THE THEORY OF EMULSIFICATION. VI

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In the preceding paper[1] of this series I showed that the liquid A will be the dispersing phase and liquid B the disperse phase in an emulsion in case the surface tension between liquid A and the emulsifying agent C is lower than the surface tension between liquid B and the emulsifying agent. It was also shown that a corollary of this is that an aqueous colloid will tend to make water the external phase while a non-aqueous colloid[2] will tend to make water the internal phase. I did not take up specifically the conditions under which a substance acts as an emulsifying agent; but this is important both in its bearing on the formation of emulsions and in its bearing on the allied problem of ore flotation. For a substance to be an emulsifying agent, it must tend to pass into the surface separating the two liquids and form a coherent film there. If the emulsifying agent does not form a coherent film the emulsion will crack; if it does not pass into the liquid interface, it will not form a film round one of the liquids. Since the adsorption of air plays an important part in ore flotation and since it may be of importance in the formation of emulsions, I propose to consider the general problem of the concentrating of a dissolved or suspended substance at an interface between liquid and liquid or between liquid and vapor. To avoid circumlocution the surface separating two liquid phases will be called a dineric interface[3]

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[1] Bancroft: Jour. Phys. Chem., **17**, 501 (1913).

[2] In the preceding paper I used the term hydrophobe colloid to denote a substance forming a colloidal solution readily in some non-aqueous solvent and not doing so in water. This is not the usual sense of the term; but the usual distinction between hydrophile and hydrophobe colloids becomes meaningless if we no longer distinguish between emulsion colloids and suspension colloids. It seems foolish to invent new words when we have two perfectly good ones with no meanings attached to them. I suggest, therefore, that hydrophile be used for colloidal solutions in water and hydrophobe for colloidal solutions in non-aqueous solutions.

[3] Bell: Jour. Phys. Chem., **9**, 531 (1905).

and the surface separating liquid and vapor a foam interface. We will begin with the concentrating of a dissolved substance at a dineric interface. An interesting case of this sort has been studied by Wilson,[1] whose paper seems generally to have been overlooked.[2]

"When chloroform is placed in a test-tube, or other vessel of glass, standing on a horizontal surface, it exhibits, like other substances which wet that solid, a curved surface with the concavity upwards. If water or an aqueous solution of nitric, sulphuric, or muriatic acid, be poured upon the stratum of chloroform, the surface of the latter immediately changes the direction of its curve, and becomes convex upwards, the convexity induced being much greater however than the previous concavity. If, on the other hand, an aqueous solution of potash, soda, or ammonia be placed above the chloroform, the latter ceases at its upper limit to present a sensible curvature upwards or downwards, and shows a surface which, to the unassisted eye, appears to be flat. It is to this property of an acid to round, and of an alkali to flatten the surface of various liquids, of which chloroform is one, that I seek specially to direct attention.

"The phenomena referred to, cannot seem remarkable when merely described; but they have appeared striking and, I may say, startling to most who have witnessed them. They are best observed by dropping into a perfectly clean, flat-bottomed glass vessel containing pure water, a quantity of chloroform too small in amount to touch the walls of the vessel on every side. The heavier liquid then shows itself as a brilliant, highly mobile globule. If alkali be now added the globule in a moment collapses, sinks as if exposed to a crushing force, and flattens out on the bottom of the glass. On slightly supersaturating the alkali with an acid, the flattened chloroform starts into its previous globular shape, with a momentum and rapidity, such as might be exhibited

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[1] Jour. Chem. Soc., 1, 174 (1848).

[2] It is given among the references to the literature in Winkelmann's Handbuch der Physik, 1, 498 (1891).

by a highly elastic substance, like a ball of caoutchouc suddenly
relieved from enormous pressure. When the acid in its turn
is supersaturated with alkali, and flattening again occurs,
and by alternating the addition of these reagents, the same
globule may be successively flattened and rounded for any
number of times.

"It is necessary here to mention that the employment
of an acid is not essential to the development of the phenomena
described. In distilled water, chloroform exhibits a con-
vexity of upper surface as marked as in the aqueous solution
of an acid. The alternate addition to it of water, and re-
moval from it of alkali, are as efficacious accordingly as the
successive addition of alkali and acid. But the washing
away of the former by repeated effusions and decantations
of water, is a tedious and unsatisfactory process, which has
the great disadvantage of changing the form of the globule
by slow graduations from a flat to a convex surface, whilst an
acid effects the conversion *per saltum*. I shall confine my
observations, accordingly, to the action of alkalies and acids,
although the effect of the latter in altering the shape of the
chloroform globule, is not greater but, as I incline to think,
less than of water.

"Change in configuration, however, is not the only
alteration which the globule of chloroform undergoes. Some
of the other physical properties are markedly altered by its
contact with acids and alkalies. These changes are best
seen when a deep white saucer, or flat-bottomed porcelain
basin, is made use of as the containing vessel. When acid-
ulated water is placed in this, and chloroform let fall into it,
the denser fluid is scarcely wetted and, although nearly half
as heavy again as pure water, sinks reluctantly. If the drops
indeed be small, they never reach the bottom but, by floating
on the surface, evaporate away. Those which descend
form globules very mobile, and readily obeying the solicita-
tion of gravity. When separate globules melt, they rapidly
flow together, and scarcely one is to be seen without a bubble
of air attached to its upper surface and adhering tenaciously.

I have already referred to the brilliancy of the drops of chloroform at the bottom of the water; they retain this character when the water is acidulated.

"When the water, on the other hand, is alkaline, the chloroform is quickly wetted, and sinks swiftly. The drops, if small, become circular discs with rounded edges; if large, they are oval, or spread out into elongated, irregularly ovoidal, or flattened cylindrical forms. Their shape, however, is changed by the slightest impulse, or inclination of the containing vessel, in a way which, perhaps, I may best illustrate by comparing it to the ever-varying elongation, contractions and irregular swellings, which alter the configuration of an active living leech in a glass of water. The flattened globule, moreover, is much less mobile than the rounded one in acid. The former moves sluggishly, even down an inclination, clings to the vessel; and when compelled to move rapidly, leaves a tail behind it, like foul mercury. No air-bells attach themselves to it and its brilliancy is sensibly diminished, as if its refractive index had altered."

Some further experiments were made by Swan[1], who obtained the following results:

1. Olive oil floating on the surface of water or of hydrochloric acid has its under surface convex, but with solution of potash its surface is apparently flat. It has also, in contact with alcohol or sulphuric ether, a much flatter surface than with solution of potash.

2. Spermaceti oil also exhibits a convex surface in contact with water and hydrochloric acid, and a flat surface with solution of potash.

3. Oil of cloves sinks in water and has a highly convex surface, which becomes nearly flat on the addition of alcohol to the water; but the liquids mingle so readily that their mutual surface is not very well defined.

4. Oil of cassia sinks in water; and its surface, which is very convex, is considerably flattened by adding potash or

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[1] Phil. Mag., (3) **33**, 36 (1848).

alcohol to the water. The addition of acid in the former case, or of water in the latter, restores the convexity of the surface.

5. Oil of lavender floats on water, with its under surface convex. If alcohol is poured upon it, its upper surface is nearly flat.

