let d = thickness of the film

n_f = refractive index of the film

i and α = angles of incidence and refraction, respectively

l = path length of refracted ray through the film.

The distance traveled by the internally reflected ray OCA is

$$2\,l = \frac{2d}{\cos\alpha} \tag{1}$$

The time of traversal of this path is

$$t_2 = \frac{2\,l}{C/n_f} = \frac{2\,n_f d}{C\cos\alpha} \tag{2}$$

where C is the velocity of light in air (or vacuum). The time for ray (1) to traverse path OB (= X sin i) is

$$t_1 = \frac{X\sin i}{C} = \frac{(2\,l\sin\alpha)\sin i}{C} \tag{3}$$

The difference in traversal time of paths OCA and OB gives rise to a phase difference of $\omega(t_2 - t_1)$ where $\omega = 2\pi\nu$ (ν being the vibration frequency of the incident light in cycles per second), from which we must subtract π since beam (1) has undergone a phase shift while beam (2) has not. Subtracting equation 2 from equation 3,

$$t_2 - t_1 = \frac{2\,l}{C}\,(n_f - \sin\alpha\sin i) \tag{4}$$

or, since $\sin i = n_f\sin\alpha$,

$$\begin{aligned} t_2 - t_1 &= \frac{2\,n_f l}{C}\,(1 - \sin^2\alpha) \\ &= \frac{2\,n_f l}{C}\,(\cos^2\alpha) \\ &= \frac{2\,n_f d}{C}\cos\alpha \text{ (see Equation 2)} \end{aligned} \tag{5}$$

The phase difference then becomes

$$\phi = \omega(t_2 - t_1) - \pi = \frac{\omega 2nd}{C}\cos\alpha \quad - \pi \tag{6}$$

or, since $\frac{\omega}{C} = \frac{2\pi\nu}{C} = \frac{2\pi}{\lambda}$ where λ = the wavelength (in air) of the incident beam,

$$\phi = \frac{4\pi n_f d}{\lambda}\cos\alpha - \pi \tag{7}$$

For a reflectance maximum (constructive interference) beams (1) and (2) must be in phase so that $\phi = 2\pi k$, where k is an interger. These maxima occur when

$$\frac{4\pi n_f d}{\lambda}\cos\alpha - \pi = 2\pi k \tag{8}$$

or,

$$2 n_f d \cos\alpha = (k + \frac{1}{2})\lambda$$

For a reflectance minimum (destructive interference), beams (1) and (2) must be 180° ($=\pi$) out of phase so that

$$2 n_f d \cos\alpha = k\lambda . \tag{9}$$

For normal incidence, $\cos\alpha = 1$, and maximum reflectance occurs when d is an odd multiple of a quarter wavelength of the light in the film (λ/n), but no reflectance occurs if d is an even number of quarter wavelengths of λ/n.

2. Experimental Procedure

A 1/2 inch diameter glass magnifying lens was silvered, polished with jewelers rouge, washed, and dried. A laminate of 11 VBTAC-NaSS interfacial films was built up on the silvered surface as illustrated in Figure 46 (for description of lamination procedure, see Section III-E).

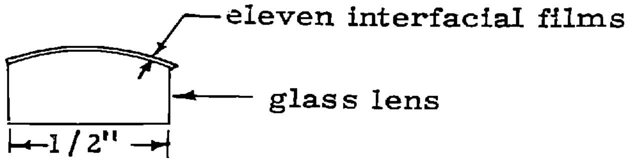


Figure 46

Because the (dried) films spontaneously adhered to solid surfaces, it was assumed that they were able to conform to even microscopic surface irregularities, so that no air gaps were present either between the individual films or between the films and the silvered surface. This assemblage was mounted in the reflectance chamber of the reflectance spectrophotometer of the M. I. T. Color Measurement Laboratory, and a continuous recording made of per cent of reflected light vs. wavelength of incident monochromatic light. Figure 47 is a sketch of the reflectance chamber of the spectrophotometer.

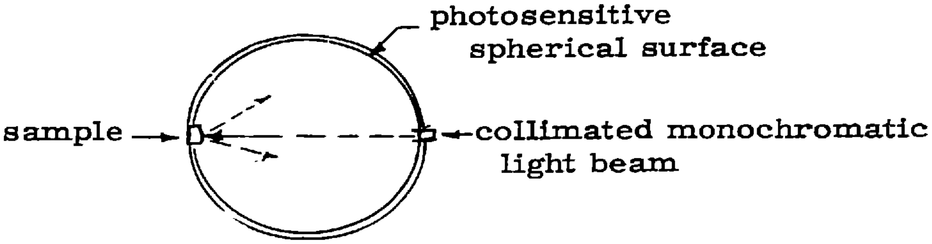


Figure 47

3. Results and Calculation of Film Thickness

Figure 48 is the plot of per cent reflectance vs. λ of incident light obtained for the 11 film laminate in the reflectance spectrophotometer. Since the reflectance of the film (film-air surface) was much less than that of the silver surface, and since the reflectance of Ag varies appreciably with incident light frequency, the plot must be corrected for the Ag reflectance. Table XXIV gives numerical values of measured reflectances, and the reflectance of Ag at the same frequencies (19). The Ag reflectance values are reduced by 20.5 per cent to account for reflectance from the upper film surface and imperfections (roughness, oxidation, etc.) in the silvered surface used (Column 4). The net reflectance of the interfacial film laminate is obtained (Column 5) by subtracting the corrected Ag reflectances from the measured reflectance of the laminate. A plot of the net reflectance of the film laminate versus incident light wavelength has been given previously in Figure 14, which is repeated here for convenience.

The reflectance minimum at about 480 millimicrons corresponds (for normal incidence) to a film thickness which is an even multiple of one fourth the wavelength of light in the film, $\frac{\lambda}{n}$. For a multiple of 2 (first order minimum), a reinforcement should occur at 860 millimicrons, where the film would be one fourth of $\frac{\lambda}{n}$ of the incident light. If the minimum were second order ($d = \lambda$), a reflectance maximum would occur at 4/3(480) or 640 millimicrons where the film would be 3/4 of λ/d of the incident light. For higher orders of reflectance, a maximum would occur at frequencies closer to 480 millimicrons than 640 millimicrons. The plot shows no peaks between 480 $m\mu$ and 700 $m\mu$, with a fairly steady rise toward an apparent maximum at 860 $m\mu$, so the minimum is first order and the laminate thickness is $480 / 2\, n_f$ (millimicrons). Although no measurement was made of the refractive index of the film, it is probably close to 1.5, by comparison with compounds of similar structure as shown in Table XXIII.

Table XXIII: Refractive indices (20) of compounds related in structure to VBTAC-NaSS polysalts

Material	Refractive index, visible light wavelengths
NH_4HSO_4	1.46 - 1.51
NH_4-malate	1.503
Gum Arabic	1.48 - 1.51
Gelatin	1.52 - 1.53
Rubber	1.52

For n_f = 1.5, the laminate thickness (λ/ 2n) becomes (480)/ (2)(1.5) = 160 mμ or 160/ 11 = 14.5 mμ = 145 Å per film.

The above calculation assumes normal incidence of the light, which cannot be exactly true for the entire surface of the laminate whose surface was curved. Light incident at angles other than 90° will give a calculated d less than the actual value (d cos α is the calculated value, which is assumed to be d), so the 145 Å represents a minimum value of film thickness.

