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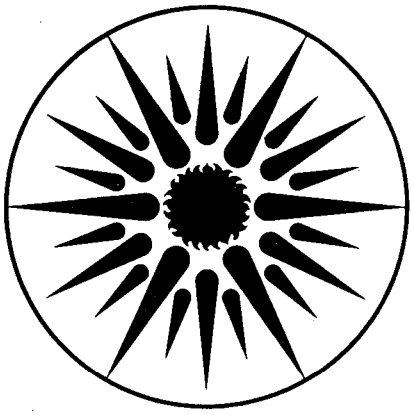

ENERGY AND ENVIRONMENT DIVISION

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Recovery of Propylene Glycol from Dilute Aqueous Solutions by Reversible Chemical Complexation with Organoboronates

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Abstract

The recovery of propylene glycol (1,2-PD) from aqueous solution using extractants containing organoboronates was studied experimentally. Extractants consisting of an ion-pair of Aliquat 336 with phenylboronate or 3-nitrophenylboronate were prepared in various diluents (2-ethylhexanol, toluene, *o*-xylene or diisobutylketone). In batch experiments 1,2-PD was very effectively extracted, even at low concentrations of 1,2-PD. The heterogeneous complexation constants β_{11} calculated from the results at 25 °C were 45-120 $(mol/l)^{-1}$ in 2-ethylhexanol, 34.8 $(mol/l)^{-1}$ in toluene, 37.6 $(mol/l)^{-1}$ in *o*-xylene and 14.4 $(mol/l)^{-1}$ in diisobutylketone. In 2-ethylhexanol, there was no significant influence of extractant concentration on the complexation constant. The equilibrium water concentration in the extractants was 8-12 wt %, and decreased with increasing uptake of 1,2-PD. Nearly all extractant/diluent systems exhibited overloading (more than stoichiometric uptake of 1,2-PD). Evidence for aggregation of the ion-pair extractant in the organic phase was found from water solubilization studies (molar solubilization ratios up to 10) and ^1H NMR spectroscopy studies. Solubilization of 1,2-PD within hydrophilic aggregate interiors may explain the observed overloading. The complexation constant decreased with increasing temperature, but not enough to make back extraction after a temperature change attractive. Back extraction may be achieved after acidification with carbon dioxide to convert the organoboronate anion to the corresponding organoboronic acid. Up to 80% of the extracted 1,2-PD was back-extracted in a batch extraction using CO_2. The extractant could then be regenerated by stripping carbon dioxide from solution at temperatures exceeding 110 °C. However, at these temperatures the extractant appears to undergo a transformation in which its color changes and the extraction capacity is reduced to about 60% of its original value.

Extractant regeneration by extracting CO_2 into an aqueous sodium carbonate solution does not lead to a noticeable chemical alteration. Regeneration effectiveness increases with increasing aqueous pH.

1. Introduction

1.1. Recovery of hydroxylated compounds from aqueous solutions

Recovery of compounds bearing multiple hydroxyl groups from aqueous solutions is important in many areas of the process industry. Recovery of fermentation chemicals from a complex and dilute broth (*e.g.*, glycerol can be recovered as a byproduct from ethanol fermentations; Cygnarowicz-Provost and Shapouri, 1994), removal of these chemicals from waste streams generated by a variety of industrial processes and recovery of glycols from the aqueous solutions in which they are produced as petrochemicals are typical examples, each with their own set of complicating issues. Recovering such chemicals with low volatility and strongly hydrophilic characteristics from dilute aqueous solutions is a difficult separation problem, one that in many fermentation processes causes downstream processing to account for 40% or more of the final product cost.

The most straightforward approach is multiple-effect evaporation or distillation. All the water must be evaporated, but by using the multiple-effect approach the required heat load is reduced. However, even in a triple-effect evaporation system, the heat required per pound of recovered chemical is high, especially for dilute aqueous solutions, since it is, to a first approximation, inversely proportional to the concentration of the aqueous solution. Also, the chemical of interest is often just one of many non-volatile chemicals in the solution; differentiation among these can be difficult and inefficient.

More economical separation methods are required, especially in cases where fermentation chemicals must compete with synthetically produced chemicals that have relatively low downstream processing costs. To remove them selectively and efficiently from solution, such methods must capitalize on specific properties of the chemicals to be recovered.

Chemicals of interest include glycerol and diols (which have boiling points well above that of water) and saccharides (which are non-volatile). The research described in this report focuses on propylene glycol (1,2-propanediol, 1,2-PD), which is a large-scale petrochemical product and a potential commercial fermentation chemical. Furthermore, its optical isomers (an *R*- and an *S*- form) do not differ in their physical properties. Another important fermentation glycol is 2,3-butanediol, which has a *meso* form with different properties than the *R*- and *S*- forms. The study of a mixture of two chemicals which differ in such areas as reactivity and residence time on a chromatography column would be a complex task. The use of 1,2-propanediol avoids these complications.

Propylene glycol is used in the production of polyester resins. It also has applications in the food and pharmaceutical industries. Currently it is produced from propylene oxide in a high-temperature, high-pressure hydrolysis reaction. The molar ratio of water to propylene oxide must be high to minimize dipropylene glycol formation. A compromise between yield and recovery costs leads to a *ca.* 15% aqueous solution of propylene glycol as the product stream (Wagner, 1978). The water is removed by multiple-effect evaporation.

A fermentation which produces *R*-propylene glycol from glucose, using the bacterium *Clostridium thermosaccharolyticum*, is described by Cameron and co-workers (Cameron and Cooney, 1986; Cameron *et al.*, 1990). The concentration of propylene glycol in the product mix is about 0.8% by weight.

Other glycols that can be produced by fermentation include 1,3-propanediol (trimethylene glycol), using glycerol as a substrate (Cameron and Cooney, 1986; Saint-Amans *et al*, 1994), and various butylene glycols, *e.g.* 2,3-butylene glycol from glucose (Senkus, 1946a).

Chemical properties of glycols that may allow them to be selectively recovered include their hydrogen-bonding capability, their characteristics in Lewis acid-base interactions, their ability to form specific chemical complexes with certain compounds and their ability to participate in specific reversible chemical reactions. Avenues to capitalize on these properties include chemical extraction and adsorption with extractants and adsorbents of well-chosen functionalities, adductive crystallization and reversible selective chemical reaction, followed by separation and back-reaction.

1.2. Solvent extraction

Munson and King (1984) compiled data on the equilibrium distribution of ethanol between an aqueous phase and a range of organic solvent phases. Solvents that combine a high molar distribution ratio D_{EtOH} (defined as the ratio of the equilibrium solute concentrations in the organic and the aqueous phase, respectively) with a high separation factor ($\alpha=D_{EtOH}/D_{H2O}$) would be effective in a liquid-liquid extraction process. However, nearly all solvents exhibit an unfavorable (<1) distribution ratio for ethanol. Lewis acid solvents give more favorable combinations of α and D_{EtOH} than do Lewis bases. Since glycols are more hydrophilic than ethanol, they distribute into the organic phase to an even lower extent.

Phenols are the solvents exhibiting the highest distribution ratios for ethanol, up to as high as 2.2. They would be candidates for a simple extraction process, as long as solvent toxicity and residual solvent solubility are not issues. Arenson and King (1989) investigated the extraction of several alcohols and diols into an organic phase containing *m*-cresol. The distribution ratio for extraction of propylene glycol into pure *m*-cresol is only *ca.* 0.7; this ratio decreases as the concentration of *m*-cresol in an organic diluent (chloroform, *m*-xylene) decreases. So even though phenolic compounds are the most

efficacious simple extractants found, their utility in a solvent extraction process for recovering glycols is limited. It is necessary to identify compounds that form stronger complexes with glycols.

1.3. Complexation with organoboronates

Borates and organoboronates are a class of compounds known to form complexes with *cis*-vicinal diols. They react reversibly with the diols to form a five-membered ring, as shown below for phenylboronate.

For the reaction to proceed, the boronic acid must be in the anionic form. The complexation may take place in an aqueous phase (Randel and King, 1991) or in an organic phase (Randel *et al*, 1994) in which the organoboronate ion must be coupled with an organic cation to maintain electroneutrality.

1.4. Extraction with a boronate-containing extractant

Such a system was previously investigated in this research group (Randel *et al.*, 1994; Randel and King, 1991; Chow, 1992). Polyhydroxy compounds were extracted into an organic phase containing the nitrophenylboronate (NPB^-)/Aliquat 336 ($A336^+$) ion pair. Aliquat 336 is a quaternary ammonium compound, trialkylmethylammonium

chloride, in which the alkyl groups are primarily n-octyl and n-decyl. The nitro group in nitrophenylboronic acid serves to reduce both the solubility and the pK_a relative to phenylboronic acid. NPB^- was shown to have a strong affinity for propylene glycol, the extractant being loaded to near its stoichiometric capacity even at low aqueous diol concentrations.

Since the complexation of NPBA with glycols occurs only when NPBA is in the anionic form, an extraction process can be envisioned in which the glycol is taken up from a dilute aqueous solution into a solution of the $NPB^-/A336^+$ extractant. The extractant can be regenerated by a pH swing that converts NPB^- to NPBA, releasing the glycol in the process.

Loss of NPBA to the aqueous phases during extraction and back-extraction due to the non-neglibible aqueous solubility of NPBA poses a problem that must be addressed. NPBA is an expensive chemical, and any significant process loss of NPBA may prove to add significant cost to the process.

1.5. Using boronates in an adsorption mode

Since organoboronates are the most effective extractants for diols, boronated adsorbents are likely to show a good selectivity and affinity for diols. Adsorbents with this functionality are available commercially only in the form of column packing resins for use with high-performance liquid chromatography (HPLC). Applications for these resins include the analysis of mixtures of sugars and organic biomolecules such as proteins and nucleotides. Boronate HPLC packings are manufactured by Bio-Rad (Affi-Gel 601) and Pierce (Glyco-Gel II). They consist of gel beads functionalized with phenylboronate groups *via* spacer groups of varying length and chemical composition. Singhal *et al.* (1991) describe a nitrophenylboronate HPLC packing that complexes with diols at a pH

just slightly higher than neutral (pK_a 7.4), with good binding capacity. Gel polymers of the kind used for HPLC are difficult to implement in an industrial adsorption process, due to factors such as their low capacity, their tendency to swell and the necessity for solutes to diffuse through the gel to complex with the boronate functionality. Macroreticular resins with an easily accessible adsorption surface and limited swelling characteristics would be better for industrial use, but are currently not commercially available.

Elliger *et al.* (1975) produced boronated adsorbents by several methods. Those obtained by coating porous polystyrene beads with poly(*p*-vinylbenzeneboronic acid) by interstitial polymerization had higher capacities than those produced by copolymerization of *p*-vinylbenzeneboronic acid with styrene. The uptake of *L*-DOPA (a biomolecule containing a vicinal diol functionality) from a 1 mM solution onto the coated polymer increased from 130 μmol/g at pH 7.0 to 400 μmol/g at pH 9.0. These uptakes are per weight of coating; 0.36 g of the boronic acid polymer is coated onto 5 g of polystyrene.

In their patent, Carobbi and Innocenti (1991) describe boronated resins prepared from a polyacrylic matrix functionalized with quaternary ammonium groups. The degree of crosslinking of these resins is 4%, and the degree of functionalization is 4.4 meq/g dry resin. Their selectivity in sugar uptake can be used for the purification of sugar syrups.

Research at TNO Zeist, Netherlands (Schneiders *et al.*, 1989; Hanemaaijer, 1992) aimed at continuous recovery of NAD (nicotinamide-adenine dinucleotide) from a fermentation broth investigated the uptake of NAD through a membrane into a solution of a water-soluble polymer functionalized with boronate groups. The spacer group between the hydrophilic polyethylene imine polymer and the phenylboronate function was engineered to maximize the binding capacity for NAD at the fermentation pH of 7.

In the overview above, the boronate functionality is an integral part of the polymeric resins. An alternate approach would be to load an anion-exchange resin with

borate or boronate anions, and to use this loaded resin to adsorb glycols. Since in this case the boronate functionality is not chemically bonded to the adsorbent matrix, the loss of boronate anions to the aqueous phase may be a problem. Hydrophobic attraction of the organoboronate anion to the exchange resin could limit this loss of activity.

1.6. Goals of the research described here

As was stated in Section 1.4, ion-pair extractants involving nitrophenylboronate in organic diluents are effective in the recovery of glycols from aqueous solutions. The research described in this report builds on the results of Chow (1992), and sets out to answer some additional questions and challenges.

Nitrophenylboronic acid is an expensive chemical, and its production requires several reaction steps. Phenylboronic acid, from which NPBA is derived, requires one less reaction step, and would therefore be less expensive. Most recent experiments have been carried out with PBA as the organoboronate compound, sacrificing the lower aqueous solubility of NPBA. The other characteristic of NPBA, its lower pK_a as compared to PBA, is not necessarily an advantage, since the back extraction must probably be carried out by pH swing, and the optimum pK_a cannot be easily predicted *a priori*.

Previous research left several questions about the chemistry and mechanism of the complexation reaction unanswered. This work takes a closer look at the reaction stoichiometry, the role of water in the extraction process and the effect of the diluent in which the extractant is prepared.

The back extraction is effected by a downward shift in pH, by which the phenylboronate anion is converted to phenylboronic acid. The $A336^+$ cation is then paired with the anion provided with the acid, *e.g.*, if hydrochloric acid is used to shift the

pH, $A336^+$ is paired with chloride anions. To reconvert this to the phenylboronate form, an upward shift in pH is required, during which a salt is formed, *e.g.* if the acid and base used in the back extraction and regeneration are hydrochloric acid and sodium hydroxide, respectively, then sodium chloride will be formed in the process. To avoid the consumption of chemicals and the formation of byproducts which must be separated and disposed of, acidification with a recoverable substance such as carbon dioxide to effect the back extraction , followed by stripping of the CO_2 to regenerate the extractant, is envisioned as an alternative. Back-extraction and regeneration were investigated. Extraction, back-extraction and regeneration results are presented in Chapter 2.

Two approaches to glycol recovery with solid sorbents using phenylboronate complexation were also studied experimentally; one on the basis of an anion exchange resin loaded with phenylboronate anions, the other on the basis of a phenylboronate affinity chromatography gel. The results are presented in Chapters 3 and 4.

2. Extraction

2.1. Experimental procedures

2.1.1. Analytical procedures

2.1.1.1. Titration of PBA in aqueous solutions

The concentrations of PBA in aqueous solutions were determined by titration with a sodium hydroxide solution of approximately 0.1 N concentration, using a Metrohm 655 Dosimat titrator. The progression of the titration was monitored by a pH meter and a pH combination electrode. The endpoint was determined from the inflection point (around pH 5) of the pH *vs.* volume curve.

2.1.1.2. Gas chromatographic analysis

The concentrations of 1,2-PD in aqueous solutions and in 2-ethylhexanol solutions were determined by gas chromatrography (GC). A Varian Model 3600 gas chromatograph was used, equipped with a flame ionization detector (FID). Samples of 1 µl volume were injected onto a 1/8-in., 5-ft stainless steel column packed with Waters Porapak PS, 80-100 mesh. The column temperature was set at 170°C. The FID output was processed by Varian's Star Chromatography Workstation software. Propylene glycol exhibited a nearly linear response on the FID over the entire range of concentrations used, up to 1.9 mol/L. However, more accurate results could often be obtained by using different linear two-parameter calibration fits for low-concentration (< 0.10 mol/L) and high-concentration analyses.