Swan also made some experiments to see "whether the results were modified by altering the nature of the containing vessel. I have found that on immersing a slip of recently ignited platina foil, or clean iron or brass wire in the liquids, the surface of the chloroform is highly convex in contact with them under water or hydrochloric acid, but apparently flat under solution of potash. If the metal is not perfectly clean, the surface of the chloroform is apt to become concave in contact with it under water or acid. On lining a glass tube with a thin coating of wax, I found that chloroform placed in it under hydrochloric acid had a very *concave* surface, while on supersaturating the acid with solution of potash the surface became sensibly flat. Similarly chloroform under water in a quill has a very *concave* surface which becomes sensibly flat on the addition of potash, and the concavity is restored by adding a sufficient quantity of hydrochloric acid. It will be observed that the coating of wax, or the substitution of a tube of quill for one of glass, while it completely reverses the curvature of the chloroform in contact with water and acids, exerts apparently no influence on the power of the alkali to flatten its surface; and the conclusion seems inevitable, that this effect depends upon a mutual action of the liquids, and is quite independent of the nature of the containing vessel for it takes place equally in contact with surfaces of glass, platina, iron, wax, or quill."

Having eliminated everything else, as he thought, Swan concluded that the flattening of the surface must be due to the affinity between caustic potash and the organic liquid, an affinity which is shown independently by the fact that caustic potash reacts with chloroform and with vegetable oils. Swan says: "In conclusion it may be remarked, that

if the phaenomenon of the flattened surface of two immiscible liquids has received a correct explanation on the hypothesis of a strong mutual attraction of their molecules, and if this phaenomenon is found to appear only in cases where the liquids have a decided chemical affinity for each other, an interesting connexion is thereby established between chemical affinity and the mechanical force of adhesion, tending to prove that they are modifications of the same force; while the whole subject of the mutual attractions of two liquids opens up an interesting, and, so far as I am aware, a new field of inquiry in capillary attraction."

Swan's hypothesis, that the flattening takes place only when chemical action is possible, is proved to be wrong by the fact that benzene behaves in exactly the same way.[1] While the flattening is clearly due to a change in surface tension, it cannot depend on the absolute value of the surface tension of the water phase because Wilson found the effect of alkali to be the same qualitatively whether sodium chloride was present or not, whereas the addition of salt increases the surface tension of the water phase. What happens is that hydroxyl is adsorbed at the dineric interface lowering the surface tension and causing the organic liquid to flatten. This is confirmed by the experiments of von Lerch,[2] who determined the surface tension between benzene and water by means of the rise in capillary tubes. The surface tension between pure benzene and pure water was found to be 32.6 dynes/cm at $15°-16°$. With $M/4$ NaOH the value dropped to 20.7 and with $M/2$ NH$_4$OH to 27.3. The lowering of the surface tension is greater with sodium hydroxide than with ammonia owing to the greater electrolytic dissociation of the former. The surface tension was also lowered by hydrochloric acid but only slightly, $M/2$ HCl bring it down to 31.5. This is in accord with Wilson's qualitative conclusions that acids do not increase the surface tension quite as much as

[1] von Lerch: Drude's Ann., **9**, 434 (1902).
[2] Drude's Ann., **9**, 434 (19 02).

pure water. Von Lerch also found a marked effect due to acetic acid; but this acid is miscible in all proportions with benzene and causes benzene and water to become more miscible, so there is nothing surprising about its behavior. The surface tension measurements are confirmed by the electrical ones, for von Lerch found that benzene drops in caustic soda moved fairly readily under electrical stress, whereas there was almost no movement in presence of sodium chloride or hydrochloric acid. It is possible that other ions might be adsorbed markedly by benzene, but I know of no experiments to show this.

The adsorption of hydroxyl means practically a concentrating of alkali at the surface of the benzene and consequently a closely adhering film of water. This accounts for Wilson's observations that the drops of chloroform were readily wetted by an alkaline solution. The presence of the surface film of caustic soda solution also accounts for the decreased mobility observed by Wilson.

The amount of adsorption has not been determined quantitatively in the preceding cases; but Patrick[1] has studied the adsorption of new fuchsine, picric acid, salicylic acid, and mercurous sulphate from solution by mercury. In all four cases the amounts adsorbed varied with the concentration approximately according to the exponential formula and in all four cases the surface tension of the mercury was lowered by the adsorption.

Tomlinson's experiments upon the action of oils on supersaturated solutions would come under the heading of a dissolved salt concentrating at a dineric interface if one were only certain of the accuracy of the work. Tomlinson[2] found that oils start crystallization in supersaturated solutions of sodium sulphate in case the oil spreads out in a film over the water; but do not if it remains lens-shaped. "Four ounces of Glauber's salt in four ounces of water was boiled

[1] Zeit. phys. Chem., **86**, 545 (1914).
[2] Phil. Trans., **161**, 51 (1871).

and filtered into four flasks, covered with watch-glasses and left until cold. A clean glass rod was dipped into a bottle of clear, pale seal oil, and the watch-glass being gently removed from off one flask, a drop of the oil was carefully delivered to the surface solution; the glass rod was withdrawn, and the watch-glass restored to its place. The drop of oil expended into a well-shaped film, with a display of iridescent rings; and immediately from the lower surface of the film there fell large well-shaped prisms with dihedral summits of the ten-atom sodic sulphate, being the normal salt. The prisms were an inch or an inch and a half in length, and three-eighths of an inch across. The crystallization proceeded from every part of the lower surface of the film, and as one set of crystals fell off another set was formed, until the whole solution became a mass of fine crystals in a small quantity of liquid. This effect is entirely different from the usual crystallization which takes place when a supersaturated solution of Glauber's salt is subjected to the action of a nucleus at one or two points in its surface, as when motes of dust enter from the air, or the surface is touched with a nuclear body. In such cases small crystalline needles diverge from the point touched, and proceed rapidly in well-packed lines to the bottom, the whole being too crowded and too rapid to allow of the formation of regular crystals. But in the case before us, where the whole surface of the solution and the surface only, is subjected to nuclear action by the spreading of the oil film, the action is not so rapid as in the former case, because it is not downwards but parallel with the surface; the crystals mould themselves, as it were, upon the oil-film, and, falling off, allow fresh portions of the solution to come into contact with the film, until at length a very fine crop of crystals is produced. This experiment was repeated on the solutions in the other three flasks with the same result.

"Similar experiments were tried on solutions of Glauber's salt of different strengths, with drops of ether, absolute alcohol, naphtha, benzole, oil of cajuput, oil of turpentine, and other volatile oils, herring oil, sperm oil, olive oil, castor oil,

and some other fixed oils of animal and vegetable origin, with this general result, that, whenever the oil spread out into a film, it acted as a powerful nucleus.... A solution of two parts of Glauber's salt to one part of water was boiled and filtered into three flasks, which were covered with watch-glasses and left until the next day. A drop of castor oil was then placed upon the surface of each; it formed a lens which gradually flattened; but there was no separation of salt, even when the flasks were shaken so as to break up the oil into small globules. The necks of some clean flasks were oiled inside with castor oil, and the boiling solution of Glauber's salt filtered into them; the oil formed into globules, and some of it ran into the solution. Next day there was no separation of salt. The flask was turned round quickly so as to form a whirlpool, in which the globules of oil descended to the bottom and were broken up and diffused so as to form a kind of emulsion; but by repose the solution became clear again, the oil collected into larger globules, and there was no separation of salt. If, while the flask is being turned round, a sudden jerk be given to it, so as to flatten some of the globules against the side into films, the whole solution instantly becomes solid; or if by strong pressure with the finger against the interior of the neck a smear of oil be made, the solution crystallizes as soon as it is brought into contact with such smear. But if it be objected that the finger may introduce nuclear matter, then a catharized wire, which, dipped into the solution is inactive, will, if rubbed against the side so as to flatten some of the small oil globules, leave a number of minute crystals of a chalky white color filling up the lines traced by the wire, and these serve as nuclei to the rest of the solution."