Table XXIV: Reflectance of polysalt interfacial film laminate; corrections for reflectance of silver substrate

λ (mμ)	% refl. of laminate	% refl. of silver (1)	% refl. of silver - 20.5% (2)	Net refl. of film (col. 3 - col. 4) (%)
400	65.0	83.6	63.1	1.9
420	67.0	86.6	66.1	0.9
450	70.5	90.5	70.0	0.5
500	71.0	91.3	70.8	0.2
550	73.0	91.7	71.2	1.8
600	78.5	92.6	72.1	6.4
650	83.5	94.7	74.2	9.3
700	87.0	95.4	74.9	12.1

(1) Data from Handbook of Chemistry & Physics (19)

(2) Value of 20.5% chosen to give film reflectance of 0% at minimum (ca. 480 mμ).

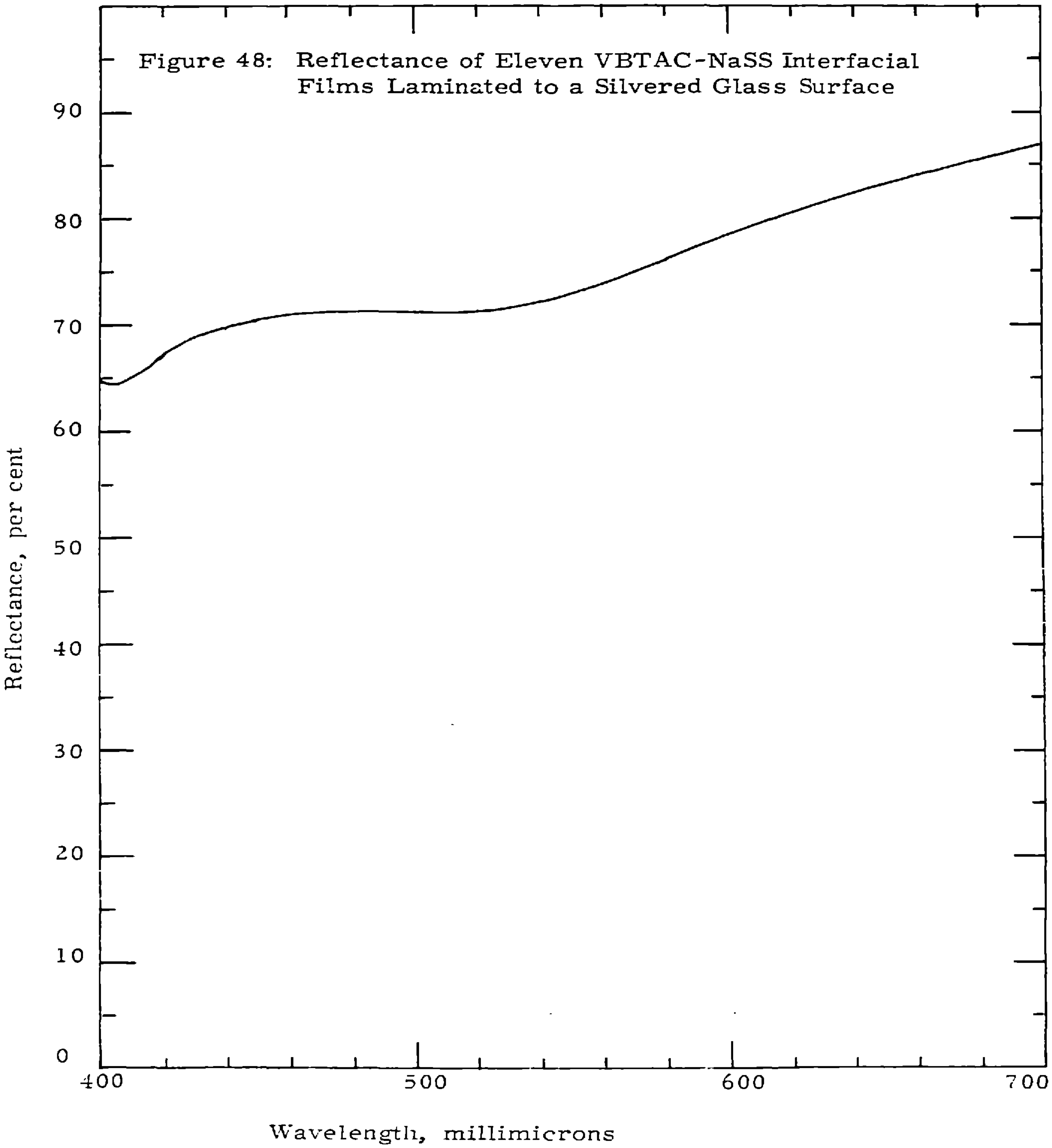
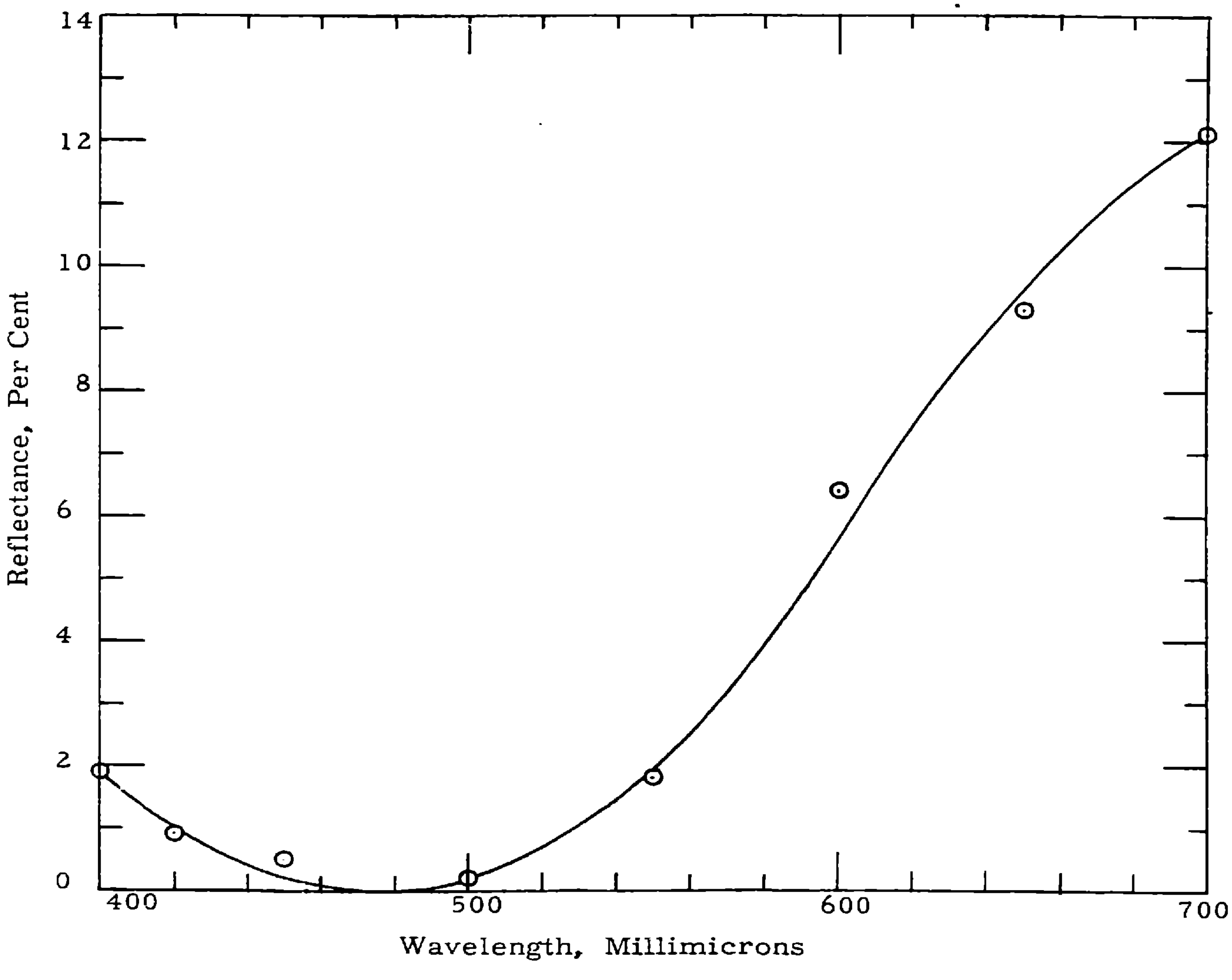