2.1.1.3. Chloride ion analysis

The concentration of chloride ions in aqueous solutions was analyzed using an Orion Model 94-17B combination chloride electrode and an Orion Model SA 720 pH/ISE meter. Standards were prepared by dissolving sodium chloride in aqueous solutions of sodium hydroxide. It was found that the electrode response was a function not only of the chloride ion concentration, but also of the hydroxide concentration. Both concentrations varied in the aqueous wash solutions analyzed by this method, thus complicating the analysis. Calibration results with standards varying in chloride and hydroxide concentrations are presented in Appendix A.

Later it was decided that a more accurate method of chloride analysis was preferable. The method chosen was Mohr's precipitation titration of chloride with silver nitrate, using a buffer of potassium chromate and potassium bichromate as the indicator (Vogel, 1989). Basic wash solutions were first neutralized by addition of 1 N sulfuric acid. A silver nitrate solution of 0.100 N titer (standardized against a sodium chloride solution) was used for the titrations.

2.1.1.4. Titration of aqueous wash solutions

Titration with 0.100 N HCl was used to determine the sum of the concentrations of hydroxide and phenylboronate ions in aqueous wash solutions, using the same equipment as described in Section 2.1.1.1. When both hydroxide and phenylboronate are present, the titration curve shows two inflection points, the first at the point where all free hydroxide has been neutralized (around pH 10.5), and the second at the point where all phenylboronate has been protonated (around pH 5). Therefore, both concentrations may be deduced from the curve.

Theoretically, the pK_a may be determined from the pH *vs.* volume curve, since the solution pH should equal the pK_a of PBA (8.86) at the point where half of the initial PB^- ions have been protonated. However, this method is imprecise because of the sharp change of pH at the end point, and it gave somewhat inconsistent results, possibly due to the effect on the pH exerted by other buffering components of the solution, such as dissolved CO_2.

2.1.1.5. UV/VIS spectrophotometry

Due to their aromatic character, phenylboronic acid and nitrophenylboronic acid and their anions absorb light in the UV region. Analyses of phenylboronate concentrations in aqueous solutions were made using a Hewlett Packard Model 8452A diode array spectrophotometer. Standards were prepared by dissolving PBA in sodium hydroxide solutions of approximately the same strength as the samples to be analyzed. A sodium hydroxide solution of that strength was used as a blank.

Sodium hydroxide solutions absorb UV light at wavelengths below 240 nm. Phenylboronate shows two distinct peaks, one at 222 nm and one at 258 nm. Because of its overlap with sodium hydroxide absorption, the peak at 222 nm is not useful for quantification purposes. The height of the peak at 258 nm is proportional to phenylboronate concentration in a relatively narrow concentration region; deviations from linearity start at concentrations above 6 mM PB^-. On the other hand, background absorption by low-concentration contaminants becomes significant at concentrations of PB^- below 1 mM. Between these limits, the analyses are very reproducible and yield results with less than 2% error. Occasionally nitrophenylboronate was analyzed instead of phenylboronate. Nitrophenylboronate absorbs even more strongly than does phenylboronate, which shifts the concentration range for linear response down to 0.02-

0.3 mM. Its spectrum exhibits peaks at 222 and 282 nm. Absorbance is related to concentration via the relationship $A = \epsilon\, l\, c$, in which l is the path length through the absorbing solution and ϵ is the molar absorbance coefficient. The path length of the cuvet used in these experiments was 1.00 cm. The value of ϵ was determined to be 226 l/mol·cm for PB^-, $7.19 \cdot 10^3$ l/mol·cm for NPB^-.

Attempts were made to develop a UV technique for direct analysis of the phenylboronate concentration in extractant solutions. The method yielded only approximate results, due to complications such as absorption by Aliquat 336 in the UV region. Details of the method are presented in Appendix B.

2.1.1.6. Boronate analysis by atomic absorption spectroscopy

The boron content of chemicals may also be analyzed by atomic absorption (AA) spectroscopy. Aqueous wash phases were analyzed using a flame AA instrument at the UC Berkeley College of Chemistry Micro-analytical lab. Because of the highly fluctuating response of the instrument, it was decided that this method of analysis could not provide concentration measurements of sufficient precision, and subsequent measurements were done by UV spectrophotometry and by titration. Since neither of those techniques is effective for analysis of organic phases, an attempt was made to analyze extractant solutions by AA. The Micro-analytical Lab could not obtain accurate results on the AA instrument. A subsequent attempt at analysis by Ion-Coupled Plasma Atomic Emission analysis by Desert Analytics, Inc. (Tucson, AZ) was also not successful. An alternative direct boron analysis for liquid phases was not found.

2.1.1.7. Karl Fischer titration for water concentration

The concentration of water in organic solutions was determined by Karl Fischer titration, using a Quintel CompuTrac MS-1 titrator. KF solvent and titrant (2 mg/mL standard) were obtained from GFS Chemicals.

2.1.1.8. Elemental analyses

Analyses for carbon, hydrogen and nitrogen content of organic chemicals were performed by the UC Berkeley College of Chemistry micro-analytical laboratory using a combustion analyzer. Analyses for chlorine and boron were carried out by Desert Analytics using the Schoniger Flask method and flame atomic absorption spectroscopy, respectively.

2.1.2. Purity of materials

2.1.2.1. Water

Deionized water with a resistivity of 18 MΩ-cm was generated by a Millipore Milli-Q water purification system. This water was used in preparing all the solutions mentioned hereafter.

2.1.2.2. Phenylboronic acid

A lot of phenylboronic acid (F.W. 121.93) was obtained from Aldrich Chemical Co. The specified purity was 97%, with a melting point of 217-220°C. The label also indicated that phenylboronic anhydride may be present in addition to phenylboronic acid. By acid/base titration with 0.0986 N NaOH the effective molecular weight was found to be 120 g/acid equivalent, which may indicate that some anhydride (F.W. 103.91) is indeed

present. Elemental analyses for carbon, hydrogen and boron showed 57.90 wt% C, 5.77 wt% H and 8.40 wt% B. The atomic H/C ratio calculated from these numbers is 1.19, which provides no evidence for the presence of anhydride (formula H/C is 1.17 for the acid, 0.83 for the anhydride). The atomic C/B ratio is 6.19. Since the experimental error in the analyses, especially for boron, is not well-known, it is difficult to draw conclusions from the fact that C/B deviates from 6. The boron content may be expressed as 129 g/mol B, which could indicate the presence of water (or some other inorganic compound which doesn't contain boron). Since the outcomes of the several analyses do not present a clear picture of the presence of impurities, the stated formula weight of the acid was used in all calculations, and 100% purity was assumed. Where reference is made to PBA in the experimental procedures, phenylboronic acid was used as is.

2.1.2.3. Nitrophenylboronic acid

Two lots of 3-nitrophenylboronic acid were obtained from Aldrich Chemical. Randel and King (1991) concluded from several analyses, including titration of aqueous solutions and elemental boron analysis, that the most accurate molecular weight to use was close to the molecular weight of the acid anhydride, 148.91 g/mol. The experimentally determined formula weight for the second lot, which was used in the experiments described here, was 149.7 g/mol. This value was used in all calculations. In this report, the designations nitrophenylboronic acid and NPBA both refer to the *meta* compound.

2.1.2.4. Aliquat 336

Aliquat 336, manufactured by Henkel Corporation, obtained from Aldrich Chemical Co., is labeled as trioctylmethylammonium chloride ($TOMA^+Cl^-$), with a formula weight of 404.17. Previous findings in this research group (Chow, 1992) revealed that the actual composition of Aliquat 336 differs considerably from pure $TOMA^+Cl^-$. The lot of Aliquat used for the experiments described here (lot number 05611MW) was analyzed for the carbon, hydrogen, nitrogen and chlorine contents. The analyses found 71.00 wt% C, 14.13 wt% H, 2.87 wt% N and 7.43 wt% Cl. This totals to 95.43 wt%.

Since this result is similar to previous analyses reported by Randel and King (1991) and Chow (1992), the presence of oxygen as a fifth element was suspected. Analysis by Karl-Fischer titration showed a water concentration of 5.50 wt%. This translates to 4.89 wt% O, and a total of 100.32 wt%, which is an acceptable result when experimental errors are taken into account.

The overall formula for this lot of Aliquat 336 is then $C_{28.9}H_{65.5}NCl_{1.02}\cdot 1.49\ H_2O$, which corresponds to 488 g/mol N, or 477 g/mol Cl. An average value of 483 g/mol for the formula weight was used in all subsequent calculations, with the assumption that all nitrogen atoms are present in the quaternary ammonium form with chloride as a counterion.

2.1.3. Solubility of PBA

An excess of PBA was stirred with water for 2 days at room temperature. The supernatant solution was analyzed by titration with 0.0986 N NaOH.

2.1.4. Preparation of extractant solutions - caustic wash method

PBA and Aliquat 336 were dissolved in the diluent (2-ethylhexanol, toluene, *o*-xylene or diisobutylketone), then repeatedly washed with sodium hydroxide solutions of a molarity close to that of Aliquat 336 in the organic phase, and finally washed with pure water. An overview of the concentrations and other relevant experimental conditions used in the various extractant preparations, and a detailed step-by-step experimental procedure, are presented in Appendix C.

The aqueous and organic phases were contacted in a separatory funnel by manual shaking. In the final water wash, and to a lesser degree in the caustic washes, a persistent emulsion often formed and would not settle by gravity. In these cases the phases were separated by centrifugation, sometimes for as long as an hour in a Damon IEC S II centrifuge operating at full speed (2200 RPM). The difficulties with emulsion formation were most pronounced in the preparation of low-concentration extractants. At higher concentrations of Aliquat 336 and PBA, settling of the phases was usually faster and the amounts of stable emulsion were insignificant.

The wash solutions were analyzed for pH, chloride ion concentration and boronate concentration by the techniques described in Section 2.1.1.

Several experiments were carried out with nitrophenylboronic acid replacing phenylboronic acid. Additionally, a number of experiments were carried out in which Aliquat 336 solutions, without any boronate, were washed repeatedly with sodium hydroxide solutions varying in concentration between 0.1 M and 0.5 M. These sets of experiments are also documented in Appendix C.

2.1.5. Preparation of extractant solutions - methanol method

An alternative method for the preparation of phenylboronate extractants was also investigated. In this method, a solution of sodium phenylboronate in methanol was prepared by dissolving 3 g phenylboronic acid in 50 mL methanol and adding 1.16 g sodium hydroxide. Then 14 g Aliquat 336 was added to this solution, and the mixture was stirred for several minutes, during which sodium chloride precipitated out. The solids were removed by filtration, washed with methanol and analyzed for chloride content.

Next, 60 mL 2-ethylhexanol was added and most of the methanol was distilled out of the mixture, until the liquid temperature reached 85°C (at atmospheric pressure). The additional solids precipitated during the distillation were again removed by filtration, washed with 2-ethylhexanol and analyzed for chloride. The organic phase was washed with water twice (50 mL and 25 mL), to remove residual methanol, sodium chloride and sodium hydroxide. The aqueous wash phases were analyzed for phenylboronate, hydroxide and chloride as described above.

2.1.6. Preparation of an extractant loaded with inorganic borate

In one series of experiments, a solution of 0.50 M Aliquat 336 in 2-ethylhexanol was contacted twice with an aqueous solution of 0.46 mol/kg sodium borate (prepared by dissolving 7.74 g of boric acid and 5.01 g of sodium hydroxide in 250 mL water). The amount of borate taken up by the Aliquat 336 was determined by titration of the aqueous phases after contacting.

2.1.7. Measurement of the distribution ratio of 1,2-PD

The partition coefficient of 1,2-PD between water and 2-ethylhexanol was measured in batch equilibrium experiments. Standard 1,2-PD solutions were prepared in water that had been presaturated with 2-ethylhexanol. Known volumes of the 1,2-PD solution and water-saturated 2-ethylhexanol were contacted at room temperature with vigorous stirring, for at least 4 hours. The concentrations of 1,2-PD in both phases were measured by GC. The concentration of water in the organic phase was measured by Karl-Fischer titration.

In order to correct accurately for physical distribution into high-concentration extractants, the distribution ratio for 1,2-PD between 30.6 vol % Aliquat 336 (chloride form) in 2-ethylhexanol was also measured. In this case it was not possible to analyze the organic phase for 1,2-PD directly. Instead, the aqueous-phase concentrations of 1,2-PD before and after extraction were measured, along with the water concentration in the organic phase. Similar experiments were also carried out with solutions of Aliquat 336 in various other organic diluents.

2.1.8. Extraction studies

A number of standard 1,2-PD solutions were prepared. For each extraction experiment, known volumes of one of these standards and one of the extractants were pipetted into a 20-mL scintillation vial. In the experiments reported here, the actual quantities of each phase were determined by weight measurement, since pipetting the viscous extractant yielded inconsistent results.

The phases were contacted on a shaker bath, shaking at a rate of 80 rpm, for at least 16 hours. The shaker bath temperature was controlled to either 25 or 55 °C. The agitation was not strong enough to cause emulsification problems.

The final 1,2-PD concentration of the aqueous phase was measured by GC, using the original 1,2-PD solution as a standard. The conditions of all batch extraction experiments are reported in Appendix D.

To investigate the co-extraction of water into the extractant phase, the water concentration of the final organic phase was measured in many of the experiments. Also, the distribution of 1,2-PD and water between an aqueous phase and 2-ethylhexanol was measured at several 1,2-PD concentrations.

2.1.9. Back extraction with hydrochloric acid

Several milliliters of extractant Q (Table 2.1) were contacted with 0.7456 M 1,2-PD at room temperature, to load the extractant fully. The extractant phase was then contacted with 0.5 N hydrochloric acid. The concentration of 1,2-PD in the resulting aqueous phase was measured after the back extraction.

2.1.10. Back extraction by acidification with carbon dioxide

Experiments in which carbon dioxide was used to force back extraction were carried out using extractants that had been pre-loaded with 1,2-PD. The experimental conditions and results of the pre-loading steps are given in Appendix D. Back extractions were carried out on a system consisting of a 30-mL sparge vessel (glass vial) containing known quantities of the loaded extractant phase and water.

Carbon dioxide from a liquid CO_2 cylinder (purity 99.98%) was presaturated with water and 2-ethylhexanol by passing it through an absorption flask containing both an aqueous and a 2-ethylhexanol phase. The saturated gas was then passed through the sparge vessel. During the experiment the two phases inside the vessel were dispersed by

magnetic stirring. The experiments were carried out at atmospheric pressure and ambient temperature.

The absorption of CO_2 was monitored by measuring the weight of the sparge vessel set-up. Experiments were ended when no further weight increase was seen, usually after 1 to 2 hours. In fact, the weight sometimes slowly decreased from its maximum value, presumably due to evaporation of water.

After the experiment, the aqueous phase was analyzed for 1,2-PD. Conditions and results for the CO_2 back-extraction experiments are summarized in Appendix F.

2.1.11. Kinetics of extraction and back extraction

In one extraction experiment (expt. W15, see Appendix D) the propylene glycol uptake was followed by repeated sampling of the aqueous phase. The phases were contacted in a 20-mL vial, on a shaker bath controlled to 25 °C and operating at 120 rpm. Samples were analyzed by GC for 1,2-PD.

