The lyotropic series

https://hdl.handle.net/1874/294318

THE LYOTROPIC SERIES

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PROEFSCHRIFT TER VERKRIJGING VAN DEN GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKS-UNIVERSITEIT TE UTRECHT OP GEZAG VAN DEN RECTOR MAGNIFICUS, Dr. H. Th. OBBINK, HOOGLEERAAR IN DE FACULTEIT DER GODGELEERDHEID, VOLGENS HET BESLUIT VAN DEN SENAAT DER UNIVERSITEIT TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP MAANDAG 1 JULI 1929, DES NAMIDDAGS TE 3 UUR

DOOR

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GEBOREN TE CHATHAM (ENGELAND)

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TO
MARGARET
HELEN
ROBINSON

The researches here described were carried out in the laboratory of Professor H. R. Kruyt to whom I shall always feel greatly indebted. I would like to thank him for having taken so much interest in the work. His extraordinarily stimulating personality was at all times a source of inspiration and I shall look back upon the time spent in his laboratory as the most valuable period of my scientific training.

Further I wish to take the opportunity of saying how much I appreciated the friendliness shown to me by all those in the van 't Hoff laboratory with whom I came in contact, this having contributed very greatly to the pleasantness of my stay in Holland.

I wish to thank Professor Ernst Cohen (Director of the van 't Hoff Laboratory) for his unfailung kindness and courtesy to me while a guest in that laboratory. I also wish to thank Dr. A. L. T. Moesveld, conservator of the laboratory, for his trouble in helping me to obtain apparatus and for his kindness on many occasions. Also Dr. H. J. C. Tendeloo and Dr. P. C. van der Willigen, formerly assistants to Professor Kruyt, whose friendship will be amongst my most pleasant memories of Utrecht.

I particularly wish to thank Professor I. M. Kolthoff whose suggestions and advice lead to the successful development of the methods of determining the aromatic nitro compounds and the p-phenylenediamine used in the solubility experiments.

My thanks are also due to Mr. Emil Hatschek for his kindness in allowing me to complete the experiments on gelatin in his laboratory at the Sir John Cass Technical Institute (London) after I had returned from Holland.

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INTRODUCTION

The word *lyotropic* was introduced by H. Freundlich [1] to describe those properties of solutions which have their origin in the interaction of the molecules of the solute and the molecules of the solvent. This interaction of the two kinds of molecules brings about a change in the internal pressure of the solution and consequently we may describe all those properties such as surface tension, compressibility, solubility, etc. as lyotropic properties, and the influence that a dissolved substance has upon these properties as a lyotropic influence.

It will be seen that none of these properties can be explained by the van 't Hoff theory of dilute solutions, the reason being that in the van 't Hoff theory the possibility of the interaction between solute and solvent is neglected.

It will be the aim of this thesis to deal with several of these lyotropic properties and the influence of strong electrolytes on them in both true and colloidal solutions.

IONIC SERIES

If we investigate the influence of, say, lithium, sodium, and potassium chlorides on the lyotropic properties of a liquid, we will find that this differs for each salt, and, consequently, it is possible to arrange the cations in a series. Similarly if we take salts having the same cation and different anions it will be possible to obtain an anion series.

The effect of the cation and anion are additive. In general it will be found that these series are the same as the series for the hydration of the ions or these series reversed, i. e.

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$$

for the cations, and

$$\mathrm{SO_4} > \mathrm{Cl} > \mathrm{Br} > \mathrm{NO_3} > \mathrm{I} > \mathrm{CNS}$$

for the anions.

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[1] H. Freundlich, Kapillarchemie, 1st Ed. 1909 p. 56.

As will be mentioned later, secondary influences will sometimes bring about irregularities, and one or two of the ions will be found out of place, so that we may find Na $>$ Li $>$ K or Cl $>$ NO_3 $>$ Br, but in general, where we are dealing with the influence of these ions on a lyotropic property of a true solution or a colloidal solution, these two series will appear. We will hereafter refer to them as the lyotropic series. If we find the influence of ions at the extreme ends of the series almost the same, we may consider the lyotropic influence to be small; if, on the other hand, their influence differs considerably and we find a "spreading" of the series, we may consider the lyotropic influence to be large.