Figure 48: Reflectance of Eleven VBTAC-NaSS Interfacial Films Laminated to a Silvered Glass Surface

Figure 14: Net Reflectance of an 11-Film Polysalt Interfacial Film Laminate vs. Wavelength of Incident Monochromatic Light



C. Summary of Data and Calculated Values

Table XXV: NaSS Equivalent Weight Determinations

Sample	g. HSS (1 g/dl solution)	g. NaSS (after titration)	Ml NaOH	Normality NaOH	M l 0.1000N potassium biphthalate (back titration)	Meq. polymer	Eq. wt. HSS	Eq. Wt. NaSS
Batch A								
1	0.10	--	5	0.1123	0.76	0.485	206	228[1]
2	0.10	--	5	0.1123	0.78	0.483	207	229[1]
3	0.10	--	5	0.1123	0.84	0.477	209	231[1]
4	0.10	--	5	0.1123	0.84	0.477	209	231[1]
5	0.10	--	5	0.1123	0.83	0.478	209	231[1]
								230±1(avg)[2]
Batch B								
1	--	0.2626	13.66	0.0855	--	1.67	--	225
2	--	0.2614	13.40	0.0855	--	1.145	--	228
3	--	0.2531	13.50	0.0855	--	1.153	--	220
4	--	0.2194	11.55	0.0855	--	0.987	--	222
5	--	0.2199	11.45	0.0855	--	0.979	--	225
								224±2(avg)

[1] Eq. wt. HSS + 22

[2] Because of a calculation error, this value was originally thought to be 234, and is reported as 234±8 in Table I. The small correction (1.3%) involved does not materially affect the experimental results, so all results in the thesis have been calculated using the originally assumed eq. wt. of 234 for NaSS Batch A.

Table XXVI: VBTAC Equivalent Weight Determinations

VBTAC Batch	Normality of $AgNO_3$	g. VBTAC titrated	Ml $AgNO_3$ at endpoint	VBTAC Eq. wt.
A	0.00316	0.003	4.13	230
A	0.00406	0.003	3.11	238
A	0.00406	0.003	3.16	234
A	0.00403	0.003	3.08	242
A	0.0050	0.01	8.25	242
A	0.0050	0.0099	8.10	243
B	0.00298	0.0016	2.02	265
B	0.00298	0.0016	2.03	264

Table XXVII: Determination of VBTAC-NaSS mixture supernatant liquid chloride concentrations

	Mixture Titrations				Titrations of VBTAC stock solutions					
Mixture No.	g. VBTAC*	$AgNO_3$ Normality	Ml$AgNO_3$ at end-point	Apparent eq. wt. VBTAC	g. VBTAC	Normality of $AgNO_3$	Ml$AgNO_3$ at end-point	Eq.wt of VBTAC	(Cl^- per g. VBTAC in mixt.) / (Cl^- per g. VBTAC in stock)	(Cl^- per g. VBTAC in mixt.) / Cl^- per g. VBTAC of eq. wt. 234)
10	0.0030	0.00403	3.14	237				242		
3	0.0024	0.00338	3.00							
			3.08	234(avg)	--	--	--	--	--	1.00
4	0.0032	0.00338	3.90							
			3.95	242(avg)	--	--	--	--	--	
			3.87							
8	0.001	-	0.91	--	0.001	--	0.91	--	1.02	--
			0.94				0.92			
			0.95				0.915 avg			
			0.93 avg							
9	0.0020	--	1.89	--	0.001	--	0.915	--	1.03	--
			1.89							
			1.89 avg.							

* g/ ml VBTAC in mixture times ml of supernatant liquid used.

Table XXVIII: Supernatant liquid specific viscosities of NaBr-free VBTAC-NaSS mixtures at 25.00 ± 0.02°C (Cannon-Fenske capillary viscometer, size 100)

Mixture	Mixture Composition VBTAC Meq/dl	 NaSS Meq/dl	Control sample comp. Ionic excess VBTAC or NaSS Meq/dl	 Max. supern. NaCl conc. Meq/dl	θ Flow time of mixture supern. seconds	θ_c Flow time of control sample, seconds	η_{sp}* $= \frac{\theta - \theta_o}{\theta_o}$	$\eta_{sp_{theo}}$ $= \frac{\theta_c - \theta_o}{\theta_o}$
1	0.0855	0.427	0.342	0.086	486.4	482.5	5.94	5.95
2	0.171	0.427	0.256	0.171	258.2	258.5	2.68	2.69
3	0.256	0.427	0.171	0.256	154.5	155.8	1.20	1.22
4	0.342	0.342	--	--	70.2	--	0.001	(0.000)
5	0.384	0.249	0.135	0.249	84.0	84.5	0.198	0.206
7	0.384	0.166	0.218	0.166	101.0	102.1	0.442	0.456
7	0.384	0.0829	0.301	0.083	136.1	136.6	0.943	0.949

*θ_o = flow time of solvent (water) = 70.1 seconds

Table XXIX: Specific viscosities of aqueous VBTAC-NaSS mixtures containing 0.1 M NaBr, at 25.00 ± 0.02°C (Cannon-Fenske Capillary Viscometer, Size 100)

Mixture	VBTAC Meq/dl	NaSS Meq/dl	Age of mixture	θ Flow time of mixture supern., seconds	$\eta_{sp} = \frac{\theta - \theta_o}{\theta_o}$ *	η_{sp}/c_p (Meq/dl)$^{-1}$
0.1 - 1	0.379	0.0	fresh	83.3	0.101±.002	0.267
			10 days	83.3	0.101 "	0.267
0.1 - 2	0.379	0.085	fresh	81.35	0.075 "	
			10 days	81.2	0.373 "	
0.1 - 3	0.379	0.171	fresh	79.15	0.046 "	
			10 days	78.9	0.042 "	
0.1 - 4	0.379	0.171	fresh	78.84	0.041 "	
			10 days	78.6	0.038 |	
0.1 - 5	0.379	0.256	fresh	77.63	0.026 |	
			10 days	76.8	0.015	
0.1 - 6	0.379	0.427	fresh	75.9	0.003 |	
			10 days	75.9	0.003	
0.1 - 7	0.379	0.427	fresh	79.2	0.046 |	
			10 days	77.7	0.026 |	
0.1 - 8	0.227	0.427	fresh	85.3	0.127 |	
			10 days	84.7	0.119	
0.1 - 9	0.152	0.427	fresh	87.25	0.153 |	
			10 days	86.7	0.147	
0.1 - 10	0.152	0.427	fresh	89.1	0.177 |	
			10 days	88.0	0.163	
0.1 - 11	0.0758	0.427	fresh	92.9	0.227 |	
			10 days	92.2	0.218 |	
0.1 - 12	0.00	0.427	fresh	96.2	0.271 |	0.635
			10 days	95.6	0.263 |	0.617
0.1 - 13	0.141	0.171	fresh	75.77	0.00 |	
			10 days		0.00 |	
0.1 - 14	0.304	0.197	fresh	75.9	0.00 |	
			10 days	76.05	0.00 |	
0.1 - 15	0.227	0.00	fresh	80.4	0.062 |	0.273
			10 days	80.3	0.061 |	0.268
0.1 - 16	0.152	0.00	fresh	78.8	0.040 |	0.263
			10 days	78.8	0.040 |	0.263
0.1 - 17	0.00	0.256	fresh	87.8	0.160 |	0.625
			10 days	87.5	0.156 |	0.610
0.1 - 18	0.00	0.171	fresh	83.75	0.106 |	0.620
			10 days	83.6	0.104 "	0.609