Similarly, in a back extraction experiment (expt. Rg19, see Appendix F), the aqueous-phase glycol concentration and the mass increase due to absorption of CO_2 were measured as a function of time. The phases were dispersed by magnetic stirring.

2.1.12. Extractant regeneration by stripping

Batches of extractants that had been treated with CO_2 were regenerated by immersing them in a temperature-controlled glycol bath. Nitrogen was sparged into the vial at a low rate to maintain a low partial pressure of CO_2 and to prevent degradation of the extractant by contact with oxygen. The temperature of the glycol bath was set at values ranging from 80 to 130°C. In most experiments, the duration of the regeneration was around 1 hour. In one experiment, no nitrogen was sparged through. Instead, a

boiling aqueous phase was maintained at the bottom of the vial, to simulate steam stripping of the extractant.

The effectiveness of the regeneration was determined by reloading the extractant with propylene glycol and measuring the change in aqueous-phase glycol concentration. In several experiments, the same batch of extractant was repeatedly cycled through loading, back-extraction and regeneration steps.

2.1.13. Extractant regeneration with sodium carbonate solutions

Sodium carbonate solutions were prepared using analytical grade $Na_2CO_3 \cdot H_2O$. Solutions of 0.86 mol/kg, 1.6 mol/kg and 2.6 mol/kg (saturated at 25 °C) were prepared in purified water and analyzed by titration with 0.0976 N HCl. From the titration results, the amount of bicarbonate in solution was determined. Just enough sodium hydroxide was added to the solutions to convert the bicarbonate to carbonate.

Extractant solutions were loaded and carbonated as described in Sections 2.1.8 and 2.1.10. Measured quantities of such extractant solutions and sodium carbonate solutions were contacted on a shaker bath at 25 °C or by magnetic stirring at ambient temperature for a minimum of 16 hours. The final pH of the aqueous phase was measured using a pH probe. In experiments using 0.86 mol/kg Na_2CO_3 the concentrations of carbonate and bicarbonate in the aqueous phase were measured by titration. The extractant phase was then contacted with an aquous solution of 1,2-PD, to determine the reloading in the same way as described in Section 2.1.12. In one experiment a larger batch of extractant was regenerated in several batch stages; the regeneration effectiveness was determined after each stage. Experimental conditions and results are given in Appendix G.

2.2. Results

2.2.1. Solubility of PBA

The concentration of the aqueous solution saturated with PBA at 25 °C was 0.181 mol/L, or 22.1 g/L This compares to an aqueous solubility of NPBA of 0.027 mol/L, or 4.5 g/L (Randel and King, 1991). Both g/L values pertain to the acid (not anhydride) form of the compounds.

2.2.2. Extractant preparation - caustic wash method

The tables in Appendix C summarize the experimental results for the various extractant preparations, including the pH, chloride concentration and phenylboronate concentration of the aqueous wash phases. Analysis of these results to obtain understanding of equilibrium distribution of chloride and phenylboronate between the aqueous and extractant phases was not successful. Either equilibrium was not reached in the amount of contacting time provided, or the distribution equilibria are complex functions of the concentrations of many of the species involved and not just of the solution pH.

For the majority of the extractants that were used the amount of chloride exchanged was greater than the final remaining boronate concentration; *i.e.* these extractants had some Aliquat 336 in the hydroxide form. It was assumed that all the PBA in these extractants was ionized and paired with Aliquat 336.

Since the final boronate concentration was inferred from a number of aqueous-phase measurements rather than a direct organic-phase measurement, the error in this

Table 2-1. Extractants prepared by the caustic wash method.

Symbol	Diluent	(PB^-) (mol/L)	Remarks
Q	2-ethylhexanol	0.325	first high-concentration extractant
S	2-ethylhexanol	0.261	
T	2-ethylhexanol	0.284	
U	2-ethylhexanol	0.357	
V	2-ethylhexanol	0.252	
W	2-ethylhexanol	0.272	
X	2-ethylhexanol	0.212	
Y	2-ethylhexanol	0.298	
XX	2-ethylhexanol	0.042	prepared by direct dilution of X
F	2-ethylhexanol	-	no phenylboronate; 0.198 mol/L $A336^+OH^-$
NH	2-ethylhexanol	0.350	3-nitrophenylboronate
TOL	toluene	0.321	
XYL	*o*-xylene	0.295	
DBK	diisobutylketone	0.353	

value may be large, because of errors in the measurements of the aqueous-phase boronate concentrations, incomplete phase separation between washes or volume changes due to the extraction process. A detailed error analysis would be difficult to carry out since the magnitude of each of these errors is hard to estimate. However, an indication of the overall magnitude of the error due to individual concentration measurements is given by the difference in calculated phenylboronate concentration by the two analytical methods – UV spectrophotometry and titration, evident from the data in Appendix C. When results were obtained by two methods, the phenylboronate concentration used in further calculations was the average value.

Table 2-1 summarizes the characteristics of several of the most-used batches of extractants.

2.2.3. Extractant preparation - methanol method

The alternative method for extractant preparation, described in Section 2.1.5, is based on the low solubility of sodium chloride in methanol, compared to the solubilities of sodium hydroxide and sodium phenylboronate. As a result, the reaction in which phenylboronate replaces chloride on Aliquat 336 is thermodynamically driven by the simultaneous precipitation of sodium chloride, keeping the activity of chloride in solution at a low value.

The precipitate resulting from the mixing of sodium hydroxide, phenylboronic acid, Aliquat 336 and methanol was recovered by filtration. Chloride analysis revealed that the precipitate was at least 87% sodium chloride. Incomplete removal of Aliquat 336 by washing may account for the remainder of the solids weight. More sodium chloride precipitated during the removal of methanol, indicating that the solubility of sodium chloride in 2-ethylhexanol is lower than in methanol. Additional chloride was removed in the aqueous washes, along with sodium hydroxide and sodium phenylboronate. The details of the preparation are given in Appendix C.

From the data in Appendix C, the phenylboronate concentration in the extractant may be estimated. According to this estimate, the capacity of the extractant is of the same order as the capacity of extractants made by the caustic wash method, while the amount of phenylboronic acid used in the preparation is less than half of the amount used in that method. Also, using this method it would be possible to prepare extractants with higher boronate concentrations. For an industrial application, this process would therefore probably be preferable. Note that in this research, it was not attempted to optimizè the methanol method. A procedure with lower phenylboronate losses could probably be developed; optimization of the caustic wash method is much less likely to result in a significant decrease in phenylboronate losses.

2.2.4. Preparation of an extractant loaded with inorganic borate

An attempt was made to prepared an extractant by exchanging chloride anions paired with Aliquat 336 in 2-ethylhexanol with inorganic borate anions, by contacting the organic phase with aqueous sodium borate solutions. The amount of borate exchanged for chloride was very low: The uptake of borate from the aqueous phases was determined by titration to be 0.005 mol/L in the first wash and 0.015 mol/L in the second wash. The conclusion from these results is that the Aliquat 336 cation has a much larger affinity towards chloride anions than towards borate anions when surrounded by 2-ethylhexanol. Since the borate concentration of the organic phase was so low, no extraction experiments were carried out.

2.2.5. The distribution ratio of 1,2-PD

The partition coefficient P of 1,2-PD between water and 2-ethylhexanol, defined as the ratio of 1,2-PD concentrations in the organic and aqueous phases, had previously been reported by Randel and King (1991) and Chow (1992). Because of the large difference between these values (0.080 and 0.010, respectively), it was decided to measure the value of P again.

The batch equilibrium experiments were set up in such a way as to allow a mass balance check from the concentrations of both phases. After finding deviations from the mass balance in early experiments, the water content of the 2-ethylhexanol phase was measured before and after equilibration. It was found that additional water enters the

Table 2-2. 1,2-PD partition coefficient between 2-ethylhexanol and water

c_{aq} (mol/L)	c_{org} (mol/L)	$P_{1,2\text{-PD}}$	GC error
1.320	0.103	0.078	3.1%
0.710	0.058	0.082	6.8%
0.541	0.040	0.074	4.1%

organic phase upon the uptake of 1,2-PD. When corrections are made to take this into account, the mass balance on 1,2-PD closes to within 1%.

Three experiments yielded three values for P, which are summarized in Table 2-2. The GC error included in the Table was calculated from the standard deviation of repeated GC injections of the same sample.

In equilibrium extraction calculations for low-concentration extractants, the mean value 0.078 was used as the value for P. One experiment was carried out at 50 °C, and yielded a partition coefficient of 0.121.

However, most extraction experiments were carried out using high-concentration extractants, in which Aliquat 336 constituted a sizeable volume fraction. This complicates the estimation of physical distribution of propylene glycol considerably, especially since in the final extractant Aliquat 336 is paired with both chloride and phenylboronate ions. The assumption was made that these ion-pairs have equal physical affinities for propylene glycol. Experiments were carried out in which propylene glycol was extracted into a phase consisting of 30.6 vol % Aliquat 336 (chloride form) in 2-ethylhexanol, in a concentration representative of the actual organoboronate extractants used. The results

Table 2-3. 1,2-PD distribution ratio into 2-ethylhexanol/Aliquat phase

[1,2-PD] (mol/L)	(1,2-PD) (mol/L)	$D_{1,2\text{-PD}}$	GC error
0.412	0.046	0.112	10%
0.775	0.082	0.106	5%
0.208	0.020	0.096	9%

of the three experiments are presented in Table 2-3. As there appears to be no trend in the value of D with aqueous-phase concentration, the average value of 0.105 was used for the physical distribution ratio in equilibrium loading calculations for extractions involving high-concentration extractants.

In the determination of the distribution ratio, the assumption was implicit that the physical distribution of propylene glycol between a phase containing Aliquat 336 is the same, regardless of the paired anion, *i.e.* chloride or phenylboronate. The fact that propylene glycol interacts chemically with phenylboronate makes it impossible to independently measure the physical distribution of 1,2-PD into a phase containing Aliquat 336/phenylboronate. To test the assumption noted above, ethanol, which does not

Table 2-4. Distribution ratios for ethanol between aqueous and extractant phases

Organic phase	[1,2-PD] (mol/L)	(1,2-PD) (mol/L)	D
2-ethylhexanol	0.143	0.0571	0.399
30.6% $A336^+Cl^-$	0.123	0.0587	0.480
31.0% $A336^+Cl^-$	0.178	0.0753	0.424
extractant U	0.171	0.0890	0.520
extractant W	0.160	0.0731	0.457

Table 2-5. Distribution ratios of 1,2-PD between aqueous and organic phases. Unless otherwise stated, the data are for 25 °C.

Diluent	P	($A336^+Cl^-$) (vol. %)	D
2-ethylhexanol	0.078	30.6	0.105
	0.078	23.0	0.103
	0.121 (50 °C)		
	-	23.0	0.181 (60 °C)
toluene	-	26.9	0.095
o-xylene	-	26.8	0.112
diisobutylketone	0.0056	26.8	0.124
chloroform	0.0073	26.5	0.080
Aliquat 336		100	0.360

interact chemically with phenylboronate, was distributed between an aqueous phase and several organic phases. The results of these experiments are presented in Table 2-4.

The ion pair with phenylboronate appears to interact with ethanol somewhat more strongly, but due to the large scatter in these results, it is impossible to draw solid conclusions. The assumption of equal distribution into both Aliquat forms was used in all further calculations. Partition coefficients were also measured for several other organic diluents, as well as the distribution ratio into solutions of 26-27 vol% Aliquat 336/chloride in these diluents and one distribution ratio and a partition coefficient at a higher temperature. The distribution ratio into pure Aliquat 336/chloride was also determined. The results are summarized in Table 2-5.

2.2.6. Batch extraction results

2.2.6.1. Theory, definitions and calculations

The uptake of 1,2-PD from the aqueous into the organic phase may be attributed to both physical distribution of 1,2-PD between the two phases and chemical complexation of 1,2-PD within the extractant phase. The expected stoichiometry of complexation in a glycol-organoboronate system is 1:1, *i.e.* one molecule of 1,2-PD complexes with one phenylboronate/Aliquat 336 ion pair. Data for the uptake of 1,2-PD obtained by Chow (1992), when interpreted using the correct value for the distribution coefficient for 1,2-PD, show Z rising to a value near unity for an aqueous glycol concentration of 0.08 mol/L. No accurate data are available at higher concentrations. The corrected data from Chow are included in Appendix D.

The 1:1 complexation may be described by a heterogeneous complexation constant β_{11}, defined as

$$\beta_{11} = \frac{(PB^- \cdot 1,2\text{-}PD)}{(PB^-)[1,2\text{-}PD]} \qquad (2\text{-}1)$$

in which (PB^-·1,2-PD) and (PB^-) are the organic-phase concentrations of the complex and the uncomplexed phenylboronate, respectively, and [1,2-PD] is the aqueous-phase 1,2-PD concentration. Another useful quantity is the extractant loading Z, defined in Equation 2-2. If each boronate anion can take up no more than one glycol molecule, then Z will take on values between 0 and 1. The expression in the denominator is the total organic-phase phenylboronate concentration, $(PB^-)_{tot}$.

$$Z = \frac{(PB^- \cdot 1,2\text{-}PD)}{(PB^- \cdot 1,2\text{-}PD)+(PB^-)} \qquad (2\text{-}2)$$

Equations 2-1 and 2-2 may be combined to find the relationship between Z and [1,2-PD].

$$Z = \frac{\beta_{11}[1,2\text{-PD}]}{1+\beta_{11}[1,2\text{-PD}]} \qquad \textbf{(2-3)}$$

The extraction equilibrium is determined by measurements of the aqueous-phase 1,2-PD concentrations before and after extraction. These concentrations are related through the mass balance in Equation 2-4,

$$V_{aq,0}[1,2\text{-PD}]_0 - V_{aq}[1,2\text{-PD}] = V_{org}D[1,2\text{-PD}] + V_{org,0}Z(PB^-)_{tot} \qquad \textbf{(2-4)}$$

in which V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively. The subscript 0 denotes initial, pre-extraction quantities. In this equation the value for the physical distribution ratio D is either the partition coefficient measured for 2-ethylhexanol, for low-concentration extractants, or the distribution ratio determined for Aliquat 336 in 2-ethylhexanol, for high-concentration extractants.

The simplification that may be made by assuming $V_{aq} = V_{aq,0}$ and $V_{org} = V_{org,0}$ is not strictly correct, since the transfer of 1,2-PD and water between the aqueous and organic phases changes the volumes of both phases, most notably at high extractant concentrations. The volume change was not measured directly, but could be inferred from the change in the aqueous-phase 1,2-PD concentration and the organic-phase water concentration. In practice, the effects of the transfer of 1,2-PD into and water out of the organic phase cancel to a large extent (see Section 2.2.7), so that the phase-volume correction is generally not an important one. In the extraction experiments in which the water concentration was not measured, no correction for volume change was made.