While discussing these and other experiments, Tomlinson[1] says: "It can be shown experimentally that a clean inactive rod immediately becomes active simply by drawing it through the hand: so also a clean surface, such as the inside of a flask, smeared with a little oil, becomes power-

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[1] Phil. Trans., **161**, 66 (1871).

fully nuclear; but if the smear on the surface of the rod or on the inner wall of the flask can gather itself up into globules, these are not nuclear. Phenomena of this kind seem to be explained by reference to the surface tension of liquids. In the case of a film formed by depositing a drop of an oil on the surface of a supersaturated saline solution, the surface tension of such solution being diminished at the point touched by the oil, the surface of the solution surrounding the point touched exerts a tractive force on the oil, and spreads it into a film, with adhesion to the surface and a nuclear action on the solution; because being brought into contact with the saline particles, but not with the aqueous (seeing that oil and water do not combine, while adhesion readily takes place between oil and salt), the saline molecules are separated from the aqueous, and the action once begun is propagated. When, on the other hand, an oil deposited on the surface of the solution assumes the form of a well-shaped double convex lens, or even a disk, there is no adhesion properly so-called, and no nuclear action, since the lens is separated from the solution by surface tension, and is not nuclear because it is really not in contact with the solution. Even when the solution is shaken so as to break up the lens into globules and to submerge them, each globule is as completely separated by surface tension from contact with the solution as if it were outside the flask, at least so far as any nuclear action is concerned. Whether a drop of oil form a film or a lens depends on several variable circumstances, such as the temperature of the solution, its degree of supersaturation, its surface viscosity, and so on."

In a series of papers Tomlinson[1] brought forward further evidence in support of his views and answered the objections of others. He found that many oils did not cause crystallization when freshly distilled; but did after standing a sufficient length of time or after being exposed to ozone for a short

[1] Proc. Roy. Soc., **20**, 342 (1872); **21**, 208 (1873); **27**, 121, 189, 290 (1878); **29**, 24, 326 (1879).

time. It is therefore the oxidized oils which are active in overcoming supersaturation. The accuracy of Tomlinson's experiments has been questioned by Liversidge,[1] Gernez,[2] and Violette;[3] and Ostwald[4] speaks very contemptuously of Tomlinson's work. There is, however, nothing theoretically impossible about Tomlinson's experiments. If a given oil adsorbs sodium sulphate very strongly, it might easily raise the concentration at the dineric interface to such a point that solid salt would separate spontaneously. It is rather surprising that Tomlinson's experiments coincide very closely with what we might expect from our knowledge of colloid chemistry. On the other hand, Tomlinson was more sceptical as to the existence of particles of sodium sulphate in the air than was safe. As I see it, the whole thing turns on the question whether there is or is not marked adsorption at the dineric interface. Tomlinson[5] states that oil adheres much more strongly to salt than to water; but he gives no evidence in support of this statement. If it were true, very fine crystals of sodium sulphate ought to be raised by oil either to the dineric interface or should be carried out of the water phase into the oil phase.[6] Some experiments were made in my laboratory. Finely ground crystals of sodium sulphate were added to to a saturated solution of this salt and the whole shaken with kerosene and with commercial olive oil. With the kerosene there was no sign of the sodium sulphate being carried up by the oil. The experiments were not quite so convincing with olive oil; but the amount of salt carried up by the oil is either zero or very small. It is therefore probable that Tomlinson's results with olive oil are due to experimental error, which naturally throws doubt on his experiments with the other oils. It is always possible, however, that some

[1] Proc. Roy. Soc., **20,** 497 (1872).
[2] Comptes rendus, **75,** 1705 (1872).
[3] Ibid., **76,** 171 (1873).
[4] Lehrbuch allgem. Chemie, 2nd Ed., **2** II, 739.
[5] Proc. Roy. Soc., **29,** 328 (1879).
[6] Hofmann: Zeit. phys. Chem., **83,** 385 (1913).

of the other oils may show marked adsorption effects with
sodium sulphate. It has seemed to me worth while to discuss
Tomlinson's results in spite of their probable inaccuracy,
because the theory involved is sound and a case illustrating
it satisfactorily may be found some day.

We can now consider the second division of the subject,
the adhesion of small particles to the dineric interface. A
careful study of this phenomenon has been made recently by
Hofmann.[1] As a typical case he cites the behavior of finely
divided red lead when shaken with chloroform and water.
The red lead adheres to the surface of the benzene or of the
chloroform forming a practically continuous coating around
the organic liquid in case proper relative amounts of red lead
and organic liquid are taken. The theory of the phenomenon
is that given by Des Coudres[2] though I am going to put it
in a somewhat simpler form than Hofmann does. If a given
solid is wetted by water much more strongly than by
benzene or chloroform the water will displace the benzene
or chloroform and will form a water film around the particles.
Owing to the adhesion of water to water, work must be done
on the particle to carry it out of the water phase into the or-
ganic liquid. In other words, the particle will tend to stay
in the water phase. If the other liquid is less dense than water,
benzene for instance, the solid particles will stay in the water
phase irrespective of size. If the organic liquid is more
dense than water, chloroform for instance, the particles will
stay in the water phase unless they are so large that the force
of gravity carries them down out of the water phase through
the chloroform to the bottom of the containing vessel. If,
on the other hand, the solid under consideration is wetted
more strongly by chloroform or benzene than by water, a
surface of chloroform or benzene will form round the parti-
cle and will tend to prevent the carrying of the particle from
the organic liquid into the water phase. The solid particles

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[1] Zeit. phys. Chem., **83**, 385 (1913).
[2] Arch. Entwicklungsmechanik, **7**, 325 (1898).

will therefore pass into the water phase only when the water is the more dense of the two liquid phases and when the particles are so large that the force of gravity overcomes the adhesion of the liquid film to the organic liquid.

Since the solid particles tend to remain in the non-aqueous liquid when they are wetted exclusively by the non-aqueous liquid and since they tend to remain in the water phase when they are wetted exclusively by the water, it follows logically that they will remain in the surface separating the two liquids if they are wetted partially[1] by each liquid. This is the conclusion drawn by Des Coudres and by Hofmann. While this is perfectly sound as a matter of logic, it seems to me somewhat unsatisfactory from a physical point of view unless we specify clearly what we mean by partial wetting by each liquid. We may mean that the surface of the solid particles is arranged like a checker board with the organic liquid adhering to the red squares and the water to the black squares. I think that this is Hofmann's conception of the matter so far as he has one, though I admit that he does not say so. This seems probable because Freundlich cites dirty glass as a case of partial wetting, the water wetting the clean places and not wetting the greasy ones. This cannot be what occurs with our solid particles because they are not dirty. If we are not to have the two liquids scattered over the surface of the solid particles as distinct phases, they must be present as a single phase. It seems to me therefore more satisfactory to say that the solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they tend to adsorb the other liquid to the practical exclusion of the water; while the particles tend to go into the dineric interface in case the adsorption of the two liquids is sufficiently intense to increase the miscibility of the two liquids very considerably at the surface between solid and liquid.