* θ_o = flow time of solvent (0.10 M NaBr solution) = 75.7 seconds

Table XXX: Specific viscosities of aqueous VBTAC-NaSS mixtures containing 0.01 M NaBr, at 25.0 ± 0.05°C (Cannon-Fenske Capillary Viscometer, size 100)

Mixture	Mixture Composition VBTAC Meq/ dl	 NaSS Meq/ dl	θ Flow time of mixture supern. seconds	η_{sp}, = $\frac{\theta-\theta_o}{\theta_o}$ *	
0.01 - 1	0.427	0.00	81.1	0.294	± .002
0.01 - 2	0.427	0.086	85.8	0.219	± .002
0.01 - 3	0.427	0.171	80.8	0.142	± .002
0.01 - 4	0.427	0.256	75.6	0.073	± .002
0.01 - 5	0.427	0.342	71.4	0.014	± .002
0.01 - 6	0.427	0.427	72.1	0.024	± .002
0.01 - 7	0.342	0.427	79.5	0.129	± .002
0.01 - 8	0.256	0.427	87.3	0.240	± .002
0.01 - 9	0.171	0.427	97.9	0.391	± .002
0.01 - 10	0.086	0.427	110.4	0.568	± .002
0.01 - 11	0.00	0.427	125.1	0.776	± .002

* θ_o = flow time of solvent (0.01 M NaBr solution) = 70.4 seconds

Table XXXI: Specific viscosities of VBTAC-NaSS mixtures containing 1.0 M NaBr, at 25.0 ± 0.05°C (Cannon-Fenske Capillary Viscometer, size 100)

Mixture	Mixture Composition		θ Flow time of supern. seconds	$\eta_{sp} = \frac{\theta - \theta_o}{\theta_o}$ *	
	VBTAC Meq/ dl	NaSS Meq/ dl			
1-1	0.427	0.00	72.20	0.044	± .002
1-2	0.427	0.086	71.31	0.031	± .002
1-3	0.427	0.171	70.37	0.017	± .002
1-4	0.427	0.256	69.35	0.0025	± .002
1-5	0.427	0.342	69.32	0.002	± .002
1-6	0.427	0.427	69.2	0.00	± .002
1-7	0.342	0.427	69.32	0.002	± .002
1-8	0.256	0.427	71.5	0.035	± .002
1-9	0.171	0.427	71.9	0.039	± .002
1-10	0.086	0.427	73.2	0.059	± .002
1-11	0.00	0.427	74.55	0.079	± .002

* θ_o = flow time of solvent (1.0 M NaBr solution) = 69.17 seconds

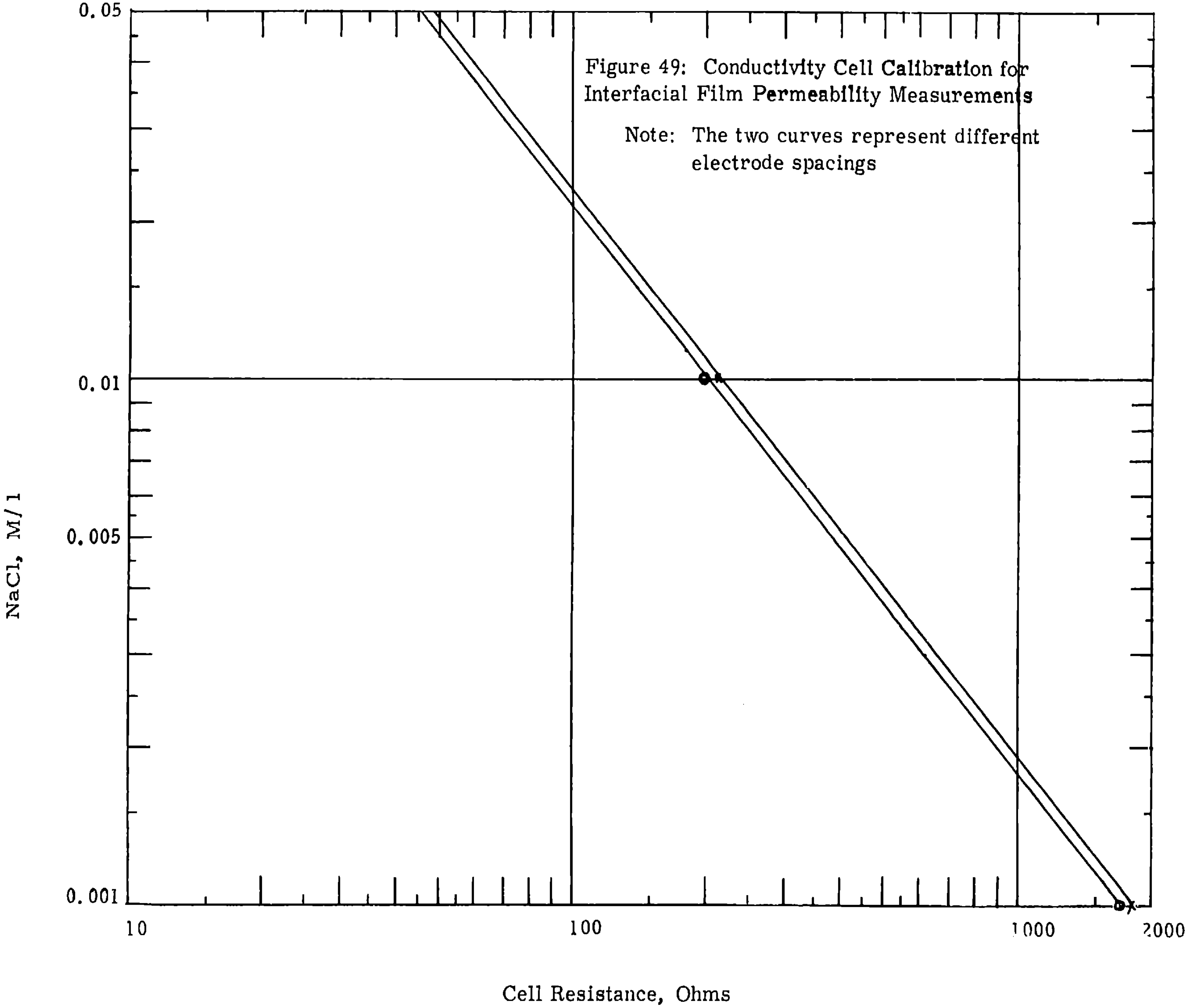


Figure 49: Conductivity Cell Calibration for Interfacial Film Permeability Measurements

Note: The two curves represent different electrode spacings

Table XXXII: NaCl diffusion through supported polysalt interfacial films at 25.0 ± 0.02°C. Membrane area = 0.442 sq. in.