The extractant loading Z may be calculated from the experimental extraction results and Equation 2-4. The error in the calculation in Z results primarily from either

an error in the estimate of D, or an error in the measurement of [1,2-PD]. It is useful to investigate the impact that these errors may have on the error in Z. If volume changes are ignored, the error due to an inaccurate value of D may be expressed as

$$\frac{\Delta Z}{\Delta D} = \frac{[1,2\text{-PD}]}{(PB^-)_{tot}} \qquad \textbf{(2-5)}$$

The error due to an inaccurate value of [1,2-PD], estimated by ignoring the term for physical distribution in Equation 2-4, may be expressed as

$$\frac{\Delta Z}{\epsilon[1,2\text{-PD}]} = \frac{V_{aq}}{V_{org}} \cdot \frac{[1,2\text{-PD}]}{(PB^-)_{tot}} \qquad \textbf{(2-6)}$$

where ϵ[1,2-PD] is the relative error in the final aqueous-phase glycol concentration. Note that in both Equation 2-5 and 2-6, the ratio of [1,2-PD] to $(PB^-)_{tot}$ is important. Measurements at high glycol concentrations are likely to have large uncertainties in the value of Z if the concentration of boronate in the organic phase is not sufficiently high, and possibly a high systematic error due to the error in the value of D. This explains why initial experiments with low-concentration extractants showed significant scatter at high concentrations. After that, the emphasis shifted towards high-concentration extractants.

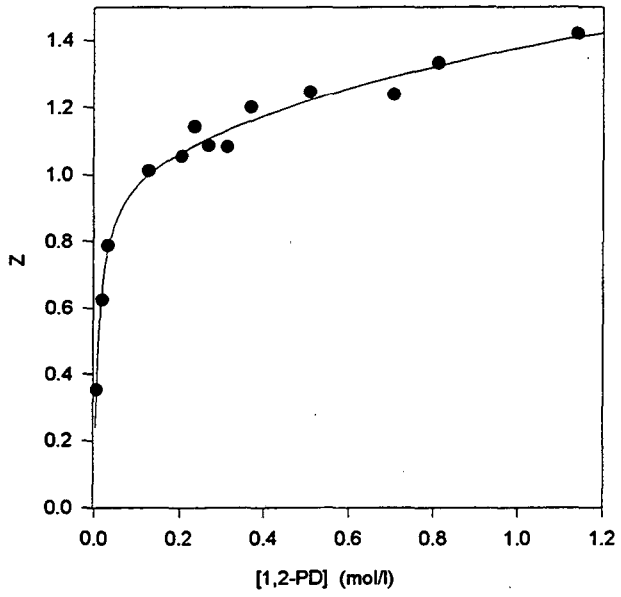

Figure 2-1. Loading curve for extractions at 25 °C with extractant V

Unless otherwise stated, all extraction experiments were carried out at 25 °C. Exact conditions, results, calculations and assumptions related to batch extraction results are presented in Appendix D.

2.2.6.2. An example of a series of extraction experiments

Figure 2-1 shows an example of a typical series of extraction experiments, carried out with one extractant (V from Table 2-1) at 25 °C. The figure shows the loading, Z, plotted against the aqueous-phase concentration of 1,2-PD at the end of the experiment. The final [1,2-PD] was varied primarily by varying the initial [1,2-PD], but in some experiments also by variation of the phase volume ratio.

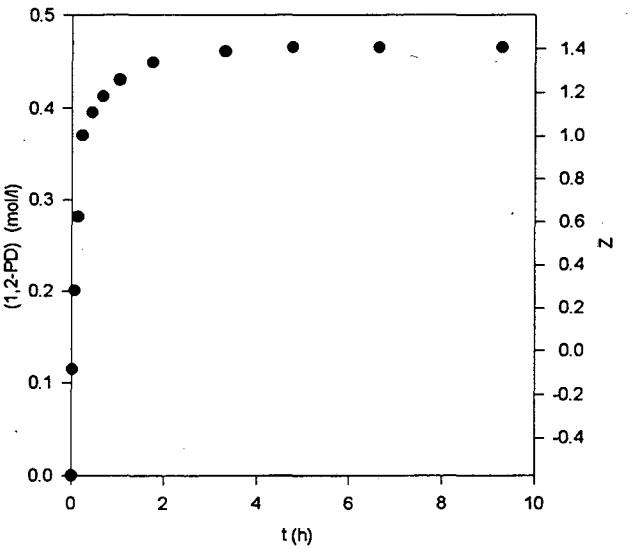

Figure 2-2. Kinetics of extraction experiment W15, with extractant W at 25 °C

The loading rises rapidly at low [1,2-PD], then levels off somewhat at higher concentrations. When two extractants differ in complexation strength, the difference between their loading curves will be most pronounced at low [1,2-PD]. For this reason, when extractants are compared the loading is usually plotted *vs.* the logarithm of the concentration, to emphasize the low-concentration region.

2.2.6.3. Extraction kinetics

In one extraction experiment, the aqueous-phase concentration of 1,2-PD was measured at several times during the extraction. From this information, the concentration of (1,2-PD) in the extractant and the loading Z was calculated as a function of time, as shown in Figure 2-2. The data indicate that a near-equilibrium extent of extraction is

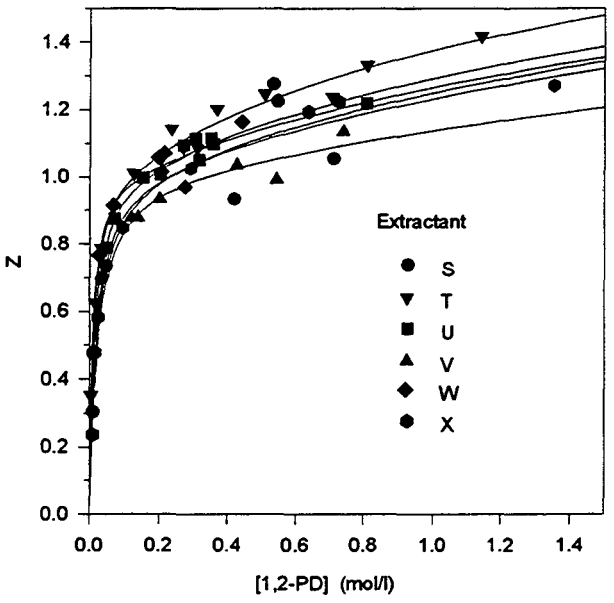

Figure 2-3. Loading curves for extractants prepared with 2-ethylhexanol as the diluent, from extraction series at 25 °C

reached in approximately 3 hours. A small additional amount of glycol is extracted after that. Extraction equilibrium appears to be reached after 6 hours. All batch extractions reported here were allowed to equilibrate for at least 24 hours.

2.2.6.4. Overloading

The results from the batch extraction experiments with several extractants that were prepared with 2-ethylhexanol as diluent are presented as loading curves in Figure 2-3. These results are in conflict with the notion of simple 1:1 complexation stoichiometry, as evidenced by values of Z that exceed unity. The degree to which this occurred appears to vary with the particular batch of extractant. After the initial rapid increase of Z with the concentration of 1,2-PD the loading did not level off to a constant

value, but continued to increase with concentration. Several explanations may be offered to explain this phenomenon:

a) The value of $(PB^-)_o$ used in the calculations may be incorrect. If $(PB^-)_o$ is underestimated, the entire loading curve will be stretched upward, and the loading would level off at a value equal to *real* $(PB^-)_o$/*calculated* $(PB^-)_o$. This is not in agreement with the continuing upward slope of the loading curve.

b) The value of the physical distribution ratio D used in the calculations may be incorrect. If D is underestimated, the value of Z will not be completely corrected for uptake of 1,2-PD by physical distribution, resulting an error that increases linearly with the aqueous-phase 1,2-PD concentration. Assuming the error in Z is completely due to this effect, the error in D may be calculated from the linear portion (at high concentration) of the plots in Figure 2-3. This calculation suggests that D is underestimated by 0.12. There is no other evidence for such a large deviation from the experimental value (0.105). It is therefore highly unlikely that this effect alone could explain the overloading.

c) The Aliquat 336/hydroxide ion pair, which is present in the extractants in a concentration that varies with the particular batch of extractant (see Appendix C), may have a greater affinity for glycol, either physical or chemical, than the Aliquat 336/chloride ion pair. If this interaction is chemical in nature, with a fixed 1:1 stoichiometry, total concentration of Aliquat 336 converted from the chloride form to either the boronate or the hydroxide form would be reflected in the loading curve.

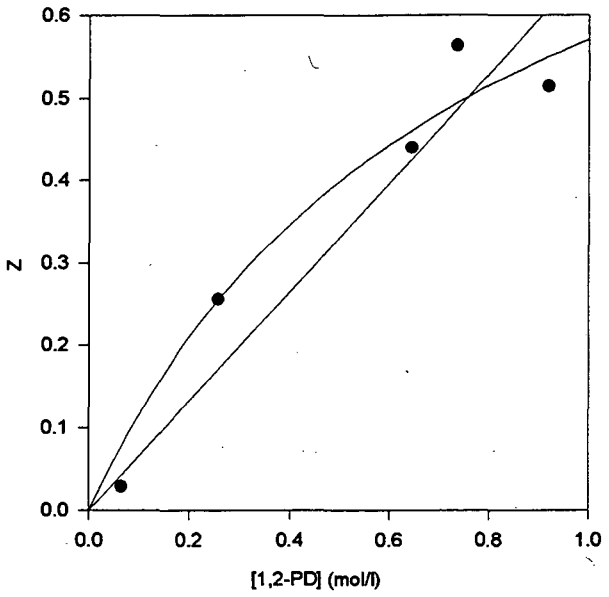

Figure 2-4. Extraction results with Aliquat 336/hydroxide extractant (extractant F in Appendix C), at 25 °C

To investigate the affinity of Aliquat 336/hydroxide for 1,2-PD, an extractant was prepared by repeatedly washing a mixture of 2-ethylhexanol and Aliquat 336 with sodium hydroxide solution, with no organoboronate present. Details of the preparation can be found in Appendix C. The results of several extractions using this solution are presented in Figure 2-4, where Z is now calculated relative to the concentration of Aliquat 336/hydroxide. The results of two one-parameter regressions, one a first-order linear regression through the origin, the other a curve-fit to Equation 2-3, are also plotted. At [1,2-PD]=0.3 mol/L, $Z_{A336/OH}$ does not exceed 0.25. At typical concentrations of Aliquat 336/hydroxide (0.05 mol/L) and Aliquat 336/phenylboronate (0.30 mol/L), the uptake by the hydroxide form could account for an apparent increase in Z of 0.04, not enough to explain experimental loadings exceeding 1.30.

Furthermore, the fact that there appears to be overloading of the same order of magnitude with extractant U, which had no excess of Aliquat 336/hydroxide and extractant V, which had a significant excess, also suggests that this reasoning by itself is incapable of explaining the phenomenon.

d) Aggregates of Aliquat 336 ion pairs in the extractant phase, *e.g.* reverse micelles, may form. Water and other hydrophilic molecules, such as 1,2-PD, could be solubilized in the interior of the aggregates. Experimental evidence for the existence of aggregates and a discussion of the effect aggregates may play in this system are presented in Section 2.2.8.

e) The phenylboronate/Aliquat 336 ion pair may in fact exhibit overloading, *i.e.* one boronate anion may take up (by chemical complexation or solvation) more than one 1,2-PD molecule. In the case of stoichiometric complexation it would be appropriate to define a second complexation constant, β_{21}, to describe the equilibrium of 2:1 complexation. When β_{21} is defined as in Equation 2-7, the resulting expression for Z is given by Equation 2-8. The loading Z is still defined relative to 1:1 complexation; its maximum value is now 2.

$$\beta_{21} = \frac{(PB^- \cdot (1,2\text{-PD})_2)}{(PB^-)[1,2\text{-PD}]^2} \qquad \textbf{(2-7)}$$

$$Z = \frac{\beta_{11}[1,2\text{-PD}] + 2\beta_{21}[1,2\text{-PD}]^2}{1 + \beta_{11}[1,2\text{-PD}] + \beta_{21}[1,2\text{-PD}]^2} \qquad \textbf{(2-8)}$$

The numerator in Equation 2-7 is the concentration of the 2:1 complex in the organic phase.

The curves drawn in Figure 2-3 are fits of Equation 2-8 to the batch extraction data, a separate curve for each extractant. The values of β_{11} and β_{21} obtained by non-linear least-square fitting are given in Table 2-6. Units of $(mol/L)^{-1}$ for β_{11}, and $(mol/L)^{-2}$ for β_{21} are implied through the remainder of this chapter.

Table 2-6. Complexation parameters fitted to extraction series at 25 °C

Extractant	β_{11} $(mol/L)^{-1}$	β_{21} $(mol/L)^{-2}$
Q	72.6	5.0
S	57.0	18.8
T	75.1	32.8
V	99.6	62.2
W	116.9	43.9
X	49.6	18.3
Y	46.9	12.8
NH	29.9	1.9
TOL	34.8	8.4
XYL	37.6	23.7
DBK	14.4	-0.3

The fact that the two-parameter model appears to fit the experimental data well does not provide proof for the hypothesis of 2:1 complexation. Other modes of interaction between the Aliquat 336/phenylboronate ion pair and propylene glycol, such as solvation by glycol of the ion pair/glycol complex or solubilization of glycol inside aggregates, could probably explain the observed behavior as well, or for that matter, any combination of complexation and solvation. The distinction between these modes cannot be made from phenomenological data such as loading curves. Direct investigation on a more fundamental level, such as spectroscopic methods to investigate the interactions in the extractant system, are needed to provide the information needed to discriminate

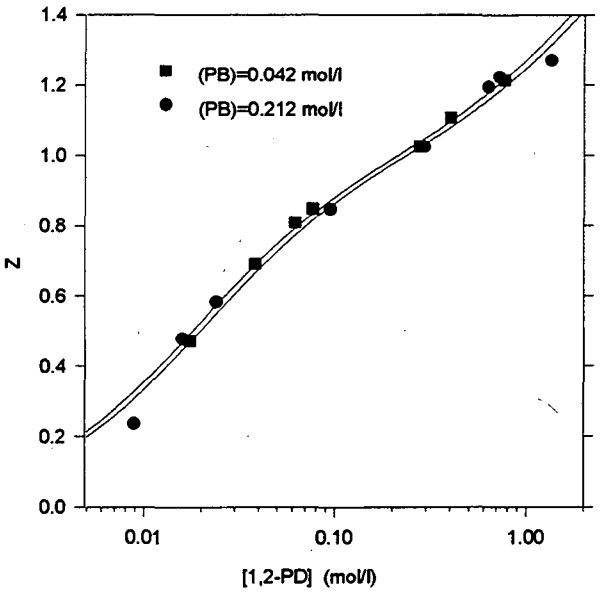

Figure 2-5. Loading curves for extractants X and XX, at 25 °C

between the modes of association. However, it is convenient to fit the data with Equation 2-8, since this resultsin two parameters, the first of which is a good measure of the extraction affinity at low glycol concentrations, the second a measure of the degree to which overloading occurs.