These conclusions as to the way a given pair of liquids

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[1] Cf. Freundlich: Kapillarchemie, 18 (1909).

will behave with a given solid refer to the relations prevail-
ing under the conditions of the experiment.   Hofmann's
experiments with two liquid layers in glass test-tubes (soda-
lime glass) showed that the time factor might be an important
one.   If a few cubic centimeters of an aqueous potassium
bichromate solution are shaken up in a carefully cleaned glass
test-tube, there remains on the walls of the test-tube a con-
tinuous uniform coating of solution recognizable by its yellow
color.   This film gradually becomes thinner and paler but does
not break at any point until the water disappears completely
through evaporation.   If one adds a layer of xylene or kerosene
to the aqueous bichromate solution in the test-tube, it is easy
to see that there is a coating of aqueous solution between the
organic liquid and the glass.   If water is allowed to flow
in at the bottom of the test-tube, the organic liquid can be
forced out at the top and there will be no sign of its having
adhered to the glass wall at any point.   If, however, the test-
tube containing the aqueous bichromate solution and the
xylene or kerosene be left standing quietly for a long time,
6–10 hours, it will be found that the organic liquid has diffused
through the water film to some extent and now adheres firmly
to the glass wall nearly everywhere, having displaced the
aqueous film almost completely.   If the contents of the test-
tube are shaken violently, the water displaces the organic
liquid from the glass surface practically completely.   The
glass is therefore wetted more readily and more rapidly by
water than by xylene or petroleum; but a large mass of xylene
or petroleum will gradually displace a water film from the glass
surface.   One would therefore expect to get a slightly differ-
ent behavior with glass powder according as one treated at
first with water or with the organic liquid.   This was ex-
actly what Hofmann found.   If the glass powder were treated
first with water and then shaken with kerosene, practically
all the glass went into the water phase.   If the glass powder
were allowed to stand a long time with kerosene, or if it were
heated with it to hasten the removal of the air film, some of
the glass powder would remain in the dineric interface.   Vigor-

ous shaking would, of course, cause the water to displace the kerosene. Chloroform behaves towards glass and water somewhat like xylene or kerosene though the tendency to displace the water layer from the glass is less than with kerosene. Small drops of chloroform do not break through the water film at all. With increasing amounts of chloroform the force of gravity causes it to break through at the bottom of the test-tube, the surface wetted by the chloroform increasing as the column of chloroform increases in height.

Hofmann[1] describes a number of interesting experiments with thin plates and with powder. "If a freshly-split molybdenite (molybdenum bisulphide) scale be placed on water, it floats on the surface. If it is pushed quickly under water, bubbles of air remain clinging to it. If the air film on the scale is removed by boiling with water, the molybdenite scale sinks under the water and does not remain in the surface. If a layer of xylene or kerosene is placed over the water or a layer of chloroform under it, the molybdenite scale is held fast at the dineric interface when brought in contact with it. If the scale is brought from the air into chloroform, xylene or kerosene, it sinks at once, but adheres to the liquid interface when brought into contact with it. The adhesion at the dineric interface is evidently very great, for if one brings merely a portion of the surface of the scale in contact with the interface the plate is drawn up at once. A molybdenite scale therefore behaves with these pairs of liquids like a small glass plate which has been heated in kerosene. . . . If one shaves some molybdenite off a fresh cleavage plane, one gets a powder made up of little plates of different sizes and can therefore compare the behavior of these directly with that of the larger plates or scales. At the foam interface only the finest powders are held up; the coarser ones sink at once in the water, showing that the adhesion at the water surface is very small indeed. These finest particles sink also if they are shaken with the water and still more

[1] Zeit. phys. Chem., **83**, 409 (1913).

readily after boiling.[1]   The powder can be shaken out of the water phase quantitatively by xylene, kerosene, or chloroform, the powder forming a film round these liquids.   Even the coarser particles cannot be shaken off from the interface without carrying drops of the second liquid with them....   We thus find that, in this case where the clinging of the larger plates at the interface pointed to a marked surface adhesion, the powder goes quantitatively into the interface when it is shaken with the two liquids.

"While molybdenite is a typical instance of the simultaneous partial wetting by water and the other liquid, gypsum behaves more like clean glass.   When thin plates of gypsum are brought out of water[2] into a xylene or kerosene interface, the gypsum plate is not held there but remains entirely covered with a thin film of water.   On the other hand, if one puts a gypsum plate first into kerosene or xylene and then brings it carefully into the water interface, it adheres to this though not very firmly.   A slight blow causes it to sink into the water, after which it will not adhere to the interface....   When calcium sulphate powder, suspended in water, is shaken with kerosene, a very small amount of powder does unquestionably cling to the interface and this also happens if a sodium sulphate solution is added to a calcium chloride solution and the mixture is shaken with kerosene at once.   There is no question therefore but that occasional particles will adhere to the interface when a powder is shaken with two liquids even though thin plates of the same substance remain covered with a continuous film of the two liquids when brought into the interface.   A possible explanation is that the viscous emulsion layer which forms under the petroleum layer after vigorous shaking with water, slows down the rate of sinking of the powder so much that there is time for the thin adher-

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[1] During the boiling the molybdenite powder and also many others are carried up in relatively large amounts to the surface.

[2] In order to make this experiment comparable with those with powdered gypsum, a saturated solution of calcium sulphate was used instead of water.

ing water film to be removed by the kerosene. It is also possible that the particles are held fast by the surface film[1] which forms when kerosene is shaken with pure water. It is also conceivable that the water films around the grains of gypsum are broken mechanically by shaking with kerosene. At the water-chloroform and the water-xylene interfaces there adhere only traces of a calcium sulphate powder suspended in water. In the water–chloroform system the chloroform which does not wet the gypsum, is the more dense liquid and consequently the particles, on standing, settle apparently upon the interface; but they are not really in contact with it as is shown by the fact that a mild shaking whirls them up into the body of the upper liquid. If one suspends gypsum powder first in kerosene, xylene, or chloroform, and then adds water carefully, the same phenomena are obtained as in the similar experiment with glass powder. The powder clings at first to the interface with the exception of the coarser particles which fall at once from the xylene or kerosene into the water. When the tube is shaken, nearly all the gypsum goes into the water phase and only a little is left at the interface. Just as with glass powder, the amount remaining at the interface is greater the longer the powder is left in contact with the organic liquid. If the gypsum were only suspended for a couple of minutes in the organic liquid, the amount that remained in the interface was scarcely larger than if the gypsum had been suspended in water from the first. If the gypsum is left several weeks in the organic liquid, distinctly more powder remains in the interface. Just as with glass, heating the gypsum with the organic liquid cuts down the time enormously.

"Calcium carbonate behaves entirely differently from calcium sulphate. If one brings a plate of Iceland spar out of water[2] into a xylene or kerosene interface, it adheres there

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[1] [This is due to impurities in the kerosene and should have been eliminated in these experiments. W. D. B.]

[2] When these pieces are laid on the surface of water they float there but sink into the water if jarred. The finest particles of calcium carbonate powder also float at the foam interface but can easily be shaken into the water.

even when considerably thicker than a gypsum plate, and is not easily shaken off. From this experiment the adhesion of Iceland spar to xylene or kerosene must be considerably greater than that of gypsum. In accordance with this is the fact that calcium carbonate powder suspended in water goes quantitatively into the dineric interface provided the coarser particles have been removed by sedimentation. The experiment comes out the same way with olive oil in place of kerosene or xylene, the powder being retained quantitatively at the interface.[1] On shaking, a fine emulsion is formed which carries the whole of the powder up with it. When calcium sulphate is used, only a small amount of powder clings to the oil."