Run	Supporting membrane	Conditions at start of run	Low conc. side of diffusion cell			Time Interval used	Avg.conc. difference across membrane	NaCl diffusion rate, moles/hr/sq. in. per 0.1 M/1 conc. difference across membrane
			Time, minutes	Resis.of conduc. cells, ohms	NaCl conc. M/1 (fig. 49)			
1-a	Filter paper, S&S 576	100.0 ml 0.1 M NaCl diffusing to 100.0 ml 0.001 M NaCl, no interfacial film	0	1870	0.00100	10 min -120 min	0.0964 M/1	3.0 x 10^{-4}
			10	1670	0.00113			
			15	1570	0.00121			
			20	1475	0.00130			
			25	1373	0.00140			
			30	1290	0.00150			
			35	1225	0.00159			
			40	1155	0.00170			
			45	1093	0.00180			
			50	1035	0.00190			
			55	984	0.00200			
			60	935	0.00213			
			70	855	0.00235			
			80	790	0.00255			
			90	738	0.00275			
			100	691	0.00295			
			110	640	0.00320			
			120	600	0.00343			
1-b	Same as 1-a	Same as 1-a except filter paper treated to contain imbedded interfacial film	0	1835	0.00100	10 min-120 min.	0.0963 M/1	3.0 x 10^{-4}
			3	1770	0.00103			
			10	1620	0.00115			
			20	1380	0.00135			
			25	1285	0.00146			
			30	1205	0.00157			
			35	1140	0.00166			
			40	1080	0.00176			
			45	1022	0.00190			

			50	795	0.00196		
			55	928	0.00205		
			60	892	0.00217		
			70	819	0.00238		
			80	755	0.00260		
			90	705	0.00280		
			100	660	0.00300		
			110	614	0.00326		
			120	585	0.00352		
			0	1820	0.00100			
2-a	Filter	100.0 Ml 0.1M	10	1540	0.00120	10 min-	0.0961	3.24 x 10^{-4}
	paper,	NaCl diffusing	15	1416	0.00132	120 min	M/1	
	S&S 576	to 100.0 ml	20	1318	0.00143			
		0.001 M NaCl	25	1219	0.00156			
		no interfacial	30	1121	0.00170			
		film	40	1010	0.00191			
			50	910	0.00213			
			60	827	0.00236			
			70	757	0.00259			
			80	703	0.00281			
			90	655	0.00302			
			102	607	0.00330			
			120	543	0.00372			
			0	1790	0.00100	5 min-	0.0960	
2-b	Same as	Same as 2-a,	5	1525	0.00118	120 min	M/1	3.22 x 10^{-4}
	2-a	except filter	15	1285	0.00143			
		paper treated	20	1195	0.00154			
		to contain	25	1120	0.00167			
		imbedded	30	1053	0.00176			
		interfacial	35	995	0.00189			
		film	40	934	0.00201			
			45	892	0.00213			
			50	845	0.00221			
			55	807	0.00234			
			60	779	0.00244			
			70	713	0.00269			

			80	664	0.00287			
			90	615	0.00314			
			100	581	0.00337			
			110	547	0.00357			
			120	518	0.00380			
			0	620	0.003			
3-a	Type "SM" millipore filter (5.0 micron pore size)	100.0 ml 0.1M NaCl diffusing to 100.0 ml 0.003M NaCl no interfacial film	5	555		30 min-300 min	0.0775 M/l	9.46 x 10^{-4}
			10	503				
			20	422				
			30	353	0.0054			
			40	316				
			50	288				
			60	263				
			70	248				
			80	228				
			90	214				
			120	182				
			150	161				
			180	146				
			210	132				
			240	123				
			270	114				
			300	106	0.0200			
			0	620	0.00300			
3-b	Same as 3-a	Same as 3-a except filter treated to contain imbedded interfacial film	10	559		30 min-180 min	0.0849 M/l	9.50 x 10^{-4}
			15	530				
			20	480				
			30	415	0.0046			
			40	365				
			50	325				
			60	293				
			70	272				
			80	252				
			90	234				
			120	199				
			150	172				
			180	153.5	0.0135			

Table XXXIII: Solubility limits of VBTAC-NaSS polysalts and salt-out of NaSS in NaBr-acetone-water solutions at room temperature (25-30°C)

Composition of mixtures at turbidity or gelation (marked with asterisk) points			Mixture wt. (not including VBTAC & NaSS)	Per cent acetone	Per cent H_2O
g. acetone	g. H_2O	g. NaBr			
Run 1 (0.5 g. VBTAC and 0.5 g. NaSS in mixture)					
2.1*	24.8*	14.0*	40.9	5.1	60.6
12.3*	24.8*	14.0*	51.1	24.1	48.5
18.7	54.7	14.0	87.4	21.4	62.6
28.0	57.5	17.3	102.8	27.2	55.9
28.3	58.8	17.3	104.4	27.1	56.3
28.5	73.6	17.3	119.4	23.8	61.5
Run 2 (0.5 g. VBTAC and 0.5 g. NaSS in mixture)					
2.2*	28.5*	14.0*	44.7	4.93	63.8
2.5*	30.8*	14.0*	47.3	5.28	65.1
4.6*	37.9*	14.0*	56.5	8.14	67.1
5.6*	41.1*	14.0*	60.7	9.27	67.7
7.6*	45.9*	14.0*	67.5	11.3	68.0
9.6	48.6	14.0	72.2	13.3	67.3
13.1	53.2	14.0	80.3	16.3	66.3
15.1	54.3	14.0	83.4	18.1	65.1
27.6	55.7	20.7	104.0	26.5	53.6
28.8	55.7	24.0	108.5	26.6	51.3
30.0	55.7	28.2	113.9	26.4	48.9
30.7	55.7	32.0	118.4	25.9	47.0
30.7	57.0	38.9	126.6	24.3	45.0
30.7	57.9	41.1	129.7	23.7	44.6
Run 3 (0.26 g. VBTAC and 0.26 g. NaSS in mixture)					
16.0	31.6	23.5	71.1	22.5	44.4
16.0	34.9	27.2	78.1	20.5	49.6
16.0	46.8	38.2	101.0	15.8	46.3
16.0	55.5	45.4	116.9	13.7	47.4
16.0	63.4	51.9	131.3	12.2	48.2
16.0	71.1	58.0	145.1	11.0	49.0
16.0	80.0	64.9	160.9	10.0	49.7
14.0	88.1	70.6	174.7	9.2	50.4

Run 4 (0.3 g. VBTAC and 0.3 g. NaSS in mixture)

2.1	28.1	14.0	44.2	4.8	63.6
2.9	28.1	20.5	51.5	5.6	54.6
3.6	31.0	23.1	57.7	6.2	53.7
8.7	32.0	25.9	66.6	13.1	48.1
8.7	33.2	26.7	68.6	12.7	48.4
8.7	35.3	28.4	72.4	12.0	48.8
8.7	43.4	34.5	86.6	10.1	50.2
8.7	46.1	36.0	90.8	9.6	50.7
8.7	49.6	38.4	96.7	9.1	51.3
8.7	63.5	48.7	120.9	7.2	52.5
8.7	71.9	54.0	134.6	6.5	53.4
8.7	75.6	56.6	140.9	6.2	53.6
8.7	82.0	60.7	151.4	5.7	54.1

Run 5 (0.15 g. VBTAC and 0.15 g. NaSS in mixture)

4.3	50.8	36.2	91.3	4.7	55.7
4.3	57.6	40.8	102.7	4.2	56.1
4.3	70.8	49.7	124.8	3.4	56.8
4.3	82.2	58.3	144.8	3.0	56.8
4.3	100.8	58.3	163.4	2.6	61.7

Run 6 (0.1 g. VBTAC and 0.1 g. NaSS in mixture)

2.0	30.0	15.2	47.2	4.2	63.6
2.0	31.8	16.5	50.3	4.0	63.2
2.0	34.9	18.7	55.6	3.6	62.8
2.0	45.6	26.4	74.0	2.7	61.6
2.0	54.6	37.9	94.5	2.1	57.8

Run 7 (0.1 g. VBTAC and 0.2 g. NaSS in mixture)