2.2.6.5. The effect of extractant concentration

The individual loading curves shown in Figure 2-3 correspond to different batches of extractant, all differing slightly in their preparation procedure and therefore possibly in properties important to their extraction behavior. Because of the variation in parameters with an unknown effect on extraction properties, there is a scatter in the shape of the curves, and therefore in the fitted complexation constants. This complicates

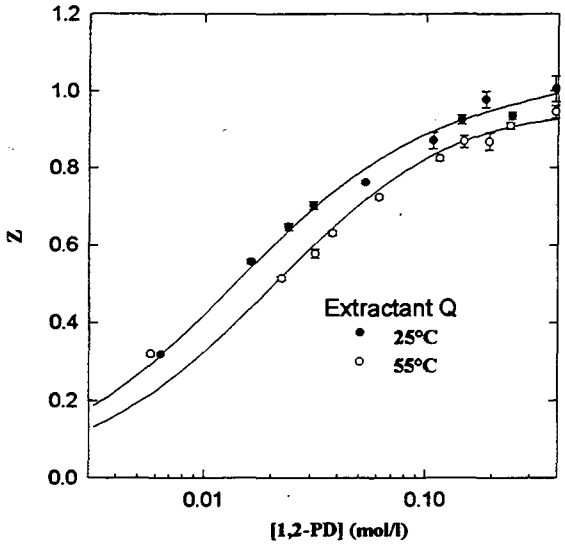

Figure 2-6. Loading curves for extractant Q at 25 °C and 55 °C

making comparisons between individual extractants. Therefore, the influence of extractant concentration was not studied using two separately prepared extractants, but rather with one batch of extractant (X) and a dilution in 2-ethylhexanol of the same extractant (XX). The phenylboronate concentrations were 0.212 mol/L and 0.042 mol/L, respectively. Loading curves for both extractants are shown in Figure 2-5. The curves nearly overlap, and the calculated complexation constants differ from each other by less than the standard errors. In other words, no concentration dependence of extraction behavior was observed in 2-ethylhexanol as a diluent.

2.2.6.6. The effect of temperature

Figure 2-6 shows the results of series of extraction experiments at 25°C and 55°C. Equation 2-8 was fitted to the experimental results by non-linear least-squares regression. The results are presented as the curves in Figure 2-6. The parameter values (β_{11}, β_{21}) obtained by this analysis were (72.8, 10.6) at 25°C and (48.7, 8.7) at 55°C. Through the Van 't Hoff equation, this indicates a heat of complexation of *ca.* 13 kJ/mol for the 1:1 complexation. In these experiments, the same value of the physical distribution ratio was used for calculations at both temperatures.

Another experiment was carried out with a different batch of extractant at 25 °C and 60 °C. In this case, the distribution ratio was also measured at the higher temperature (see Table 2-5) and used in subsequent calculations. The parameter values obtained from these experiments were (49.6, 18.3) and (36.5, 6.0), respectively. The calculated heat of complexation in this case is 7 kJ/mol.

Although these results indicate that there is a temperature effect, back extraction following a temperature increase could not provide enough driving force for such a process to be effective, if it is desired to concentrate the glycol solute.

2.2.6.7. The effect of the diluent

Results of series of extractions carried out with extractants in which toluene, *o*-xylene and diisobutylketone replaced 2-ethylhexanol as the diluent are shown in Figure 2-7. The experimental results were processed in the same way as for 2-ethylhexanol diluent, using the physical distribution ratios of propylene glycol between an aqueous phase and organic phases given in Table 2-3. The parameter values (β_{11}, β_{21}) obtained from a curve fit are (39.9, 2.7) for the toluene extractant, (37.6, 23.7) for the *o*-xylene extractant and (18.3, 0.6) for the diisobutylketone extractant. These results indicate that

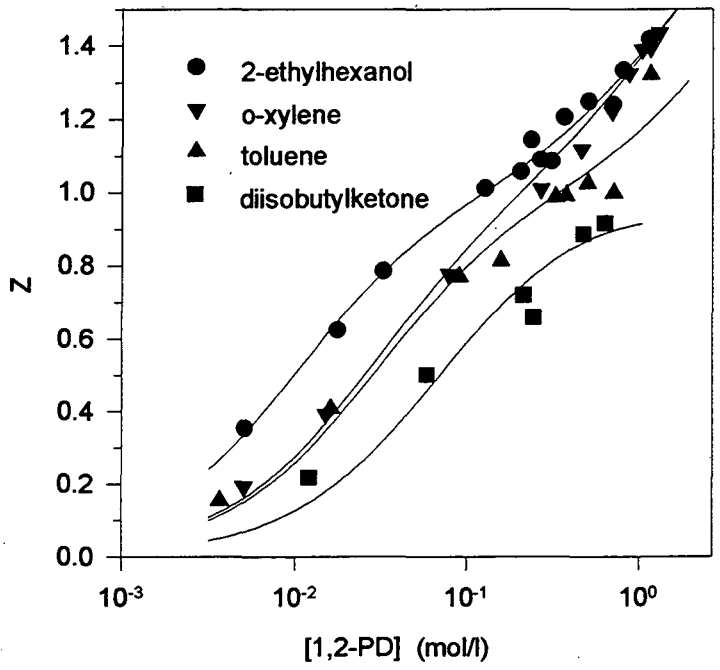

Figure 2-7. Loading curves for extractants V, TOL, XYL and DBK at 25 °C

complexation in the aromatic solvents is not as strong as in a 2-ethylhexanol environment, and is even weaker in diisobutylketone. Overloading occurred in the aromatic solvents, but was not observed in diisobutylketone.

Batches of the *o*-xylene and diisobutylketone extractants were kept for several weeks. Both extractants underwent a spontaneous discoloration (towards a darker color), and seemed to exhibit a different, slightly sweet smell. Analysis of aqueous phases contacted with "old" xylene extractant caused degradation of GC performance. An extraction carried out with "old" diisobutylketone extractant showed that the extraction capacity had decreased to 60% of its original value. Extractants with 2-ethylhexanol as diluent did not appear to degrade in any way, even when stored for considerable lengths of time. Apparently the Aliquat 336/phenylboronate ion-pair is preferentially stabilized in 2-ethylhexanol solution, due to either the higher polarity or the hydrogen-bonding capability of the diluent.

2.2.6.8. The capacity of methanol-method extractant

The extractant prepared with the methanol method described in Section 2.2.3 was loaded with propylene glycol in an extraction experiment. With the assumption that the rough calculation of the phenylboronate content presented in Appendix C is accurate, the loading Z may be calculated as above. At an aqueous-phase concentration of 0.25 M 1,2-PD, the value of Z is 0.98. This indicates that this extractant is about as effective for recovery of propylene glycol as extractants prepared by the caustic-wash method.

2.2.6.9. Extraction into a nitrophenylboronate extractant

One high-concentration extractant was prepared with NPBA instead of PBA. Extraction results using this extractant are presented in Figure 2-8. The parameters for the least-squares curve fit are β_{11}=29.9, β_{21}=1.9. These values are lower than the range observed for phenylboronate extractants. This effect may be due to the electron-attracting effect of the nitro group, which stabilizes the boronate functionality, making it less reactive towards diols. More extensive research would be needed to provide more evidence for weaker complexation and to confirm the electronic structure explanation for the difference.

2.2.7. Water content of extractants

The water concentration of each extractant, after the final aqueous wash, was measured by Karl-Fischer titration. Additionally, the final water contents of the extractant

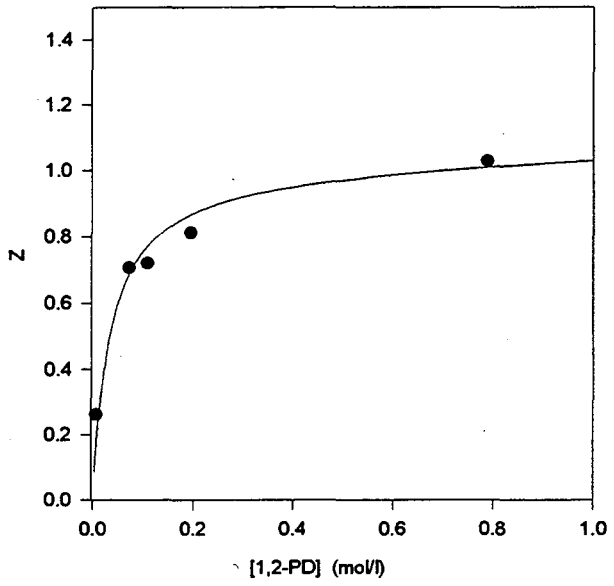

Figure 2-8. Loading curve for extractant NH, prepared with 3-nitrophenylboronic acid

phases were measured in most batch extraction experiments. It was found that the water concentration decreased as the 1,2-PD concentration increased. The available data of this type are summarized in Figure 2-9, in which the concentration of water is plotted against the concentration of 1,2-PD for a variety of extractants. In most cases the relationship between the two concentrations is apparently linear; linear first-order regressions to the data are also shown. For the 2-ethylhexanol-based extractants, the slope of the line suggests that for each mole of glycol taken up into the extractant between 3 and 4 moles of water are displaced.

To investigate whether this phenomenon is related to glycol uptake by physical distribution or by chemical complexation, the water concentration was also measured in the experiments to determine the physical distribution of 1,2-PD into Aliquat 336/chloride-containing extractants, described in Section 2.1.5. In this case the slope indicates a co-extraction of 1.3 moles of water into the organic phase with each mole of

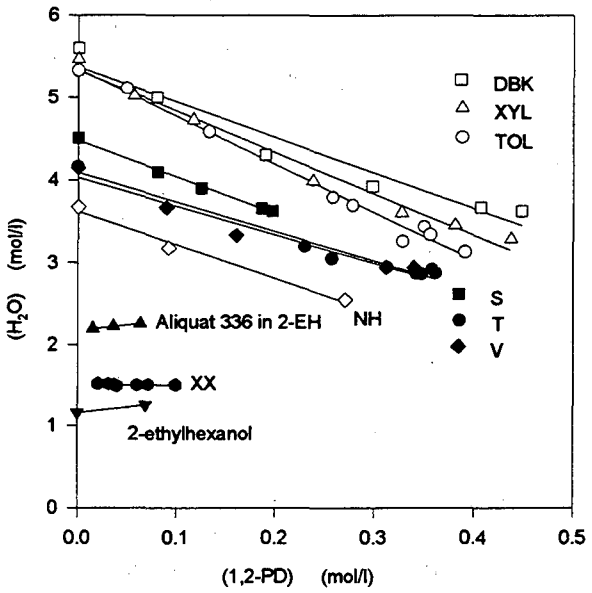

Figure 2-9. Equilibrium concentration of water *vs.* the concentration of 1,2-PD, in the extractant phase

1,2-PD. In other words, the trend is reversed in this case without boronate present, as shown in Figure 2-9. The same experiment was also carried out with just 2-ethylhexanol as the organic phase, with a similar result (also shown in Figure 2-9). These results suggest that the displacement of water from the extractant is exclusively due to the presence of phenylboronate in the organic phase. Either many more water molecules are involved in the solvation of the uncomplexed Aliquat 336/phenylboronate ion pair than with its complex with propylene glycol, or 1,2-PD physically displaces water when it complexes with phenylboronate, *e.g.* from the interior of an aggregate structure.

The water concentration in the low-concentration extractant (XX) was measured as a function of the glycol concentration. The results are included in Figure 2-9. As evidenced by the near-zero slope of the line, the displacement of water by glycol as a result of extraction did not occur significantly in the low-concentration extractant.

Water concentration measurements were also carried out for extractions with extractants with other diluents. The water concentrations of the extractants themselves are higher than in 2-ethylhexanol, which would not be expected on the basis of the low solubilities of water in toluene (0.06 wt %), *o*-xylene (0.10 wt %) and diisobutylketone (0.66 wt %). This could be because more water molecules are needed to surround the ion pairs in the extractant phase, since toluene does not participate in solvation as much as 2-ethylhexanol does. The slope of the (H_2O) *vs.* (1,2-PD) line suggests that between 5 and 6 molecules of (H_2O) are replaced per mole of (1,2-PD).

Several measurements were also made of the water concentration in the nitrophenylboronate extractant as a function of uptake of 1,2-PD; the results are included in Figure 2-9. The absolute water concentration is somewhat lower than in phenylboronate extractants, but the slope of the line showing the decrease in water concentration with increasing glycol uptake is about the same.

2.2.8. Aggregation in the extractant phase

The high concentration of water in the extractant phase, far exceeding the solubility of water in the diluents, was noted in the previous section. Expressed in terms of moles of water per mole of Aliquat 336, the equilibrium concentration of water in *o*-xylene extractants can be as much as 10 times the concentration of Aliquat 336. It is not easy to explain such high ratios with the concept of general solvation, especially since Aliquat 336 itself is largely hydrophobic. This observation suggests that the high concentration of water may be due to solubilization inside aggregates of the amphiphilic ion pairs formed by Aliquat 336.

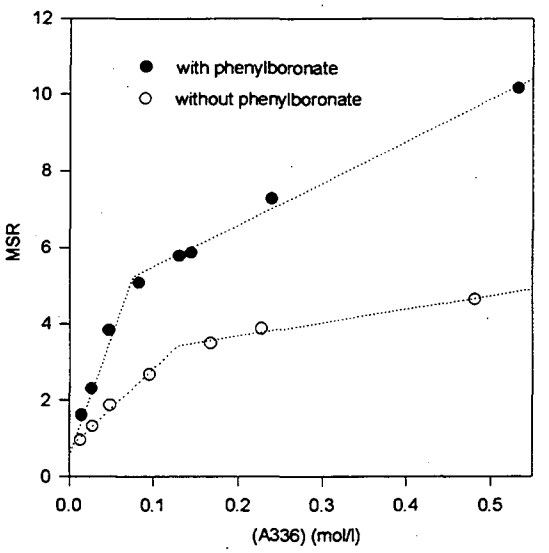

Figure 2-10. Molar solubilization ratio of water *vs.* the concentration of Aliquat 336 cation in *o*-xylene, for extractants containing phenylboronate and extractants containing only chloride.

Additional evidence for such a phenomenon was found in a series of experiments in which the equilibrium water concentration was measured in solutions of Aliquat 336/chloride in *o*-xylene, ranging in concentration from 0.01 to 0.50 mol/L Aliquat 336, and a similar set of experiments in which dilutions of the *o*-xylene-based extractant, in the same concentration range (Aliquat 336 chloride plus phenylboronate form) were used. The results are shown in Figure 2-10 as the molar ratio of water to Aliquat 336 (the molar solubilization ratio, or MSR) *vs.* the concentration of Aliquat 336. The water concentration was first corrected for physical dissolution in the xylene diluent. It is clear that the MSR for water increases with Aliquat 336 concentration, from a value close to unity at infinite dilution to values exceeding 10 above 0.5 mol/L Aliquat 336, for the extractants containing phenylboronate. This

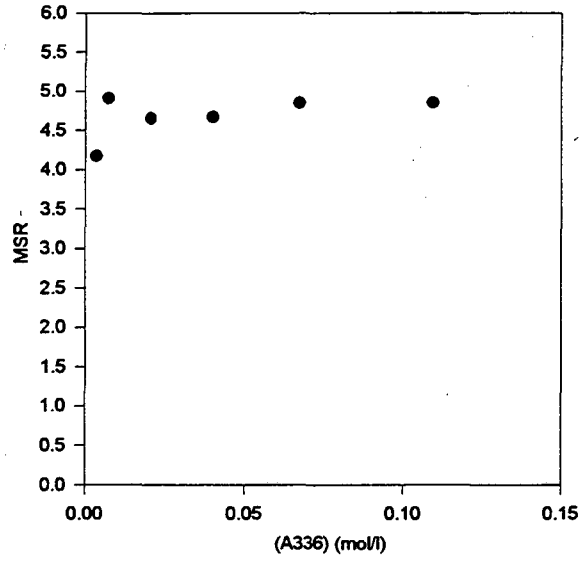

Figure 2-11. Molar solubilization ratio of water *vs.* the concentration of Aliquat 336 cation in 2-ethylhexanol

dependence of MSR on concentration suggests that some form of aggregation plays a role in the solubilization. Extractants containing Aliquat 336 in the phenylboronate form exhibit a higher MSR than simple solutions of Aliquat 336/chloride. Possible explanations would be that when coupled with phenylboronate, Aliquat 336 can more readily aggregate, or that larger aggregates form, leading to more water solubilized in each aggregate structure. In addition, there appear to be discontinuities in the slopes, most notably for extractants containing phenylboronate, at around 0.08 mol/L Aliquat 336, possibly indicating a change in aggregation behavior at that concentration.