The classical example of the occurrence of such a series is in Hofmeister's [1] researches on the salting out of a sol of white of egg. He determined the lower limit of concentration for various neutral salts at which the sol immediately became turbid, and obtained the anion series: Citrate $>$ Tartrate $>$ Sulphate $>$ Acetate $>$ Chloride $>$ Nitrate $>$ Chlorate. Hofmeister showed that a similar series existed for the influence of salts on other properties of proteins [2]. The lyotropic series is therefore often referred to as the Hofmeister series.

Jacques Loeb in his work on proteins set out to show that proteins are molecularly disperse systems and follow stoichiometric laws. He claimed that the hydrogen ion concentration was the all-important factor in determining the condition of these colloidal systems and denied the existence of the lyotropic series [3]. He claimed to have shown that the Hofmeister series has no real existence if one takes into consideration the influence of the added salt on the hydrogen ion concentration, in which case the series could be replaced by a simple valency rule, according to which only the valency and sign of charge of an ion influence the colloidal behaviour of a protein, the other properties of the ion having no influence as long as no constitutional change in the protein molecule occurs.

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[1] Hofmeister, Arch. f. experim. Pathol. und Pharmakol. *24* 247 (1888) and Lewith, ibid *24* 1 (1888).

[2] Arch. exp. Path. u. Pharm. *25* 1 (1888—89), *27* 395 (1890), *28* 210 (1891).

[3] Proteins & the Theory of Colloidal Behaviour (1922) p. 14.

Without denying the importance of this valency rule and of taking precautions that the hydrogen ion concentration remains unchanged, we will, in the following chapters, describe experiments in which the lyotropic series is very marked in spite of the fact that neutral salts which gave only monovalent ions were used throughout. It will also be seen that the hydrogen ion plays a part differing only quantitatively and not qualitatively from the other ions.

As a matter of fact the lyotropic series can be found more than once amongst the results of Loeb's own researches. Thus in a chapter which he contributed to Bogue's "Theory and Application of Colloidal Behaviour"[1] are given the results of experiments on the influence of salts on the osmotic pressure of a gelatin sol of a constant P_H of 3·8. The results are unfortunately only given graphically and no numerical values are obtainable, but from the graph we can see that the salts arrange themselves unmistakably in the lyotropic series. Thus we have in order of osmotic pressure:

$$Cl > Br > NO_3 > I > CNS$$

Loeb dismisses these facts with the remark that "the variations in the effects of the six salts with monovalent anion are chance variations".

The researches about to be described were undertaken primarily to throw some light on the lyotropic influences of salts in colloidal solutions. Kruyt and de Jong[2] have shown that the stability of emulsoids depends on two factors, the charge of the particle and the hydration (solvation) of the particle. As might be expected, the existence of this hydration, that is to say an equilibrium between the "bound" and "unbound" molecules of the solvent, means that the presence of ions, more or less hydrated, in the sol will make itself felt by the exertion of lyotropic influences. Before studying these phenomena however we found it advisable to study the somewhat simpler cases of lyotropic influence in true solution.

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[1] Bogue; „Theory and Application of Colloidal Behaviour". (McGraw-Hill, 1924) P. 65.

[2] H. R. Kruyt and H. G. Bungenberg de Jong, Zeit. phys. Chem. *100* 250 (1922).

As will be shown, the lyotropic series appears in such phenomena as the influence of salts on surface tension, viscosity, the maximum density of water, the solubility of non-electrolytes, the rate of inversion of cane sugar, etc. We will however first describe some experiments on yet another phenomenon, namely the influences of salts in lowering the critical solution temperature of phenol-water mixtures.

PART I

LYOTROPIC INFLUENCES IN TRUE SOLUTIONS

I — THE INFLUENCE OF SALTS ON THE CRITICAL SOLUTION TEMPERATURE OF PHENOL-WATER MIXTURES

EXPERIMENTAL

Kahlbaum's ("zur Analyse") phenol was further purified by distillation. This gave a product which did not turn pink on exposure to the light and which had a melting point of 41° C.