TABLE I

Water and	Ether	Chloroform	Butyl alcohol	Benzene	Kerosene	Amyl alcohol	Paraffin oil
$CaSO_4$	w	w	w	w	w	w	w
SnO_2	$w(s)$	ws	ws	$s(w)$	$s(w)$	sw	sw
$Al(OH)_3$	$w(s)$	ws	ws	s	$s(w?)$	sw	$s(w)$
SnS	ws	ws	ws	$s(w)$	$s(w)$	s	ws
$BaSO_4$	ws	ws	ws	s	s	$s(w?)$	$s(w?)$
ZnS	$w(s)$	ws	ws	s	$s(w?)$	s	$s(w?)$
ZnO	ws	ws	$s(w)$	s	s	s	s
$CaCO_3$	ws	ws	s	s	s	s	s
$Mg(OH)_2$	$s(w?)$	ws	s	s	s	$s(w)$	sw
Al	sw	$s(w)$	$s(w)$	s	s	$s(w)$	s
$BaCO_3$	ws	ws	s	s	s	sw	s
CuS	ws	$s(w)$	s	s	s	s	s
$PbCrO_4$	ws	$s(w?)$	s	s	s	s	s
$Cu_2O[?]$	ws	s	s	s	s	s	s
MoS_2	$s(w?)$	s	s	s	s	s	s
PbS	ws	s	s	s	s	s	s
Fe_3O_4	ws	s	s	s	s	s	s
$BaCrO_4$	ws	s	s	s	s	s	s
Pb_3O_4	sw	s	s	s	s	s	s
C	sw	s	s	s	s	s	s
PbI_2	s	s	os	s	s	os	s
HgS	s	s	s	s	s	s	s
HgO	s	s	s	s	s	s	o
HgI_2	s	s	s	s	s	o	os
AgI	s	s	o	s	s	o	os

[1] Of course the free acids in the rancid oil convert some of the calcium carbonate into the calcium salts of the fatty acids.

In Table I are given some of Hofmann's results. The letter w means that the liquid goes nearly completely into the water phase, while o denotes that it goes almost completely into the organic liquid; s means that the powder collects nearly quantitatively in the interface. Two letters, such as sw, mean that the powder goes partly into the interface and somewhat less into the water phase; the use of a parenthesis, $s(w)$ or $s(o)$, signifies that there is a good deal more powder in the interface than in the bracketed phase. Benzene and xylene behave alike so only one is given. In the experiments tabulated, the powder was placed in water and then shaken with the organic liquid.

Much the same conclusions have been worked out by Reinders[1] independently of Hofmann. Some of his data are given in Table II. The powder was placed in the water phase and then shaken with the organic liquid.

TABLE II

Water and	Paraffin oil	Amyl alcohol	CCl$_4$	Benzene	Ether
Kaolin	w	$w(s)$	$w(s)$	w	$w(s)$
CaF$_2$	ws	ws	$w(s)$	$w(s)$	$w(s)$
Gypsum	w	ws	w	sw	ws
BaSO$_4$	$w(s)$	ws	ws	sw	ws
Magnesium	ws	ws	ws	ws	ws
PbO	s	s	sw	s	sw
Malachite	so	s	s	s	sw
ZnS	s	s	s	s	sw
PbS	so	so	s	s	s
HgI$_2$	so	s	s	s	s
Carbon	so	s	s	s	s
Selenium	so	so	so	s	s
Sulphur	so	so	$o(s)$	so	s

Similar results were obtained with colloidal solutions. Isobutyl alcohol was added to a colloidal gold solution obtained by reducing gold chloride with carbon monoxide. When the two liquids are shaken, the gold forms a thin film

[1] Zeit. Kolloidchemie, **13,** 235 (1913).

at the interface. This film is violet blue to blue green by transmitted light and golden by reflected light. A thin water film forms between the isobutyl alcohol and the glass, and the gold concentrates in the dineric interface thus formed, making the alcohol appear uniformly gold-plated. With ether the gold film rises high above the level of the two liquids. With carbon bisulphide the adherent film of gold appears blue. When the carbon bisulphide is broken into drops by shaking, each drop appears blue. When a blue gold was obtained by reducing gold chloride with phosphorus dissolved in ether, the gold went into the dineric interface. When a brownish red gold was obtained in this way, it remained in the water phase and showed no tendency to pass into the interface. This difference is undoubtedly due to an adsorption of something at the surface of the gold because Reinders found that o.oo5 percent gum arabic prevents colloidal gold from passing into the ether-water interface. With carbon tetrachloride, carbon bisulphide, and benzene, the gold goes to the interface as before; but the gum arabic prevents its changing from red to blue.

With colloidal ferric oxide practically no iron went into the interface with any of the organic liquids. It seems probable that this is due to Reinders using a ferric oxide solution which was a year and a half old, because hydrous ferric oxide is ordinarily a pretty good emulsifying agent.[1] Colloidal arsenic sulphide goes into the dineric interface with amyl alcohol or butyl alcohol; but stays in the water phase when carbon tetrachloride, benzene, or ether is the second liquid. India ink goes completely into the interface with amyl alcohol, carbon tetrachloride, or benzene; it goes partly into the interface with isobutyl alcohol and stays entirely in the water phase when ether is the second liquid.

An interesting experiment, which has been done in my laboratory,[2] is to shake copper powder or aluminum powder

[1] Briggs: Jour. Phys. Chem., **19**, 296 (1913).
[2] Bancroft: Trans. Electrochem. Soc., **23**, 294 (1913).

with kerosene and water. The metallic powder goes into the kerosene and into the interface, producing an effect of molten copper or molten aluminum as the case may be. When the bottle is allowed to stand after having been shaken, the metallic powder in the interface creeps up the side of the bottle above the surface of the liquid, rising higher if a little alcohol has been added. I have seen an apparently coherent metallic film rise two or three inches above the surface of the upper liquid phase. If too much copper or aluminum be added the kerosene cannot hold it all up and a portion falls to the bottom of the flask carrying drops of kerosene with it. If the mixture be poured out on a piece of wood, the copper spreads over the surface of the wood just as it did over the surface of the glass. This experiment illustrates the principle involved in all bronzing liquids. A bronzing liquid consists of a volatile liquid which will hold up the metal, and some substance which will keep the metallic powder from rubbing off too readily after it has been applied. This second substance also serves the purpose of keeping the metallic powder in a better state of suspension in the volatile liquid. According to Worden[1] the best of these bronzing liquids consist essentially of pyroxylene dissolved in amylacetate, to which the metallic powder is added. For bronzing radiators and steam pipes, a pure pyroxylin would not do since it would decompose, disintegrate and allow the metallic coating to peel off. To prevent this, boiled linseed oil and resin may be added. Such preparations are of course much slower in drying than pyroxylin bronzing liquids; but that is not a serious objection for these special purposes. A much cheaper form of bronzing liquids consists of rosin dissolved in benzine while the cheapest of all is apparently a solution of sodium silicate in water. The aluminum and copper powders on the market are coated with stearin; but special experiments in my laboratory have shown that the behavior of copper and aluminum with kerosene is the same qualitatively whether the stearin coating is removed with ether or not.

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[1] Nitrocellulose Industry, **1**, 310–320 (1911).