Similar experiments were carried out using an extractant with 2-ethylhexanol as diluent. The results are shown in Figure 2-11. Here, the MSR does not seem to depend on the concentration of Aliquat 336, instead remaining at a high level even at low concentrations. This is in agreement with the fact that in 2-ethylhexanol no concentration

dependence of the loading curve has been observed (Section 2.2.6.5). However, the water concentration data (Figure 2-9) suggest that the mechanism of glycol complexation and solubilization is different at low extractant concentrations. Since 2-ethylhexanol is less hydrophobic than *o*-xylene one would expect the tendency to form reverse micelles to be lower. On the other hand, a slightly amphiphilic character can be ascribed to 2-ethylhexanol itself, so that the diluent itself could perhaps play a role in determining the aggregate structure.

Several attempts were made with instrumental techniques to ascertain that aggregates do indeed exist in extractant solutions, and to characterize them. A frequently used technique for characterizing micelles in solution is dynamic light scattering. In light scattering methods, incident light from a laser beam is scattered by structures, and detected at various angles relative to the beam. With dynamic techniques the fluctuations of scattering intensity in time are observed, and the decay of self-correlation with time is a measure of, among other things, the diffusivity of aggregates, from which their size may be deduced. Dynamic light scattering experiments were carried out using an Innova 90 2-Watt Argon laser and a Brookhaven BI-90 photomultiplier and digital correlator. A sample of about 0.10 mol/L Aliquat 336 in *o*-xylene served as a model extractant. Scattered light at a laser wavelength of 488 nm and a laser intensity of 500 mW was detected at angles between 30° and 50°. Some light scattering was observed, but the results indicated a highly polydisperse size distribution. The calculated size distribution was not reproducible in a series of identical experiments. Possible reasons for the unsatisfactory results are scattering by single Aliquat 336 molecules or multiple scattering due to the relatively high concentration of the sample.

Neutron magnetic resonance (NMR) spectroscopy was also used to obtain information on the structures existing in extractant solutions. Chemical shifts of water

hydrogens in several chemical environments were observed using ^1H NMR on a Bruker AMX-400 instrument. In benzene, these hydrogen nuclei absorbed at a chemical shift of 0.4 ppm. In solutions of Aliquat 336 in benzene, a peak around 4.2 ppm could be attributed to water. This marked difference in chemical shift is related to a difference in chemical environment. In benzene, the water is not hydrogen-bonded, leaving the hydrogen nuclei more shielded from the magnetic field. The peak at higher chemical shift is close to 4.6, the chemical shift observed for bulk water. In this state, the water molecules are part of a hydrogen-bonded structure, with less shielding of the hydrogen nuclei. From these results it may be inferred that the water in extractant solutions more closely resembles bulk water, and must therefore be present in clustered structures, such as reverse micelles. Similar experiments with 2-ethylhexanol as a diluent yielded results that could not be as readily interpreted, due to the hydrogen-bonding capability of the diluent. Experimental and instrumental procedures, as well as complete results, are presented in Appendix E.

2.2.9. Back extraction by acidification with hydrochloric acid

The results of a back-extraction experiment indicate that the extractant phase loses most of its capability for propylene glycol complexation when it is contacted with hydrochloric acid of superstoichiometric concentration. The extractant loading at an aqueous-phase concentration of 0.33 mol/L 1,2-PD was 0.02, compared to values exceeding unity when contacting with a propylene glycol solution without acid.

The reaction leading to the loss of complexation capability can be written as:

$$A336^{+}\cdot PB^{-}\cdot 1,2\text{-}PD + HCl \rightarrow A336^{+}\cdot Cl^{-} + HPB + 1,2\text{-}PD \qquad (2\text{-}9)$$

While this does release the glycol, allowing for back-extraction and recovery of the compound in a more concentrated form, it also converts the Aliquat 336 back to the chloride form. It was determined in the extractant preparation studies that reconversion to the phenylboronate form is cumbersome. In addition, it involves washing with an aqueous base, during which a waste salt solution is produced. A more efficient sequence of back-extraction and extractant regeneration would be preferable.

2.2.10. Back extraction by acidification with carbon dioxide

The production of a salt during extractant regeneration may be avoided by carrying out the back-extraction using carbon dioxide as the acidifying agent. The results of the back-extractions using CO_2 are summarized in Appendix F. Each experiment yielded two equilibrium results: the amount of CO_2 taken up into the extractant solution, and the amount of propylene glycol displaced into the aqueous phase.

The amount of CO_2 absorbed is roughly equal to (and often exceeds) the amount of Aliquat 336 in the extractant that is not in the chloride form (*i.e.* either in the hydroxide or the boronate form). A large fraction of the propylene glycol complexed with the extractant is displaced into the aqueous solution, which suggests that most of the phenylboronate is protonated, and therefore unable to complex with glycols. These results suggest the following reactions:

$$A336^{+}PB^{-}\cdot 1,2\text{-PD} + CO_2 + H_2O \rightarrow A336^{+}HCO_3^{-} + HPB + 1,2\text{-PD} \qquad \textbf{(2-10)}$$

$$A336^{+}OH^{-} + CO_2 \rightarrow A336^{+}HCO_3^{-} \qquad \textbf{(2-11)}$$

When a recently carbonated extractant was left open to the atmosphere, the

weight was found to decrease steadily. Apparently, at least some of the carbon dioxide is released readily at low partial pressures of carbon dioxide. The carbon dioxide concentration corresponding to the lower final weight is well below the concentration of Aliquat in the hydroxide and phenylboronate forms.

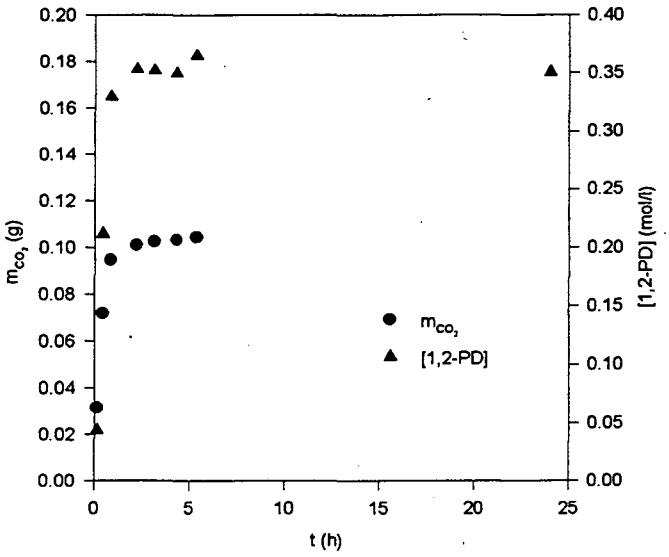

Figure 2-12. Kinetics of CO_2 uptake and 1,2-PD release during back-extraction experiment Rg19

The effectiveness of back-extraction, calculated from the amount of 1,2-PD extracted into the aqueous phase, may be expressed as Z_{be}, the loading after back-extraction. About 20 experiments were carried out with 2-ethylhexanol-based extractants. The scatter in the experimental results was considerable, values of Z_{be} varying from -0.05 to 0.24, but most values were in the range 0.02 to 0.10. The fact that the calculation of Z_{be} depends on both extraction and back-extraction calculations, with the experimental and analytical errors of both, explains some of the scatter. Also, inaccuracies due to evaporation of diluent and water from the extractant and aqueous

phases during back-extraction limited the time that CO_2 was sparged through, possibly leading to non-equilibrium results in some cases. Other factors that varied between experiments were the batch of extractant used, the age of the extractant and the organic-to-aqueous phase ratio.

In one experiment, the aqueous-phase concentration of 1,2-PD was measured several times during the back-extraction, as well as the carbon dioxide uptake. The results are shown in Figure 2-12. The back-extraction of propylene glycol follows the same trend as the uptake of carbon dioxide, with no apparent time lag. This result suggests that the transport of the glycol from the organic to the aqueous phase is a fast process compared to the kinetics of reactions 2-10 and 2-11, and that the experimental procedure in which the back-extraction is stopped not long after the uptake of carbon dioxide ceases is a sound one.

Most back-extraction experiments were carried out with extractants made using 2-ethylhexanol as a diluent. With each of the other extractants (using toluene, *o*-xylene and diisobutylketone as diluents) one or two experiments were carried out. The degree of back-extraction was particularly high in the aromatic diluents, and somewhat lower in diisobutylketone.

2.2.11. Regeneration of the extractant by stripping

Reactions 2-10 and 2-11 show that $A336^+OH^-$ and $A336^+PB^-$ are converted to the bicarbonate form in the back-extraction step. In order to reuse the extractant in an extraction mode, the Aliquat 336 must be reconverted to the phenylboronate form. Because the hydration of carbon dioxide is an exothermic reaction, reactions 2-10 and 2-11 may be reversed by an increase in temperature. This suggests regenerating the extractant by stripping out the CO_2 at elevated temperatures.

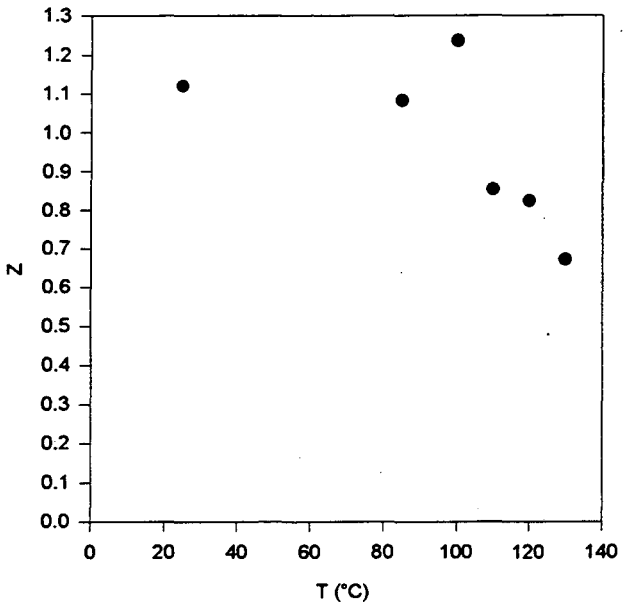

Figure 2-13. The extraction capacity of extractant W after an hour-long temperature treatment as a function of the temperature of the glycol bath

A first attempt to regenerate by stripping with nitrogen at 80°C was unsuccessful, as was an attempt to regenerate by the steam stripping from a boiling water phase underneath the extractant phase. In these cases, the degree to which the extractants reloaded upon extraction after regeneration was less than 30% of the original loading. To effect more complete regeneration, higher temperatures were used. After nitrogen stripping at temperatures between 110 and 120 °C, the degree of reloading was higher, up to 60%. Regeneration of the extractants with aromatic diluents was largely unsuccessful, degrees of reloading not exceeding 15%.

In all experiments with temperatures above 110 °C the extractant changed color from a light yellowish brown to darker shades of brown; the higher the temperature, the darker was the resulting extractant color. This indicates a chemical alteration of the extractant. In addition to the color change, an acrid odor was noticed directly after

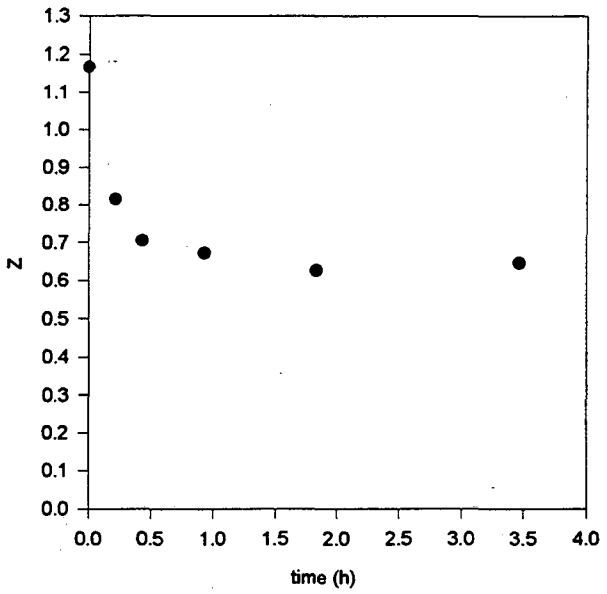

Figure 2-14. The extraction capacity of extractant W after temperature treatment at 116 °C as a function of the duration of the treatment

regeneration, and aqueous samples that had been contacted with regenerated extractant caused a deterioration in GC performance. At one time the glycol bath temperature reached 175 °C due to temperature controller failure, and an acidic gas, probably HCl, was emitted from the extractant.

To investigate whether chemical change evident from the discoloration was accompanied by a decrease in extraction capacity, several batches of extractant were heated to temperatures ranging from 80-130 °C for one hour, without having been contacted with 1,2-PD solution. Figure 2-13 shows the effect of this treatment on the resultant extraction capacity. In a similar experiment, the effect of the duration of the heat treatment was investigated by leaving samples at 116 °C for times ranging from 13 minutes to 3 hours. Figure 2-14 shows the extraction capacities of these extractants as a function of duration of regeneration. From these experiments it may be concluded that

there is no appreciable degeneration at temperatures below 100 °C, and that the capacity of the extractant reaches a level of about 60% of the original capacity in about 2 hours at 116 °C, after which no further degeneration is observed.

Several additional experiments were carried out to investigate qualitatively the degeneration process. Various samples were heated to 117 °C for at least an hour, and inspected for discoloration. No change of color was observed for phenylboronic acid in 2-ethylhexanol solution, for Aliquat 336 (chloride form) in 2-ethylhexanol, or for extractant F (without phenylboronate). Some discoloration (along with solids formation) was seen when the solution of phenylboronic acid was reheated after addition of a pellet of sodium hydroxide. Apparently, neither Aliquat 336 (chloride or hydroxide form) nor phenylboronic acid undergoes the degeneration reaction by itself. However, when the two are combined the degeneration and discoloration occur, possibly due to the presence of the anionic form (phenylboronate).

2.2.12. Repeated extraction/back-extraction/regeneration cycles

In several experiments, one batch of extractant was repeatedly cycled through the loading, back-extraction and regeneration steps. The uptake and release of propylene glycol was measured as usual. Figure 2-15 shows the results of one such cycle experiment. For each cycle, the change in loading in the extraction and back-extraction steps, Z_n-$Z_{be,n-1}$ and Z_n-$Z_{be,n}$, respectively, are shown as two bars, and the uptake of CO_2 is shown as the connected symbols. Similar plots could be constructed for all other cycle experiments; the pertinent data are included in Appendix F.