The experiments were made with mixtures containing 36·5 % Phenol and 63·5 % water or salt solution. The mixture of 36·5 % Phenol and 63·5 % water gives the maximum critical solution temperature (C. S. T.) for phenol water mixtures.

Glass tubes 1·3 cm. in diameter and 12·0 cm. in length, fitted with ground glass stoppers were used. About 2 or 3 grams of phenol was placed in the tube and weighed accurately. The corresponding quantity of salt solution was then added from a 5 cc. micro-burette graduated in hundredths of a cubic centimeter so that the mixture contained 36·5 % Phenol and 63·5 % water. The tubes were then placed in a copper stand in a four litre beaker filled with water, so arranged that the tubes were all equidistant from the thermometer in the centre of the beaker. The thermometer was a standard instrument graduated in tenths of a degree. The temperature was then raised sufficiently to bring all the mixtures above their critical solution temperature, whereupon the tubes were shaken so as to assure a homogeneous mixture. The flame was now removed and the temperature allowed to fall. The rate of cooling was found to be sufficiently constant and was less than 1° C per minute.

As the mixture cools a slight opalescence first appears which increases until the contents of the tube become opaque, the latter part of this change taking place most rapidly. It was found very convenient to take the temperature when the thermometer behind the tube could just not be seen by looking through the contents of the tube. In this way results reproducible within 0.2° C. could easily be obtained.

All determinations were made in duplicate and repeated (i. e. two tubes were filled and readings taken together as described; the temperature was then raised and again allowed to fall, so that a second reading was obtained.

When weighing the phenol it was exposed to the air as little as possible. Although it is very hygroscopic the error due to this seems to have been small as seen from the good agreement between duplicate determinations. Timmermans also found this error small [1].

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sagt 68°.

The phenol water mixture gave a C. S. T. of 66·5° C. Determinations by other workers vary from 65° C. to 70° C. (Schreinemakers and Alexejew 67° C.; Friedländer 66° C.).

For our purpose however it was more important to obtain results which were reproducible and comparable to one another than to aim at absolute values.

RESULTS

The results for a number of strong electrolytes are shown in Table I. It will be seen that for the chlorides there is for the increase in the C. S. T. a cation series:

$$\text{Li} > \text{Na} > \text{K} > \text{Rb}.$$

and for the potassiun salts an anion series:

$$\tfrac{1}{2}\text{SO}_4 > \text{Cl} > \text{Br} > \text{NO}_3,\ \text{I} > \text{CNS}.$$

Thus the increase in the C. S. T. is greatest for the most hydrated ions.

The results for HCl and HBr are of interest as showing that very large changes in the P_H of the mixtures do not bring about any appreciable change in the raising of the C. S. T. Thus the influence of O. 1 N HCl is of the same magnitude as 0.1N KC1, and, further, the addition 0.001 N HCl to 0.1 N KCl does not appreciablely change its influence on the C. S. T. This of course would be impossible if the occurrence of lyotropic series depended on the salts

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[1] Zeit. phys. Chem. *58* 129 (1907).