Instead of using a bronzing liquid to coat a solid, it can also be used, according to Worden,[1] to make imitation gold and silver leaf. "Soluble cotton ($\frac{1}{4}$ lb.) is dissolved in one gallon amyl acetate, and this combination mixed with 25 percent bronze. After very thorough mixing, the preparation is poured over a liquid heavier than the bronzing solution as water, glycerol, or carbon tetrachloride, depending upon the weight of bronze. The amyl acetate evaporates and leaves a thin film or leaf on the surface of the water. It is not stated in what manner the amyl acetate layer is placed on the water without causing precipitation of the pyroxylin before the latter assumes the solid form. By substituting aluminum powder for the bronze, it is claimed, silver leaf can be produced with equal facility.

"In the United States, this patent has passed through the experimental stage and considerable quantities of this imitation gold leaf, or 'Oriental Tissue' and 'Japanese Leaf,' as it is more often called, is prepared in the following manner: The formula stated above by the patentee has been found unduly expensive and may be replaced by amyl acetate 45 percent, refined fused oil 8 percent, and benzine (62°) 47 percent, the pyroxylin and bronzes being substantially as stated above. No readily water-soluble solvents or non-solvents must enter the formula on account of danger in rendering the film white, opaque and devoid of strength when the solution is floated on the surface of the water. A long vat of wood, from 50–75 ft. in length and about 2 ft. wide, is filled with water from 6–12 inches in depth. A hopper carrying the bronze and solvent mixture, and having a slit in the bottom which is adjustable, is filled with lacquer-bronze mixture, the diameter of the slit adjusted, and this hopper rolled over the surface of the water, but not touching, the sides of the vat acting as a track on which the hopper runs. By varying the diameter of the slit in the hopper and the speed of the movement over the surface of the water, the depth

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[1] Nitrocellulose Industry, **1**, 312 (1911).

of the film may be varied within wide limits. That gold bronze found most applicable is known in the trade as Dutch gold or 'blue elephant.' There is thus deposited on the surface of the water a gold film of some 50 ft. in length and of a width so that when trimmed it is 1 ft., and in this manner appears in commerce. The thickness is about the same as a sheet of ordinary writing paper. This imitation gold leaf is finding extensive use in the book-bindery trade in the place of real gold leaf for lettering titles."

Winkelblech[1] has proposed making use of the tendency of certain substances to go into the dineric interface in a method of analysis.

"If a solution of glue is shaken violently with benzine, the glue is precipitated. There is formed a sort of stiff emulsion of glue, benzine, and water, which separates from the water on standing, partly in consequence of entangled air. When the solution is rich in glue, a voluminous product is obtained in large lumps. If, however, a very dilute solution is taken, a number of bubbles of various sizes may be noticed resting for a considerable while on the surface of the water phase. When they break, there is left a permanent, whitish ring of very small bubbles adhering to the walls of the vessel. The further study of the phenomenon was carried out with pure gelatine.

"The following data will show that mere traces of gelatine can be made visible or precipitated in this way. A heavy precipitate was obtained when 10 cc of a solution containing 0.234 g gelatine per liter was shaken with benzine. Precipitates were also obtained when the gelatine solution was diluted tenfold, twentyfold and even fortyfold, provided 10 cc solution were taken for the test. At the highest dilution the concentration of the gelatine was 0.06 g per liter and there were consequently 0.06 mg in the 10 cc taken for the test. This seemed to be about the limit at which a precipitation could be detected definitely. The possibility of recog-

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[1] Zeit. angew. Chem., **19**, 1953 (1906).

nizing small amounts of substance is due, as stated, to the fact that these come out in the very voluminous form of very small bubbles. In order to get these last portions out, a very energetic shaking is necessary. In order to concentrate the precipitate in the smallest space, the containing vessel should not be wider than an ordinary test-tube, at any rate at the surface between the benzine and the water. For handling small amounts of liquid, a 50 cc measuring flask with a relatively wide neck was used. After shaking, the flask was inverted and the two liquid phases collected in the neck. Later a small stand glass with a glass stopper was substituted for this.

"By means of this limiting figure for the amount of gelatine which can be detected, gelatine determinations were made fairly successfully with solutions prepared by others. It was only necessary to dilute samples of the solution until the same slight amount of precipitation occurred and no precipitation occurred on further dilution. Gelatine behaves in slightly acid or slightly alkaline solutions much as it does in pure water, though the volume of the precipitate seems somewhat less in the first case and somewhat greater in the second. Such small amounts of gelatine cannot be detected, however, in presence of larger amounts of acids, alkalies or salts. Larger amounts of solution might be taken, however. If a dilute, acidified solution of gelatine be boiled for a short time, it gives no precipitate when shaken with benzine.[1]

"Some other colloids behave like the glue colloid (glutin) and can be shaken out of their solutions. Other hydrocarbons are also effective so that the phenomenon seems to be a general one. Precipitation was obtained with solutions of albumin, water-soluble starch, and soap, as well as with rosin dissolved in very dilute caustic soda. The colloids grouped as mucin can be precipitated from urine and the pro-

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[1] In making up the solutions to be diluted, heating was avoided so far as possible. The gelatine was allowed to swell in cold water and was then dissolved by shaking with warm water.

teins from beer. It is worth noting that tannin can be precipitated but not gallic acid.

"Among organic substances slight precipitates were obtained from a dilute solution of sulphur in caustic soda and from a dilute solution of water glass. With water glass the precipitate rapidly became granular and dropped into the water phase. Acidified water-glass solutions gave clear layers.[1] A sample of concentrated ammonia solution, when diluted, gave a test for silica.

"The hydrocarbons which can be used are: kerosene, liquid paraffin, benzene, chloroform, and carbon bisulphide [in addition to benzine]. The result varies somewhat from case to case. With the hydrocarbons which are lighter than water, the precipitate floats on the water; with the denser hydrocarbons the precipitate is below the water layer. The emulsions which form seem to have very nearly the same density as the organic liquid used. It is not possible to get the precipitation with all liquids which are non-miscible or slightly miscible with water. Experiments with ether were entirely unsuccessful.

"If one asks why these things happen, the most plausible explanation seems to be the following, which recognizes the surface tension as the important factor. The violent shaking breaks the second liquid into a large number of drops, which evidently have the power of condensing on their surfaces the tiny, wet, colloidal particles. The particles then coalesce to larger complexes and there is formed a rigid emulsion which also contains enclosed water.

"When the gelatine concentration was nearly down to the minimum recognizable, a few large, completely transparent and fairly permanent bubbles (drops) appeared, which were filled with hydrocarbon except for a tiny air bubble. From this it follows that the wet colloidal particles are able in some way to form surface films. This seems to be a special

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[1] Flemming found that acidified water-glass solutions gelatinize much less rapidly than alkaline ones, Zeit. phys. Chem., **41**, 427 (1902).

case of the familiar phenomenon of the foaming of many liquids when stirred, a phenomenon which also always depends on the separation of small amounts of colloids and perhaps of traces of fatty substances.

"When a colloidal solution contains suspended impurities these are carried out more or less completely with the colloidal material, so one can use this method as a means of purifying certain waters though not as a means of purifying colloids.

"As a complement to the action of hydrocarbons on aqueous colloidal solutions it was found that fats dissolved in hydrocarbons or similar liquids can be precipitated in the surface film by shaking with water. The fats therefore form colloidal solutions. Precipitations were obtained with butter, olive oil, lanolin, and vaseline. It was also found that the emulsions of heavy hydrocarbons or carbon bisulphide with the fats of low specific gravity also accumulate below the water layer, only a small portion being carried to the surface by adhering air bubbles. When water is used for shaking out, the precipitation is very slight. With a slightly alkaline solution such as dilute lime water, heavy voluminous precipitates were obtained while a transparent layer of fat is obtained when a slightly acid solution is used. With concentrated alkali or acid solutions, viscous emulsions are obtained which hold fast considerable amounts of solution."