15.7	30.6	11.8	58.1	27.0	52.7
15.7	32.4	23.8	71.9	21.8	45.1
15.7	84.7	23.8	124.2	12.6	68.2
15.7	85.2	67.3	168.2	9.3	50.0

Run 8 (0.4 g. VBTAC and 0.2 g. NaSS in mixture)

15.2	28.9	11.1	55.2	27.6	52.4
15.2	28.9	20.8	64.9	23.4	44.6
15.2	70.9	20.8	106.9	14.2	66.4
15.2	70.9	57.7	143.8	10.6	49.3
15.2	138.2	57.7	211.1	7.2	65.5

Run 9 (0.0 g. VBTAC and 0.5 g. NaSS in mixture)

19.1	37.1	28.3	84.4	22.6	44.0
27.4	47.1	28.3	94.4	26.7	45.8
31.7	57.5	28.3	117.4	27.0	48.9
38.3	76.8	28.3	143.3	26.7	53.6
44.6	97.3	28.3	170.1	26.2	57.2
51.4	118.6	28.3	198.2	26.0	59.9
58.1	139.9	28.3	226.2	25.6	61.9

Run 10 (0.0 g. VBTAC and 0.1 g. NaSS in mixture)

9.1	18.9	2.0	30.0	30.3	6.7
20.2	39.3	2.0	61.5	32.9	3.3
36.3	60.0	2.0	98.3	37.0	2.0
56.4	81.4	2.0	139.8	40.3	1.4
78.2	103.1	2.0	183.3	42.6	1.1
90.0	113.1	2.0	205.1	43.5	0.98

Run 11 (0.0 g. VBTAC and 0.1 g. NaSS in mixture)

17.0	34.5	11.4	62.9	27.0	18.1
24.9	54.8	11.4	91.1	27.4	12.5
30.7	71.2	11.4	113.3	27.1	10.1
49.5	111.5	11.4	172.4	28.7	6.6

Run 12 (0.0 g. VBTAC and 0.1 g. NaSS in mixture)

9.3	35.2	29.2	73.7	12.6	39.6
9.3	57.4	45.1	111.8	8.3	40.3

Run 13 (0.0 g. VBTAC and 0.1 g. NaSS in mixture)

0.0	24.9	15.0	39.9	0.0	37.6
1.4	24.9	17.0	43.3	3.2	39.3
3.3	24.9	19.1	47.3	7.0	40.4

Table XXXIV: Swelling of neutral polysalt in NaBr-acetone-water solutions

Sample	% acet	% H_2O	% NaBr	Sample wt. 50% hum.	Sample wt. dry*	Sample wt. soaked	Swelling, g/g	Sample appearance after swelling
B_2-A	0	100	-	-	0.118g	0.165	0.40	transparent, brittle
B	20	80	-	-	0.231	0.328	0.42	" "
C	40	60	-	-	0.357	0.500	0.40	" "
D	80	20	-	-	0.128	0.166	0.30	" "
E	100	0	-	-	0.188	0.192	0.02	" "
B_4-A	0.0	100	-	0.331	0.292	0.412	0.41	" "
B	10	90	-	0.371	0.328	0.464	0.42	" "
C	20	80	-	0.417	0.368	0.524	0.42	" "
D	30	70	-	0.170	0.150	0.211	0.41	" "
E	40	60	-	0.146	0.129	0.179	0.39	" "
B_3-A	0.0	100	-	0.229	0.202	0.282	0.40	" "
B	20	80	-	0.349	0.308	0.438	0.42	" "
C	40	60	-	0.267	0.236	0.333	0.42	
D	60	40	-	0.221	0.195	0.269	0.38	" "
B_6-A				0.857	0.756			
B_4-A	-	99	1.0	0.331	0.292	0.413	0.41	
B	-	95	5.0	0.371	0.328	0.497	0.51	
C	-	90.4	9.6	0.417	0.368	0.666	0.81	
D	-	86.1	13.9	0.170	0.150	0.343	1.29	
E	-	82.1	17.9	0.146	0.129	0.381	2.03	
B_5-A	0	98	2	0.743	0.655	0.937	0.43	transp., brittle
B	10	88	2	0.814	0.719	1.038	0.445	" "
C	20	78	2	0.353	0.312	0.448	0.435	" "
D	30	68	2	0.432	0.382	0.548	0.435	" "
E	40	58	2	0.418	0.369	0.531	0.44	" "
G	60	38	2	0.487	0.430	0.627	0.46	" "
B_4-A	10	85	5	0.331	0.292	0.462	0.58	" "
B	20	75	5	0.371	0.328	0.519	0.58	" "
C	30	65	5	0.417	0.368	0.585	0.59	" "
D	40	55	5	0.170	0.150	0.238	0.59	" "
E	50	45	5	0.146	0.129	0.255	0.97	opaque, flexible
F	60	35	5	0.171	0.151	0.413	1.74	" , soft

Sample	% acet	% H_2O	% NaBr	Sample wt. 50% hum.	Sample wt. dry*	Sample wt. soaked	Swell-ing, g/g	Sample appearance after swelling
B_5-A	0	93	7	0.743	0.655	1.056	0.61	transp., brittle
B	10	83	7	0.814	0.719	1.205	0.68	" "
C	20	73	7	0.353	0.312	0.530	0.70	" , flexible
D	30	63	7	0.432	0.382	0.701	0.83	opaque, flexible
E	40	53	7	0.418	0.369	0.863	1.34	" "
G	50	43	7	0.487	0.430	1.209	1.81	", soft
B_3-A	10	80	10	0.229	0.202	0.404	1.00	transp., flex.
B	20	70	10	0.349	0.308	0.676	1.19	" , soft
C	30	60	10	0.267	0.236	0.618	1.62	opaque, soft
D	40	50	10	0.221	0.195	0.593	2.04	opaque, tacky
E	50	40	10	0.391	0.345	1.118	2.24	opaque, tacky
F	60	30	10	0.201	0.177	fractionated		--
B_4-A	10	75	15	0.331	0.292	1.122	2.85	opaque, soft
B	20	65	15	0.371	0.328	2.862	7.72	opaque, tacky
C	30	55	15	0.417	0.368	fractionated		--
D	40	45	15	0.170	0.150	fractionated		--
B_4-A	70	28	2	0.331	0.292	0.450	0.54	translucent, brit.
B_3-A	70	26	4	0.229	0.202	0.468	1.31	opaque, soft
B_3-B	70	24	6	0.349	0.308	0.932	2.02	opaque, tacky
B_3-C	70	22	8	0.267	0.236	fractionated		--

* (dry wt.)/(50% hum. wt.) assumed same as for B_6-A

(dry wt.) = 0.883 x 50% hum. wt.)