TABLE 1

SOLUTION	Determinations of C. S. T.		Mean value of C. S. T.	Increase in C. S. T.
0.1M Li Cl.	(77·9, 77·9)	(77·8, 77·8)	77.9°	11·4°
„ Na Cl.	(73·8, 73·8)	(73·7, 73·7)	73·8	7.3
„ K Cl.	(72·4, 72·6)	(72·4, 72·6)	72·5	6·0
„ Rb Cl.	(72·4, 72·3)	(72·3, 72·3)	72·3	5.8
H_2O	(66·5, 66·6)	(66·5, 66·5)	66·5	—
0·05M K_2SO_4	(75·5, 75·6)	(75·5, 75·4)	75·5	9·0
0·1M K Cl.	(72·5, 72·5)	(72·5, 72·5)	72·5	6·0
„ KBr.	(72·2, 72·2)	(72·2, 72·2)	72·2	5.7
„ $KClO_3$	(70·6, 70·6)	(70·6, 70·6)	70·5	4·1
„ KNO_3	)70·6, 70·4)	(70·4, 70·5)	70·5	4·0
„ KI	(70·4, 70·6)	(70·4, 70·6)	70·5	4·0
„ KCNS	(67·7, 67·8)	(68·0, 68·0)	67·9	1·4
0·05M KCl.	(70·2, 70·2)	(70·2, 70·2)	70·2	3·7
0·10M KCl.	(72·5, 72·5)	(72·5) 72·5,	72·5	6·0
0.15M KCl.	(75·0, 75·1)	(75·0, 75·1)	75·1	8·6
0·20M KCl.	(77·3, 77·3)	(77·0, 77·0)	77·2	10·7
0.1 MKCl. + 0.001N HCl.	(72·8, 72·8)	(72·8, 72·8)	72.8	6·3
0·05N HCl.	(69·4, 69·5)	(69·4, 69·5)	69·5	3·0
0·10N HCl.	(71·2, 71·3)	(71·0, 71·1)	71·2	4·7
0·15N HCl.	(73·3, 73·3)	(73·3, 73·3)	73·3	6·8
0·20N HCl.	(74·6, 74·8)	(74·6, 74·8)	74.7	8·2
0.1M HBr.	(71.1, 71·0)	(71·0, 71·0)	71·0	4·5
0.05N H_2SO_4	(69·3, 69·3)	(69·2, 69·2)	69·3	2·8
0.10N H_2SO_4	(71·5, 71·5)	(71·4, 71·5)	71·5	5·0
0.20N H_2SO_4	(74·4, 74·6)	(74·4, 74·6)	74·5	8·0
0.05M K_2SO_4	(75·5, 75·6)	(75·5, 75·4)	75.5	9·0
0.10M K_2SO_4	(81·4, 81·4)	(81·5, 81·3)	81·4	14·9
0.10N NaOH.	(46.5, 46.5)	(46.5, 46.5)	46.5	—20.0

(The bracketed figures represent two determinations on the same tube).

altering the P_H of the solutions as suggested by Loeb [1]. The marked lowering of the C. S. T. in the case of 0.1 NaOH is in agreement with the findings of other investigators, that substances which are soluble in both components (i. e. phenol as well as water) lower the critical solution temperature. It is therefore not due to the lyotropic but the chemical properties of the NaOH.

These results are in close agreement with those obtained by Duckett and Paterson [2] in a paper published just after our results were completed. They found for the cation series.

$$Na > K$$

and for the anion.

$$\tfrac{1}{2}SO_4 > Cl > Br > I$$

In a later paper Carrington, Hickson & Paterson [3] found that for both chlorides and sulphates lithium was not in its usual place, the series being

$$Na > Li > K > NH_4 > H.$$

This is not in accordance with our results. It is interesting to notice that they found the lithium ion in its usual place (i.e. before sodium) in some similar experiments on the influence of salts on the C. S. T. of the system water-butyric acid. (See table 1, page 8).

THE HYDRATION OF IONS

Before attempting to explain the influence of the salts on the critical solution temperature, we must first consider the hydration of the ions involved.

It is generally assumed that many, if not all, ions are more or less hydrated. This conclusion has been forced upon the various investigators by a large number of phenomena and many attempts have been made to obtain numerical values. Generally the results are calculated so as to give the hydration as so many molecules of water to the ion. Such results have been obtained, for instance, from investigations concerning the mobility of different ions. Thus if we calculate from the mobility of the ion the apparent radius which must be assumed to make the mobility correspond with Stoke's

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[1] Proteins and the Theory of Colloidal Behaviour p. 14 (1922).

[2] Ducket & Paterson, J. Phys. Chem. *29* 295 (1925).