These results of Winkelblech are exactly what one would expect for substances which pass into the interface. The failure to obtain results with ether is undoubtedly not a general phenomenon. A glance at Table I will show that ether was found by Hofmann to be one of the least effective liquids for carrying substances into the interface; Winkelblech happened to use substances which stayed in the water phase. Reinders shook out colloidal gold with ether; but also found that very small amounts of gum arabic prevented the gold going into the interface. If one is to use Winkelblech's method to detect small amounts of gelatine, it is essential to test the pure reagents. We tried to repeat Winkelblech's experiments once, using benzene as the organic liquid. There

seemed to be no limit to the sensitiveness of the reaction until we found that the benzene alone gave a faint film when shaken with water. This was apparently due to a slight trace of rosin or similar matter dissolved in the benzene. Carefully purified benzene did not give any film. This test can be used as a means of detecting small amounts of such material in benzene.

Winkelblech's results seem not to have appeared normal or natural to other people. At a meeting of the Bunsen Society,[1] Jordis said that Winkelblech had made the very remarkable observation that all so-called colloids can be precipitated if one shakes an aqueous colloidal solution with hydrocarbons such as benzine, kerosene, etc. He wondered whether any of the members had made any experiments, for he himself could think of no explanation for the phenomenon. Biltz replied that he could confirm and amplify Winkelblech's observations. "Independently of Winkelblech, a most interesting and, at first, inexplicable observation had been made in the technical research laboratory at Mansfield during the titration of copper solutions with alkali sulphides, namely that the colloidal solution of copper sulphide clears up instantaneously if shaken with chloroform or any similar liquid. The finely divided copper sulphide coagulates and precipitates, leaving a clear solution suitable for titration.[2] I have also made a number of experiments with other colloidal solutions. Gold and platinum, for instance, can be precipitated wonderfully well, and apparently all liquids which are not miscible with water act equally well. Winkelblech has patented the use of such organic liquids as kerosene for clearing sewage. We have made tests to see how much of the putrefiable matter in the sewage can be precipitated by shaking with an organic solvent. About 20 percent was thus precipitated."

Luther remarked that "not only colloids but suspensions

[1] Zeit. Elektrochemie, **13**, 540 (1907).
[2] Koch: Zeit. anal. Chem., **46**, 31 (1907).

of microscopic particles can be made to settle wonderfully
when the water is shaken with a second non-miscible liquid.
The earliest experiments on the subject, so far as I know,
are those of the physiologist, Prof. Hofmann (now in Inns-
bruck). The experiments were made in Leipzig and were
published in abstract in Pflüger's Archiv. The whole paper
has not been published. The phenomenon can be shown
admirably by shaking an aqueous suspension of lead oxide
with toluene or chloroform."

It is not clear whether Luther means that the suspended
matter coagulates and settles, or whether it passes into the
interface. The two phenomena should be kept quite dis-
tinct.

The application of Winkelblech's method to the purifica-
tion of sewage has been studied by Biltz and Kröhnke.[1]
"Several years ago we[2] showed that a large portion of the oxid-
izable material in city sewage is in a colloidal state. The
putrefiable material which was isolated by dialyzing acted
in so many ways like colloidal material that there could be
no doubt about its colloidal nature. This seems for the first
time to give an answer to the question as to the way in which
the purifying agents really act in the technical purification
of water. Although Dunbar and his co-workers[3] have ex-
pressed the opinion that the removal of putrefiable substances
by the purifying agents was analogous to dyeing and there-
fore an adsorption phenomenon, there was no explanation
for the degree and specific nature of the purification. The
development of colloid chemistry has shown that the power
of combining by adsorption is one of the most general charac-
teristics of colloids. Once the colloidal nature of the sewage
material was established, our general knowledge in regard to
colloids could be applied to this special case and it could be
brought into line . . . .

[1] Zeit. angew. Chem., **20**, 883 (1907).

[2] Ber. deutsch. chem. Ges. Berlin, **37**, 1745 (1904).

[3] Cf. Dunbar: Vierteljahrschrift für gerichtliche Medizin und öffentliches
Sanitatswesen (3) **19**, Suppl. Bd., 178 (1900).

"Winkelblech[1] and Koch[2] have recently called attention to an adsorption phenomenon which seems to be peculiar to dissolved colloids. If one shakes an aqueous colloidal solution with an organic solvent which is not miscible with water, the finely divided drops of the organic liquid carry down with them the colloidal particles in the solution and form a foam film separated sharply from the water layer. This observation has been made successful use of technically in copper analysis to clear up copper hydrosols (Koch); independently of him Winkelblech has recommended purifying turbid water in the same way. The following experiments show that some purification is obtained when sewage is shaken with an organic liquid.[3]

"Spandau sewage was shaken for three hours on a shaking machine in 100 cc lots together with 5 cc organic liquid and 1 cc 30 percent H_2SO_4; it was then allowed to stand for an hour and a half. In order to determine the degree of purification, acidified samples of sewage were shaken by themselves and 100 cc lots of pure water were shaken with the organic liquids. The content of oxidizable material after shaking was the difference between the permanganate consumption of the sewage samples and the pure water samples, for the water required perceptible amounts of permanganate after being saturated with aliphatic solvents. In order to remove any drops of organic liquid the pipetted samples were filtered through a dry filter. The sewage samples seemed perfectly clear after being shaken and filtered. A film like an oil emulsion had formed out of organic solvent and the adsorbed albuminoids.

"Since the electrical charge on a colloid is known to be of importance in determining the precipitation of colloids, organic liquids were used having very different dielectric constants; but there was no apparent connection with this and there is really no evidence that there is any difference of

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[1] Zeit. angew. Chem., **19**, 1953 (1906).
[2] Zeit. anal. Chem., **46**, 31 (1906).
[3] Cf. Winkelblech: D. R. P. 180493 (1907).

behavior between the organic liquids because the value for carbon bisulphide is uncertain, owing to the high permanganate consumption for water saturated with this liquid."

ADSORPTION OF UNDIALYZED SEWAGE BY ORGANIC LIQUIDS

	Oxidizable matter in mg $KMnO_4$ per liter		Percentage adsorbed
	not adsorbed	adsorbed	
Benzene	165	60	27
Chloroform	174	51	23
Nitrobenzene	156	69	31
Kerosene	147	78	35

ADSORPTION OF DIALYZED SEWAGE BY ORGANIC SOLVENTS

	Oxidizable matter in mg $KMnO_4$ per liter		Percentage adsorbed
	not adsorbed	adsorbed	
Benzene	108	27	20
Carbon bisulphide	72	63	47
Nitrobenzene	98	37	27
Kerosene	89	46	34

Biltz considered the phenomenon as a straight adsorption and therefore believed that the adsorption isotherm should apply. For this reason, he did not try to find out why the purification was not more complete. Briggs[1] has shown recently that the adsorption varies with the surface exposed, as of course it should do. If the surface of the organic liquid were made sufficiently large, there seems to be no reason why the extraction should not be increased very much over the figures obtained by Biltz. If the precipitated material could be obtained in a coagulated form which was not readily peptonized by water there is no apparent reason why there should not be practically complete precipitation. I therefore

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[1] Jour. Phys. Chem., **19**, 210 (1915).

look upon Biltz's paper as a valuable bit of preliminary work but as being far from the last word on the subject. It seems to me that there is here a very important field for research.