Table XXXV: Swelling of polysalt composed of VBTAC & NaSS in the ionic ratio 2 VBTAC/ 1 NaSS, in NaBr-acetone-water mixtures

Sample	% acet	% H_2O	% NaBr	Sample wt. 50% hum.	Sample wt. dry	Sample wt. soaked	Swelling g/ g	Sample appearance after soaking
A_4- A	0	100	0	0.420	0.386^{1}	1.430	2.71	
B	0	99.9	0.1	0.313	0.288^{1}	1.235	3.28	
C	0	99.0	1.0	0.331	0.304^{1}	1.708	1.32	
D	0	90.4	9.6	0.278	0.246^{1}	0.534	1.17	
A_3-A	0	100	0	0.267	0.243^{2}	1.040	3.28	
B	0	99.7	0.1	0.343	0.312^{2}	1.419	3.54	
C	0	99.0	1.0	0.300	0.273^{2}	0.635	1.32	
D	0	90.4	9.6	0.366	0.333^{2}	0.709	0.94	
A_4- A	0	100	-	0.420	0.386^{1}	1.289	2.34^{4}	opaque
B	20	80	-	0.313	0.288^{1}	1.775	5.17^{4}	opaque
C	40	60	-	0.331	0.304^{1}	1.445	3.75^{4}	opaque
D	60	40	-	0.267	0.246^{1}	0.480	0.95^{4}	transparent
E	80	20	-		0.321	0.413	0.29	transparent
F	100	0.0	-	0.314	0.289	0.302	0.04	transparent
E	10	90	-		0.321	1.733	4.4 ^{4}	opaque
F	50	50	-	0.314	0.289	0.740	1.56 ^{4}	opaque
A_5- A	0	100	-	0.267	0.243^{2}	0.996	3.1	
B	20	80	-	0.343	0.312^{2}	2.045	5.57	
C	40	60	-	0.300	0.273^{2}	1.546	4.66	
D	60	40	-	0.366	0.333^{2}	0.617	0.85	
E	80	20	-		0.286	0.368	0.29	
E	10	90			0.286	1.475	4.16^{4}	
F	50	50	-	0.257	0.234	0.786	2.36^{4}	
A_5 - A	0	98	2	0.370	0.321^{3}	0.563	0.75	opaque, rigid
A	10	88	2	0.370	0.321^{3}	0.586	0.83	" "
B	20	78	2	0.368	0.320^{3}	0.594	0.85	" "
C	30	68	2	0.420	0.365^{3}	0.675	0.85	" "
D	60	58	2	0.397	0.345^{3}	0.545	0.58	" "
A_4 - F	40	48	2		0.289	0.496	0.71	

Sample	% acet	% H_2O	% NaBr	Sample wt. 50% hum.	Sample wt. dry	Sample wt. soaked	Swelling g/g	Sample appearance after soaking
A_5-E	0	95	5	0.399	0.346^3	0.603	0.74	opaque, rigid
E	10	85	5	0.399	0.346^3	0.636	0.84	" "
G	20	75	5	0.391	0.340^3	0.656	0.93	" "
H	30	65	5	0.557	0.484^3	1.016	1.10	opaque, flex.
I	40	55	5	0.596	0.518^3	1.061	1.05	" "
(A_3-F)	50	45	5		0.234	0.425	(0.82)	opaque, soft
A_5- A	0	93	7	0.370	0.321^3	0.597	0.86	opaque, rigid
B	10	83	7	0.368	0.320^3	0.644	1.01	" "
C	20	73	7	0.420	0.365^3	0.862	1.36	opaque, flex.
D	30	63	7	0.397	0.345^3	1.041	2.02	opaque, soft
E	40	53	7	0.399	0.346^3	0.927	1.68	opaque, soft
G	50	43	7	0.391	0.340^3	0.820	1.41	opaque, tacky
A_6-B				0.433	0.376			
A_4 -A	10	80	10	0.420	0.386^1	1.182	2.06	opaque, flex.
A_3-A	20	70	10	0.267	0.243^2	0.972	3.0	opaque, soft
A_4-B	30	60	10	0.313	0.288^1	1.312	3.56	opaque, soft
A_3-B	40	50	10	0.343	0.312^2	1.038	2.33	opaque, tacky
A_4-C	50	40	10					
A_3-C	60	30	10	0.300	0.273^2	fractionated		

[1] 0.92 x 50% hum. weight, by analogy to A_4-F

[2] 0.91 x 50% hum. wt. by analogy to A_3-F

[3] Dry weight = 0.869 x 50% hum. wt. by analogy to A_6-B

[4] Samples dessicated over P_2O_5 before measurement

Table XXXVI: Swelling of polysalt composed of 1 VBTAC/ 2 NaSS in NaBr-acetone-water solutions

Sample	% acet	% H_2O	% NaBr	Wt. room air	Wt. dry	Wt. soaked	Swelling, g/ g	Appearance
C_4- A	0	100	-	0.410	0.332^1	2.181	5.57	translucent, flex.
B	20	80	-	0.271	0.219^1	2.206	9.0	" "
C	40	60	-	0.294	0.238^1	1.248	4.21	" "
D	60	40	-	0.265	0.221^1	0.385	0.74	transparent, flex.
E	80	20	-	0.370	0.314^1	0.458	0.45	" , brittle
F	100	0	-	0.330	0.280	0.298	0.06	
C_3- A	0	100	-	0.286	0.262^2	2.003	6.64	
B	20	80	-	0.245	0.208^2	2.009	8.75	
D	40	60	-	0.267	0.193^2	1.117	4.73	
C	60	40	-	0.229	0.231^2	0.381	0.65	
E	80	20	-	0.313	0.270^2	0.391	0.45	
F	100	0	-	0.412	0.353	0.377	0.06	
C_4- D	10	90	-		0.221^1	2.012	8.05	
E	30	70	-		0.314^1	2.324	6.39	
F	50	50	-		0.280	0.665	1.39	
C_3- C	10	90	-		0.231^2	1.885	7.10	
E	30	70	-		0.270^2	2.098	6.75	
F	50	50	-		0.353	0.808	1.28	
C_4- A	-	99.9	0.1		0.332^1	2.007	5.05	
B	-	99	1.0		0.219^1	1.020	3.66	
C	-	90.4	9.6		0.238^1	0.664	1.79	
C_3- A	-	99.9	0.1		0.262^2	1.750	5.7	
B	-	99	1.0		0.206^2	0.946	3.59	
D	-	90.4	9.6		0.193^2	0.524	1.72	
C_4-A	10	85	5		0.332^1	0.993	1.98	transluc., flex.
C_3-A	20	75	5		0.262^2	0.686	1.62	" "
C_4-B	30	65	5		0.219^1	0.483	1.21	" "
C_3-B	40	55	5		0.206^2	0.405	0.96	transparent, flex.
C_4-D	50	45	5		0.221^1	0.489	1.22	opaque "
C_3-C	60	35	5		0.231^2	0.492	1.13	opaque, soft

Sample	% acet	% H_2O	% NaBr	Wt. room air	Wt. dry	Wt. soaked	Swelling, g/g	Appearance
C_4-A	10	80	10		0.332[1]	1.165	2.5	opaque, flex.
C_3-A	20	70	10		0.262[2]	0.782	1.98	transp., flex.
C_4-B	30	60	10		0.219[1]	0.623	1.85	" "
C_3-B	40	50	10		0.206[2]	0.531	1.67	" , soft
C_4-D	50	40	10		1.221[1]	0.701	2.18	tranluc., tacky
C_3-C	60	30	10		0.231[2]	0.808	2.5	" "
C_4-A	10	88	2		0.332[1]	0.997	2.0	opaque, flex.
C_3-A	20	78	2		0.262[2]	0.661	1.52	transp., flex.
C_4-B	30	68	2		0.219[1]	0.504	1.3	" "
C_3-B	40	58	2		0.206[2]	0.390	0.9	" "
C_4-D	50	48	2		0.221[1]	0.407	0.84	transluc., flex.
C_3-C	60	38	2		0.231[2]	0.415	0.79	" "

[1] dry wt. = 0.85 x wt. in room air, by analogy to C_4-F

[2] dry wt. = 0.857 x wt. in room air, by analogy to C_3-F

Table XXXVII: K+ / Na+ absorption selectivity of neutral polysalt. 0.946 g. neutral polysalt equilibrated 7 days with aqueous 0.1 M KCl-0.1 M NaCl solution, then NaCl and KCl were displaced from the polysalt by soaking it for 10 days in 50.0 ml 0.10M $MgBr_2$. Flame photometer measurements were made with a Beckman model B flame photometer using an oxy-hydrogen flame (slit width = 0.5 mm).