Since the degree of loading for each step is calculated from the results of all previous steps, the error in the absolute value of Z is probably considerable after several cycles. This effect is worsened by the fact that GC performance suffers when aqueous

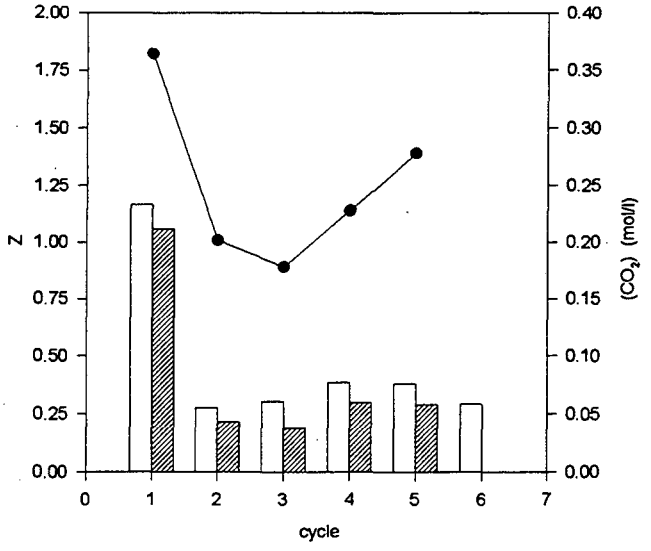

Figure 2-15. Results of 5½ cycles of extraction, back-extraction and regeneration in experiment Rg24. The bars show uptake and release of 1,2-PG, the symbols represent uptake of CO_2.

samples are analyzed that have been in contact with previously regenerated extractants.

However, the change in Z in each step, *i.e.* the uptake and release of propylene glycol, is determined directly from the corresponding concentration measurements. After the initial degradation of the extractant in the first regeneration step, no significant further deterioration of extraction performance is evident from these experiments.

The uptake of CO_2 in the back-extraction steps follows a similar pattern: The CO_2 uptake is high in the first cycle, drops considerably after the first regeneration step, but does not significantly decrease in subsequent cycles. The trend observed in Figure 2-15, with an increase in CO_2 uptake after the third cycle, is peculiar to this cycled experiment, and was not observed in other such experiments.

The combined effect of the loss of extraction capacity after regeneration, the incomplete back-extraction and the loss of overall efficiency due to the fact that the physical distribution of glycol is not influenced by the uptake of CO_2 results in extraction characteristics in the second and subsequent steps that are significantly less attractive than might be expected from the initial loading capacity. Only about 30% of the extraction capacity of the extractant used in Figure 2-15 is effectively used towards uptake and release of propylene glycol.

When extractants were first contacted with an aqueous solution of propylene glycol, a white substance often clouded the area near the phase interface. In subsequent loading steps in repeated cycles, this phenomenon was much less pronounced, or even absent. Possibly, during the first contact an irreversible reaction takes place which deactivates part of the extractant. Due to the inconsistent nature of this phenomenon, it was not studied in detail.

2.2.13. Extractant regeneration with sodium carbonate solutions

An alternative to stripping as a method of removing carbon dioxide from the extractant solution could be contacting with a high-pH aqueous phase. For example, if a sodium carbonate solution is chosen as the aqueous phase, the following reaction could take place:

$$\overline{A336^{+}HCO_3^{-}} + \overline{HPB} + CO_3^{2-} \rightleftharpoons \overline{A336^{+}PB^{-}} + 2\,HCO_3^{-} \qquad (2\text{-}12)$$

Compounds in the organic phase are shown with overbars. An analysis of the equilibria involved in reaction 2-12 shows that the overall equilibrium constant may be written as:

$$K_{regeneration} = \alpha_{PB^{-}/HCO_3^{-}} \cdot \frac{K_{a,HPB}}{K_{a2,H_2CO_3}} \qquad (2\text{-}13)$$

which means that the effectiveness of the regeneration depends on the affinity of Aliquat 336 for phenylboronate relative to bicarbonate, the dissociation constant of phenylboronic acid, and the dissociation constant of the acid complement of the basic compound in the aqueous phase. On the basis of the difference in pK_a between HPB and HCO_3^- (8.9 and 10.25, respectively) and the expectation that Aliquat 336 would exhibit a stronger affinity towards phenylboronate than towards bicarbonate due to the hydrophobic nature of the former, the regeneration effectiveness could be expected to be high, as long as a high carbonate-to-bicarbonate ratio (and therefore, a high pH) is maintained in the aqueous phase. To achieve such high effectiveness, a regenerative absorption process might be carried out countercurrently.

The advantage of this procedure for regeneration is that it could be operated at mild temperatures, avoiding possible heat degradation of Aliquat 336. A possible drawback of an absorptive regeneration procedure may be the co-extraction of phenylboronic acid into the basic aqueous phase. pH levels effective for regeneration would substantially exceed the pK_a of phenylboronic acid, so that extraction followed by dissociation in the aqueous phase competes with complexation of phenylboronate in the extractant phase. Losses of phenylboronic acid would be suppressed by the high activity coefficient of phenylboronate in the aqueous phase due to the high electrolyte concentration.

Results of experiments to regenerate extractants by absorbing CO_2 into aqueous sodium carbonate solutions are given in Appendix H. The results show considerable scatter, but in all cases the extractant was regenerated to an appreciable extent, the uptake in the reloading step corresponding to a change in loading value ΔZ of 0.32 to 0.64. Within each set of experiments (carried out using the same batch of carbonated extractant) the degree of reloading appears to increase with increasing aqueous-phase pH

(measured after regeneration). A staged experiment, in which a batch of carbonated extractant was subjected to several batch stages of regeneration, showed both the pH and the regeneration effectiveness increasing after each stage. The scatter in the results suggests that some extractant loading, back-extraction or regeneration conditions that are not taken into account explicitly have some effect on the effectiveness of regeneration.

2.2.14. Chemical losses in an extraction process

A glycol recovery process based on the extraction, back-extraction and regeneration operations discussed above would involve several steps in which the organic extractant phase is contacted with an aqueous phase. The objective of these operations is to transfer glycol out of and back into an aqueous phase. However, other components of the organic phase may also be transferred into the aqueous phase.

Aliquat 336, with its long hydrocarbon chain groups, has such a strongly hydrophobic character that the loss of this chemical to an aqueous phase should be minimal, and probably not a significant problem from a chemicals loss or a contamination perspective.

The diluent that was chosen for this research, 2-ethylhexanol, has an aqueous solubility of 0.06 w%. This is a high enough value to cause significant chemicals losses and to be of concern from an environmental point of view. In a process with equal volume flows of aqueous (0.25 M 1,2-PD) and extractant phases, the loss amounts to 0.03 grams 2-ethylhexanol per gram of propylene glycol. The current market prices of 2-ethylhexanol and propylene glycol are comparable (about $0.50/lb). Whether the solvent would be recovered in downstream processing or dealt with in a waste treatment facility would depend on the ease with which it could be recovered, *e.g.* by adsorption

onto a fixed bed, and would need to be determined by a detailed economic evaluation which is beyond the scope of this work.

Perhaps the most critical chemical from the viewpoint of process losses is phenylboronate. In several UV analyses of the final aqueous wash in the extractant preparation procedure, the concentration of phenylboronate ranged from 0.0025 to 0.005 mol/L. This value has a significant experimental error, due to the fact that the concentration, after dilution into a sodium hydroxide solution, is below the ideal range for UV phenylboronate analysis - see Section 2.1.1.5. On the basis of this phenylboronate concentration, using the same assumptions as in the previous paragraph, the loss of phenylboronate amounts to 0.02 grams phenylboronic acid per gram of propylene glycol. Most likely, the aqueous concentration of phenylboronate would be lower than the concentration in the final aqueous wash, since the aqueous phase pH of that wash is still high (10 to 11). In one UV analysis of a post-extraction aqueous phase, the concentration of PB^- was below 0.001 mol/L. Note that this was determined from an extraction experiment using a pure 1,2-PD solution. When anions with a significant affinity for Aliquat 336, such as chloride, are present in the aqueous phase, these may ion-exchange with phenylboronate, causing greater losses.

Since at this time phenylboronic acid is not manufactured in bulk quantities, it is difficult to estimate the economic value of the losses. However, since all documented preparation methods for PBA involve expensive organometallic (*e.g.* Grignard) reaction steps, it will be an expensive chemical even when made with a bulk process, and the cost of phenylboronate will be a significant consideration in the overall economic evaluation of a process using a boronate extractant.

Nitrophenylboronic acid has a significantly lower aqueous solubility than phenylboronic acid. It would therefore be expected to be extracted into the aqueous

phase to a lower extent. On the other hand, NPBA is prepared from PBA with an additional reaction step, which could significantly add to the cost of this chemical.

In the application of recovery from a fermentation broth, the depletedaqueous feed could possibly be recycled to the fermentation process, provided the organoboronate is not toxic to the organisms carrying out the fermentation.

2.3. Conclusions

The work described in this chapter confirms that extraction of propylene glycol from dilute aqueous solutions, which was previously observed by Chow (1992) in extractants with 3-nitrophenylboronate, is also effective using phenylboronate. Most extractions were carried out with high-concentration extractants; no effect of extractant concentration on extraction results was observed.

Overloading, the phenomenon in which more than one molecule of 1,2-PD is taken up for each mole of phenylboronate, was observed in all extractants at concentrations exceeding 0.2 mol/L, with the exception of one extractant in which diisobutylketone was used as a diluent. Several possible explanations were offered to explain this phenomenon. The most likely explanation is the uptake of 1,2-PD into the interior aqueous-like phase of extractant aggregate structures, *e.g.* reverse micelles.

The strength of complexation varies with the diluent in which the extractant is prepared. The highest complexation constants were observed with 2-ethylhexanol. With such extractants, the loading is 0.5 or higher at an aqueous concentration of 0.02 mol/L (0.15 wt %), and 0.33 or higher at 0.01 mol/L (0.08 wt %). On the basis of such strong complexation, it would be feasible to design a countercurrent extraction process for recovering propylene glycol from dilute aqueous streams. Currently, the concentrations achieved in fermentation processes for production of 1,2-PD would not even lead to

overloading in most extractants. A high degree of concentration could be achieved using an acceptable organic-to-aqueous phase ratio.

Back-extraction of 1,2-PD into an aqueous phase can be achieved by sparging CO_2 into a dispersion of water in a loaded extractant. Typically, around 80% of the extracted 1,2-PD can be back-extracted by this procedure. Extractants must then be regenerated by stripping at temperatures around 115 °C, to release the bicarbonate anions in the form of CO_2. At these elevated temperatures, extractants undergo some chemical change evidenced by a darkening of color and a loss of extraction capacity. The loss of capacity is limited to about 50% of the original capacity, but in combination with the capacity that remains unutilized due to incomplete back-extraction, the effective extraction/back-extraction capacity is reduced to about 30% of the initial value.

In terms of a process for recovery of glycol from aqueous solutions, this would mean that more extractant would be needed to achieve the same degree of glycol recovery, and that the overall concentrating effect between initial and final aqueous phase would be limited. For instance, if the aqueous feed contained 0.20 mol/L (1.5%) 1,2-PD, and the extractant contained 0.40 mol/L phenylboronate and cycled between Z=0.05 and Z=0.35, a minimum organic-to-aqueous phase ratio of 1.7 would be needed. The aqueous product concentration that could be achieved would depend on whether the back-extraction operation could be carried out in a countercurrent mode. Assuming that the extractant is effectively blocked by the reaction with CO_2, the highest practical aqueous product concentration would be limited by the physical distribution of 1,2-PD into the organic phase. Even in countercurrent mode, concentrations exceeding 1 mol/L (7.6%) would be impractical.

An alternative method for regenerating the extractant after back-extraction is to remove CO_2 by contacting with a high-pH aqueous sodium carbonate solution. With this

procedure the extractant does not appear to undergo chemical change. The regeneration effectiveness increases with increasing pH; a high carbonate-to-bicarbonate ratio is required to regenerate the extractant to a sufficient extent. A regeneration process would probably be carried out in a countercurrent fashion, using a saturated or near-saturated aqueous Na_2CO_3 or K_2CO_3 solution.

Extractant degradation in the regeneration step or incomplete regeneration effectiveness pose a serious problem that limits the utility of the process, as demonstrated in process calculations above. Finding optimum and effective conditions for extractant regeneration (temperature, pressure, diluent, agitation, chemical additives for regeneration by stripping; temperature, concentrations, process configuration for regeneration with carbonate solutions), would be a priority in further research into a recovery process using organoboronate extractants.

3. Adsorption onto a boronate-loaded anion-exchange resin

3.1. Experimental procedures

3.1.1. Analytical procedures and materials

Where applicable, the same materials and analytical procedures were used as for the extraction studies, detailed in Sections 2.1.1 and 2.1.2.

3.1.2. Amberlite IRA-910

Amberlite IRA-910 is a strongly basic quaternary ammonium anion-exchange resin manufactured by Rohm & Haas Corp. The resin beads are macroreticular, with a particle size of approximately 0.50 mm. The reported total exchange capacity is 3.8 meq/g dry resin, which, with the reported moisture content of 55%, translates to 1.7 meq/g wet resin. The resin is supplied as the chloride form.

In the form in which it is supplied, Amberlite IRA-910 has a wet appearance. For the experiments described below, the resin beads were washed with deionized water under suction filtration, then centrifuged at 2200 rpm for 10 minutes, which resulted in nearly free-flowing solids with a dry appearance.

3.1.3. Converting the resin to the phenylboronate form

A 0.5 M aqueous solution of sodium phenylboronate was prepared by dissolving approximately equimolar quantities of sodium hydroxide and phenylboronic acid (with a slight excess of sodium hydroxide) in water. The concentrations of phenylboronate and hydroxide were determined by titration with 0.100 N HCl.

Amberlite IRA-910 resin and sodium phenylboronate solution were weighed into vials. The solid and liquid phases were allowed to equilibrate for a minimum of 16 hours at room temperature, after which the aqueous phase was analyzed for hydroxide and phenylboronate (by titration with 0.100 N HCl) and for chloride (by Mohr's titration with 0.100 N $AgNO_3$).

The resin beads were then prepared for adsorption experiments by washing and centrifuging as described above.

3.1.4. Uptake of propylene glycol by the unconverted resin

Aqueous propylene glycol solutions of various concentrations and Amberlite IRA-910 resin in the chloride form were weighed into 20-ml vials. The aqueous and solid phases were contacted by slow stirring or shaking at room temperature for a minimum of 16 hours. The concentration of propylene glycol in the aqueous phase was then measured by GC.

3.1.5. Uptake of propylene glycol by the converted resin

Adsorption experiments similar to those described in the previous section were also carried out with Amberlite IRA-910 resin that had been previously converted (to various extents) to the phenylboronate form.