Robertson[1] has described some experiments which emphasize the emulsion formation. "If one shakes solutions of caseine, gelatine, or protein with chloroform, fine particles or drops are formed which, when numerous, form a milky layer at the bottom of the vessel; by transmitted light, they appear completely clear. These drops are extraordinarily stable and do not coalesce no matter how long they are left in contact. They can be washed repeatedly with water until all traces of protein are removed from the supernatant liquid but they remain completely stable and separated one from the other. They can even be shaken with chloroform or with $N/10$ potassium hydroxide without loss of stability. If the drops are heated under a water layer to about the boiling-point of chloroform, they burst, coalesce, and form a continuous layer of chloroform. When treated with alcohol, they dissolve at once and leave a fine filmy precipitate of protein floating on the water. If we shake chloroform with twice its volume of a one percent protamin sulphate solution, allow it to stand, separate the chloroform drops by decantation, wash them repeatedly with water, add about an equal volume of water, and stir cautiously, the drops swell and burst; and we see the fine membranes which surrounded them sink through the aqueous alcohol. If we add several volumes of alcohol, the drops of chloroform disappear completely and what we now obtain is a clear, homogeneous solution in which numberless very thin membranes can be seen floating."

From the experiments that have been described we see that wherever a suspended substance is wetted simultaneously by two liquids it will pass into the dineric interface and will therefore tend to form an emulsion. If the particles of the suspended substance are incapable of coalescing to form a coherent film, the emulsion will be very short-lived. An admira-

[1] Die physikalische Chemie der Proteine, 308 (1912).

ble illustration of this is to be found with copper, kerosene, and water. On shaking the three substances together we get a copper-plated emulsion which soon breaks down because the copper powder does not form a coherent film. We then have two liquid layers with the copper powder adhering to the liquid interface. By adding gum or something which would cause the copper particles to stick together, it would probably be possible to make a permanent emulsion if that were worth while. I don't myself know what I could do with a permanent copper-plated emulsion even if I had one, so I have not tried to get one. The surprising thing to me has always been that the copper emulsion did not break down much more rapidly than it actually does. The copper powder gives a surprisingly good imitation of a coherent film. This seems to be a general phenomenon for Metcalf[1] says that "apparently any solid, which is distributed uniformly over a liquid surface, has the power of forming a solid film. When a small amount of talc powder or lycopodium is scattered uniformly over a liquid surface, there is formed a solid film showing distinct signs of elasticity and strength."

The other extreme is represented very well by sodium oleate, kerosene, and water. By shaking these three substances vigorously, we get a fairly permanent emulsion of kerosene in water. This is because the sodium oleate forms a fairly permanent, coherent film under ordinary conditions. With ordinary soap (and probably also with sodium oleate), kerosene, and water, one can revert to the instable form of emulsion by adding sodium chloride or sodium hydroxide. These substances tend to precipitate soap from aqueous solutions; in other words, they tend to make soap cone down less hydrous. A film of less hydrous soap is brittle and lacks elasticity. For this reason it is quite impossible to get a good soap emulsion if the water contains considerable quantities of sodium chloride or caustic soda.

Briggs[2] has shown that more soap is adsorbed by a given

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[1] Zeit. phys. Chem., **52**, 45 (1905).
[2] Jour. Phys. Chem., **19**, 210 (1915).

amount of benzene the greater the surface of the benzene, in other words, the smaller the drops. It seems to be very probable that the soap film is less hydrous the more surface a given amount of soap is required to cover. While there is no direct experimental proof of this as yet, it is made very plausible by the general behavior of emulsions. Emulsions with an excess of liquid to be emulsified seem usually to be less stable than those with a marked excess of the emulsifying liquid. This hypothesis is of assistance in accounting for Winkelblech's experiments. When he shook a dilute solution of gelatine with benzene for instance, the gelatine tended to emulsify the benzene; but the benzene was present in relatively large amounts and consequently the gelatine film round the drops contained relatively little water and was correspondingly brittle. When the drops coalesced again, the gelatine was left in a precipitated or coagulated form not readily peptonized by water. Winkelblech's experiments therefore differ from those of a man making an emulsion in that Winkelblech worked, unconsciously of course, under conditions which tend to make the film form as a non-coherent mass not readily peptonized by either liquid. It does not follow that the emulsion always cracks completely. In Robertson's experiments, the drops apparently remained emulsified. The principle underlying Winkelblech's work is the partial emulsification of one liquid by a small amount of an emulsifying agent present in the other liquid. If the emulsion is moderately stable, we see it as a cream. If the emulsion is instable we may still see the membranes which had formed round the drops, provided these films are not peptonized too rapidly by either of the liquids.

There ought to be a special term for substances which pass into the interface. It is not satisfactory to call them emulsifying agents, because that term should be kept for substances which really form moderately stable emulsions and I should hardly care to call copper powder, for instance, an emulsifying agent for kerosene and water though this might be done. I suggest, therefore, that the general term be "interfacial," a

substance being interfacial for two liquids when its finely
divided particles pass into the dineric interface of those two
liquids.   A substance which was held firmly in the interface
would be strongly interfacial.

Winkelblech's method is then a test for interfacial sub-
stances.   As such it seems to me capable of wider applica-
tion than has yet been made.   It seems to me that it may
prove a valuable method for detecting colloidal solutions.
Hydrous ferric oxide is strongly interfacial for benzene and
water and we can show the presence of hydrous ferric oxide
in a ferric chloride solution by shaking with benzene.[1]   It
seems to me that the method might be used for research work,
to show the existence or non-existence of colloidal oxides when
hydrous chromium, aluminum, or zinc oxide is apparently
dissolved in an excess of alkali.   Deductions from the data
must be made cautiously, because the second liquid may in-
crease perceptibly a hydrolysis which is otherwise negligible;
but a correction can doubtless be made for this in any given
case.   I hope to be in a position before long to report on some
such experiments as these.

The general results of this paper are as follows:

1. Many organic liquids adsorb hydroxyl ions from an
aqueous alkaline solution.

2. Although it is theoretically possible that oils may
make supersaturated solutions of sodium sulphate crystallize,
it seems probable that Tomlinson's work along this line is
inaccurate.

3. When shaken with water and a non-miscible organic
liquid, solid particles tend to go into the water phase if they
adsorb water to the practical exclusion of the other liquid;
they tend to go into the other liquid phase if they adsorb the
organic liquid to the practical exclusion of the water; and they
tend to pass into the dineric interface in case they adsorb
the two liquids simultaneously.

4. The simultaneous adsorption of two liquids probably

[1] Briggs: Jour. Phys. Chem., **17,** 296 (1913).

produces a homogeneous liquid phase at the surface of the adsorbing particle.

5. A substance which passes into the dineric interface is called interfacial for those two liquids.

6. An interfacial substance can be shaken more or less completely out of its suspension in one liquid by adding a second liquid for which the substance is interfacial.

7. When an interfacial substance can form a coherent, and fairly stable, film we get a fairly stable emulsion.

8. Winkelblech's method of shaking out colloids is a method for detecting interfacial substances. It is effective in case a fairly stable emulsion is formed or if the interfacial substance is left, when the drops coalesce, in a form not readily peptonized by either liquid.

9. It seems probable that an interfacial substance comes out of the aqueous phase less hydrous, the greater the surface of the other liquid phase.

10. It seems probable that Briggs is right in suggesting that Winkelblech's method can be used as a method of research to detect peptonized substances in presence of dissolved substances.

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