Sample (numbered samples are calibrated	$MgBr_2$ conc. M/1	Na+ conc. M/1	K+ conc. M/1	"% transmission" at 589m (for Na+)	"% transmission" at 768m (for K+)
1	0.10	0.006	--	98.1	--
2	0.10	0.004	--	82.1	--
3	0.10	0.002	--	58.6	--
unknown	0.10	unknown[1]	unknown[2]	48.5	43.2
4	0.10	0.00135[3]	0.005		88.1
5	0.10	0.00135	0.003		65.6
6	0.10	0.00135	0.001		29.8

[1] Na+ conc. in unknown = 0.00135 M, from plot of % transmission at 589m vs. NaCl conc. using data of samples 1, 2, and 3 (see Figure 50).

[2] K+ conc. in unknown = 0.00170 M from plot of % transmission at 768m vs. KCl conc., using data of samples 4, 5, and 6 (See Figure 50).

[3] Na+ conc. in unknown first determined as described in footnote (1), then this conc. of NaCl was added to the KCl calibration samples. This was done because Na+ has some emission at 768 m . (K+ does not interfere with Na+ determination at 589 m).

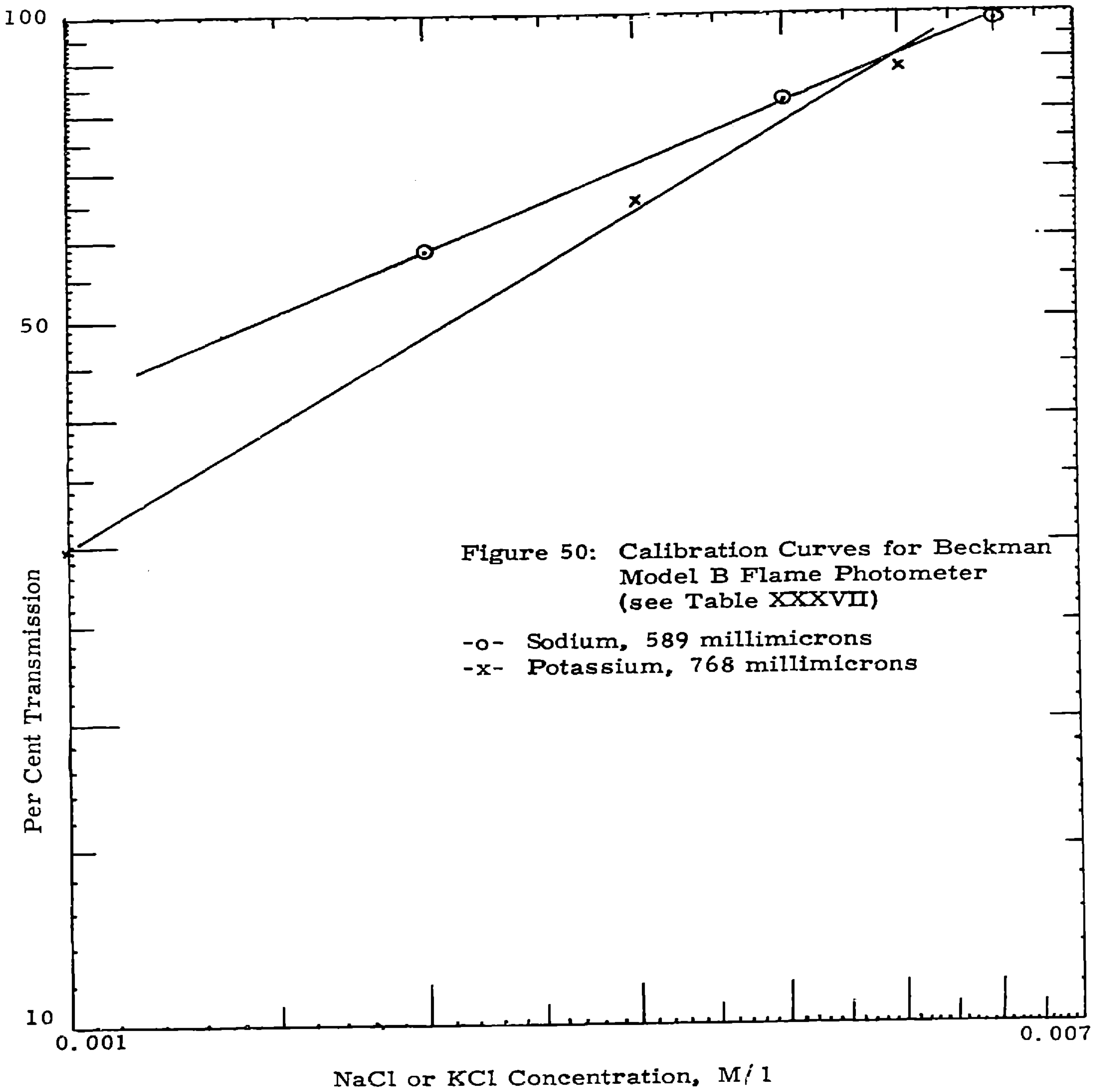


Figure 50: Calibration Curves for Beckman Model B Flame Photometer (see Table XXXVII)

-o- Sodium, 589 millimicrons
-x- Potassium, 768 millimicrons

D. Nomenclature

Å	Angstrom unit, 10^{-8} cm
c	concentration, M/l, Meq/dl, g/dl, or wt. per cent
c_i	internal concentration, wt. per cent (in liquid absorbed by polysalt)
c_o	external concentration, wt. per cent
c_p	polymer concentration, Meq/dl or g/dl
C	1.) capacitance, farads or micromicrofarads (μ μ f) 2.) velocity of light
C_o	geometric capacitance, farads or μ μ f
d	thickness, millimicrons
D	diameter, angstrom units
f	frequency, cycles per second
G"	equivalent conductance, ohms
i	angle of incidence, radians
k	integer
l	1.) path length, millimicrons 2.) liter
n_a	refractive index of air
n_f	refractive index of interfacial film
r	radius, angstrom units
$\sqrt{\overline{r_o^2}}$	root-mean-square end-to-end extension of a randomly coiled polymer molecule, cm, or angstrom units
$\sqrt{\overline{s^2}}$	root-mean-square distance of a volume element or chain segment from the center of gravity of a sphere or randomly coiled polymer molecule, cm. or angstrom units
t	time, seconds

Greek Letters

α	angle of refraction, radians
ϵ'	dielectric constant
ϵ''	loss factor, equals $\frac{G''}{2\pi fC_o}$ (C_o in farads)
η	viscosity of polymer solution, centipoises
η_o	viscosity of solvent, centipoises
η_{sp}	specific viscosity, equals $\frac{\eta-\eta_o}{\eta_o}$ or $\frac{\theta-\theta_o}{\theta_o}$
$[\eta]$	intrinsic viscosity $\equiv \lim_{c_p \to 0} \frac{\eta_{sp}}{c_p}$
$\eta_{sp\ theo}$	supernatant liquid specific viscosity corresponding to stoichiometric and ionically complete VBTAC-NaSS interaction
θ	flow time of polymer solution through viscometer, seconds
θ_o	flow time of solvent through viscometer, seconds
λ	wavelength, millimicrons
ν	vibration frequency of light, cycles per second
ω	angular velocity, radians per second

Glossary of Terms

counterion	mobile microion associated with a polyion
dl	deciliter (equals 100 ml)
NaSS	poly(sodium styrene sulfonate)
polyion	ion fixed to polymer chain
polysalt	complex formed by ionic reaction between a cationic polyelectrolyte and an anionic polyelectrolyte
PV BuPyBr	polyvinyl-N-butylpyridinium bromide
VBTAC	poly(vinylbenzyltrimethyl ammonium chloride)

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