3.2. Results

3.2.1. Converting the resin to the phenylboronate form

The Amberlite IRA-910 resin was converted from the chloride form to the phenylboronate form to various extents by varying the phase ratio of sodium phenylboronate solution to anion-exchange resin. From the initial and final concentrations of phenylboronate in the aqueous phase, the uptake onto the resin was calculated. The same calculation could be carried out for hydroxide, but its concentrations were so low that the error in the calculation was large. From the concentration of chloride in the aqueous phase after equilibration, the amount of chloride displaced from the resin was calculated. When both results are expressed in units of mmol/g resin, it is clear that the amount of chloride displaced is consistently lower than the amount of phenylboronate taken up, which suggests that some of the phenylboronate is physically adsorbed to rather than chemically complexed with the anion-exchange resin. The results of various conversion experiments are given in Appendix H, and presented graphically in Figure 3-1. The relative affinity of IRA-910 for phenylboronate and chloride may be defined as in Equation 3-1.

$$K_{PB^-/Cl^-} = \frac{q_{PB^-}}{c_{PB^-}} \cdot \frac{c_{Cl^-}}{q_{Cl^-}} = \frac{q_{PB^-}}{c_{PB^-}} \cdot \frac{c_{Cl^-}}{q_{max} - q_{PB^-}} \qquad (3\text{-}1)$$

In this equation, q_{PB} and q_{Cl} are the concentrations of phenylboronate and chloride anions associated with the resin, in mmol/g, and q_{max} is the total anion-exchange capacity. A non-linear least-squares fit of the data points in Appendix H, using the value of q_{max} given

Figure 3-1. Conversion of IRA-910 from chloride to phenylboronate form

by the manufacturer (1.70 meq/g), results in a value for $K_{PB/Cl}$ of 0.95±0.16. The corresponding fit is shown as the solid curve in Figure 3-1. A two-parameter fit (shown as the broken line in Figure 3-1), in which both q_{max} and $K_{PB/Cl}$ are determined by non-linear regression, yields q_{max}=1.24 mmol/g and $K_{PB/Cl}$=2.0. The first result suggests that IRA-910 exhibits roughly the same affinity for phenylboronate ions as it does for chloride ions. The second result, which fits the data better, suggests a higher affinity for phenylboronate ions, but a lower capacity than the manufacturer-quoted capacity.

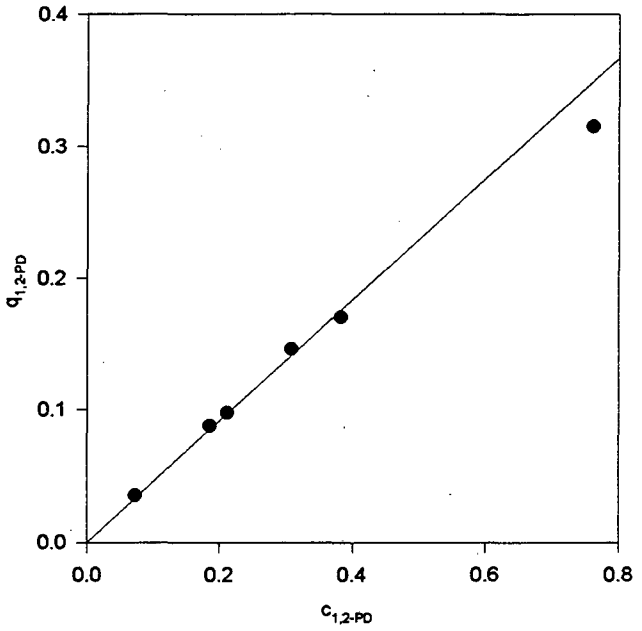

Figure 3-2. Uptake of 1,2-PD onto unconverted IRA-910 resin

3.2.2. Adsorption of propylene glycol onto the unconverted resin

The adsorption experiments with the unconverted resin are presented as an adsorption isotherm in Figure 3-2. The results are also tabulated in Appendix H. The isotherm is linear at concentrations of propylene glycol below 0.4 mol/l, with a slope of 0.458±0.007 (mmol/g)/(mol/l). This result indicates a low but non-negligible affinity of propylene glycol for the unconverted resin due to hydrophobic exclusion.

3.2.3. Adsorption of propylene glycol onto the converted resin

Batch adsorption studies were carried out with several of the converted resins. The results are summarized in Appendix H. It is assumed that the adsorption by hydrophobic exclusion is equal regardless of the anionic form of the resin. This means

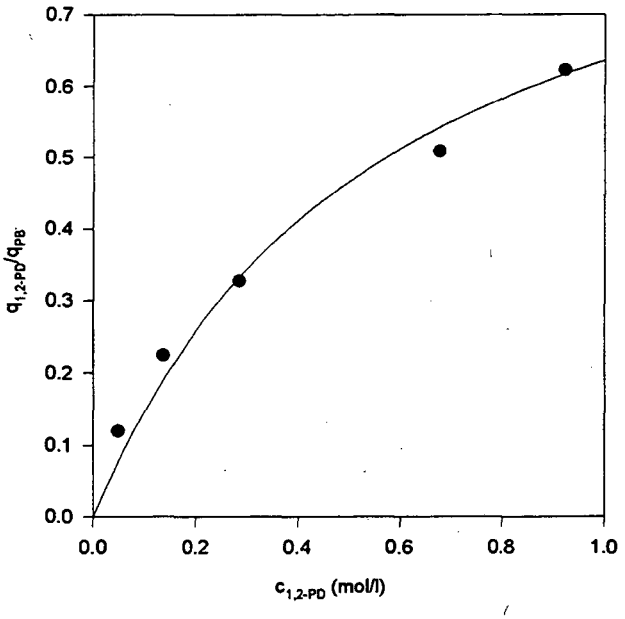

Figure 3-3. Uptake of 1,2-PD onto partially converted IRA-910

that the uptake of propylene glycol due to complexation with phenylboronate may be found by subtracting the calculated value of this adsorption from the total amount adsorbed. The amount adsorbed due to complexation, q_{comp}, is shown in Figure 3-3 as a function of the aqueous-phase concentration of 1,2-PD. The curve is a non-linear least-squares fit of Equation 3-2,

$$\frac{q_{comp}}{q_{max}} = \frac{\beta_{11} \cdot c_{1,2\text{-PD}}}{1 + \beta_{11} \cdot c_{1,2\text{-PD}}} \qquad \textbf{(3-2)}$$

representing the adsorption equilibrium for simple 1:1 complexation. The maximum adsorption q_{max} corresponds to the amount of phenylboronate taken up by the resin. Note that the quantity q_{comp}/q_{max} parallels the quantity Z defined in Section 2.2.6.1 for extraction. The best fit is obtained for β_{11}=1.75 $(mol/l)^{-1}$. The homogeneous equilibrium

constant for complexation between 3-nitrophenylboronate and propylene glycol in aqueous solution is 3.17 $(mol/l)^{-1}$ (Randel *et al*, 1994); the heterogeneous equilibrium constant for extraction found in this work is of the order of 60 $(mol/l)^{-1}$.

The large difference between the extraction and adsorption results suggests that the organic solvents used in extraction (especially 2-ethylhexanol) provide a more favorable environment for the complexation reaction, due to differences in solvation and hydrophobic interaction. The low complexation constant makes a process based on adsorption from an aqueous phase onto a phenylboronate-loaded anion-exchanger likely to be unattractive.

4. Adsorption onto a boronated gel

4.1. Experimental procedures

4.1.1. Analytical procedures and materials

Unless otherwise specified, the same materials and analytical procedures were used as for the extraction studies detailed in Sections 2.1.1 and 2.1.2.

4.1.2. Boronic acid gel

Immobilized boronic acid gel was obtained from Pierce Co. Its intended use is in affinity chromatography, for the purification of proteins, antibodies and other biological molecules (Olsson, 1979). It consists of a polyacrylamide support, functionalized with m-aminophenylboronic acid. The gel is supplied as a 50% aqueous slurry of spherical beads. According to the documentation, the loading is 100 μmol/ml gel. The gel was stored in a refrigerator at 4 °C.

4.1.3. Binding buffer

The gel documentation suggests the use of a binding buffer consisting of 0.2 M ammonium acetate solution with pH 8.8. A solution of 0.2 M NH_4Ac was prepared. Its pH, originally 7.0, was adjusted to 8.8 by the addition of several drops of ammonia.

4.1.4. Gel filtration

The slurry form in which the gel was supplied was not conducive to quantitative experiments, since the beads settled quickly, leading to a non-uniform distribution within the slurry container. Therefore, the gel was suction-filtered under a nitrogen blanket and

washed with water before each experiment. The resulting solid mass was too moist to be free-flowing, yet dry enough that the moisture distribution was assumed to be uniform. Such solids were always used within hours of filtration, and stored in a capped vial at 4 °C before use.

A small quantity of gel solids obtained by filtration was weighed into a vial and then oven-dried. The weight loss indicated that the weight fraction of dry resin in the filtered gel solids is 43%.

4.1.5. Gel titration

To investigate the content of phenylboronic acid functionality in the gel, 1.1165 g gel solids were stirred with 5.09 g of 0.0975 N NaOH solution and water, then titrated with 0.0987 N HCl solution. The pH was followed with a pH electrode. The titration was done slowly, to allow the slurry to come to an equilibrium state between titrant additions. A blank titration was also carried out, in which 4.83 g of 0.0975 N NaOH was titrated.

4.1.6. Batch adsorption experiments

Aqueous solutions of 1,2-PD and filtered gel solids were weighed into 2-ml vials and allowed to equilibrate overnight with gentle magnetic stirring. Since the loading of the gel with boronate groups is so low, high solids-to-liquid mass ratios were used, typically 0.5 to 1. The aqueous solutions were usually neutral solutions of 1,2-PD in water. Some experiments were done in other aqueous environments: (a) the binding buffer, pH 8.8; (b) the binding buffer, with pH adjusted upwards to 10 by addition of ammonia; (c) dilute hydrochloric acid.

The aqueous-phase concentrations of 1,2-PD after equilibration were measured by GC, using the initial solutions as standards.

4.2. Results

4.2.1. Gel titration

The results of the gel titration and the blank titration are shown in Figure 4-1. It is immediately obvious that the pH is strongly influenced by the presence of the gel. Where the blank titration started at a pH well above 12, the gel suppressed the pH to a value under 11. And where the blank titration exhibits a very sharp breakthrough, the gel titration exhibits a much more gradual change in pH, with two distinct inflection points, around pH 8 and pH 4. Possibly the acrylamide gel matrix itself exerts an influence on the pH, due to the slightly acidic proton of the amide group. The pH of the slurry in which the gel was provided was 4.5. In any case, it is difficult to interpret the titration curve quantitatively to obtain a value for the capacity.

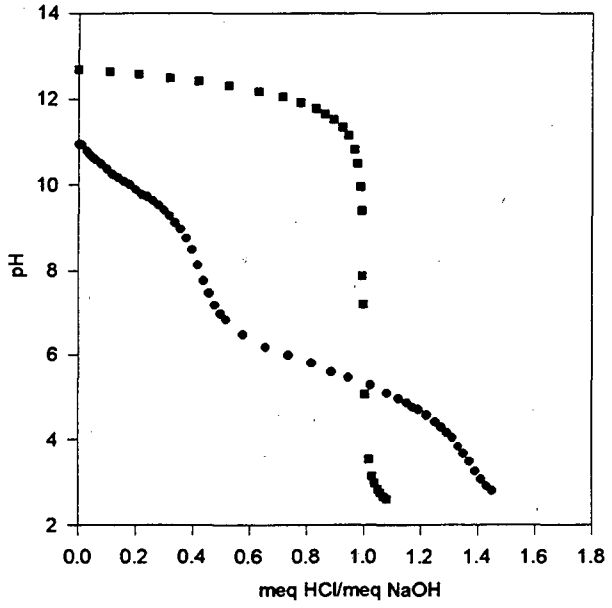

Figure 4-1. Titration of Pierce boronated gel with hydrogen chloride solution

4.2.2. Batch adsorption experiments

For each adsorption experiment the amount loaded onto the gel was calculated from

$$q = \frac{([1,2\text{-PD}]_i - [1,2\text{-PD}]_f) \cdot V_{aq}}{m_{gel}} \qquad \textbf{(4-1)}$$

The loading is expressed in mmol/g gel. The experimental data are presented in Appendix I. The gel itself contains some water at the beginning of the experiment, which causes a decrease in concentration by dilution even if no glycol is taken up. To take this effect into

account, the volume of the aqueous phase and the initial glycol concentration must be calculated from

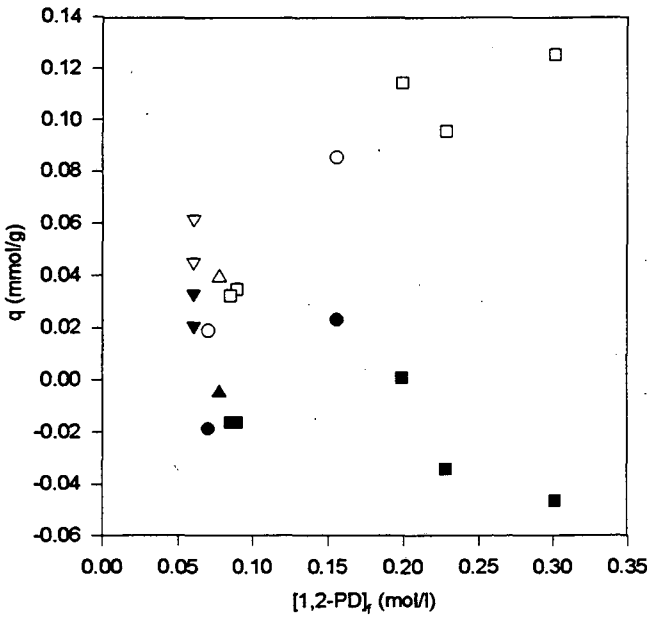

Figure 4-2. Isotherm for adsorption of 1,2-PD onto Pierce boronated gel

$$[1,2\text{-PD}]_i = [1,2\text{-PD}]_{add} \cdot \frac{V_{add}}{V_{aq}} \qquad \textbf{(4-2)}$$

$$V_{aq} = V_{add} + \frac{m_{gel} w_{H_2O}}{\rho_{H_2O}} \qquad \textbf{(4-3)}$$

in which V_{add} and $[1,2\text{-PD}]_{add}$ are the volume and concentration of the glycol solution added to the gel, and w_{H2O} is the weight fraction of water in the gel. Equation 4-2

assumes that the concentrations of 1,2-PD in the solution within the gel and in the bulk solution are the same.

The results of the experiments, calculated by Equations 4-1 to 4-3, are shown in Figure 4-2 with solid symbols. The scattered data suggest that the experimental error is significant. The fact that the calculated uptake is negative in many cases possibly indicates that the corrections introduced in Equations 4-2 and 4-3 may be inaccurate. Perhaps the concentration of 1,2-PD in the water contained in the gel is lower than the bulk concentration. This could be due to size exclusion or hydrophobic effects, prohibiting or limiting propylene glycol from entering into the same space within the gel, or due to rate effects. However, even when the corrections are not applied (shown in Figure 4-2 as open symbols), the data suggest that adsorption is weak. Adsorption in which the solute has a strong affinity for the functional group of the sorbent would result in a favorable isotherm, with a high slope at low concentrations and levelling off to its maximum uptake at higher concentrations. Here, the adsorption isotherm is roughly linear, with modest uptake at relatively high glycol concentrations. The uptake appears to be somewhat higher at pH 10 than at neutral or acidic pH, but the effect is not dramatic. It is unclear why the boronate gel, which may be used in a chromatography mode to separate glycols and other poly-hydroxy compounds, exhibits such low affinity towards propylene glycol. Evidently, once again complexation is weak in an aqueous environment. However, from the experimental data one may conclude that this type of boronated resin is not effective for recovery of propylene glycol.

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