[3] Carrington, Hickson & Paterson, J. Chem. Soc. *127* 2544 (1925).

formula, we find this radius to be greater than the "atomic" radius of the ion. Assuming this difference to be due to a "shell" of water molecules it is possible to obtain figures which represent the number of water molecules in the "shell" of each ion. In this way Remy[1] obtained the following figures:

TABLE 2

Hydration of the Alkali Cations

Ion.	Molecules per ion.
Li	< 120
Na	< 66
NH_4	17
K	16
Rb	14
Cs	13

Remy concluded that the hydrogen ion was not hydrated, a conclusion which may certainly be considered erroneous. Other values for the hydration of the ions have been deduced by other workers from the mobilities[2] in similar ways.

There is however, no agreement upon definite values for these hydration figures. Bjerrum[3] for example finds that the hydrogen ion binds eight molecules of water while the potassium ion binds none, the hydrogen ion being considered to resemble the lithium ion.

It seems to us that one reason for the discrepancies in these results is to be found in the misleading conception of the molecules of hydration of the different ions being a definite number of molecules associated with each ion. There is no evidence to justify the-

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[1] H. Remy, Zeit. f. Phys. Chem. *89* 467 (1915) and also Zeit. f. Electrochemie *29* 365 (1923).

[2] E. W. Washburn, Jahrb. Radioact. Electronik (1908) 493 and (1909) 69; E. W. Washburn and E. B. Millard, J. Am. Chem. Soc. *37* 694 (1915); Born, Zeit. f. Electrochemie *26* 401 (1920); Lorenz, Z. f. Electrochemie *29* 365 (1923)

[3] Bjerrum, Z. f. anorg. Chem. *109* 275 (1920); see also Schreiner, Ibid *121* 321 (1922).

idea that there is a definite shell of molecules of hydration immediately surrounding the ion, within which we have "bound" molecules and outside of which we have unbound molecules.

A molecule of water (or at any rate the simple molecule H_2O as distinct from the more complex nH_2O molecules) is an electrical dipole[1] with a considerable electrical moment. Consequently water molecules in the immediate neighbourhood of an ion will become orientated. If the ion is a cation their more negative ends will be pointed towards the ion. Thus there will be formed a layer of more or less firmly bound ions according to whether the ion is one largely or only slightly hydrated. Around this first layer of molecules other molecules will tend to orientate themselves, so forming a second layer (in the case of some ions) around which a third layer will tend to form (if the forces are strong enough) and so on, the water molecules being arranged round the ion in chains which may be very roughly compared to a chain of needles suspended from a magnet. We may conveniently represent a water molecule as an isosceles triangle the base of which is the more negative end of the molecule and the apex of which is the positive end. We then obtain the following scheme:

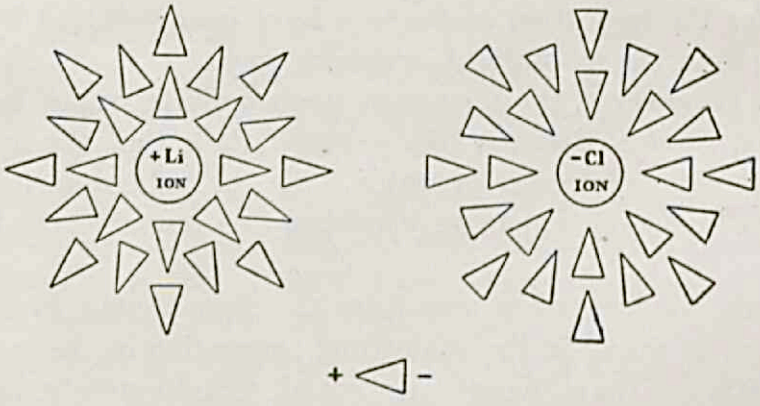

Fig. 1

(It should be noted that the representation of a molecule of water by a triangle does not presuppose a wedge-like form for the water molecule. The triangle is only used as being an easy way of representing diagrammatically the dipolar character of the molecule).

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[1] Debye, Physik. Zeit. *13* 97 (1912).

If then we consider a highly hydrated ion such as the lithium ion, we see that in its immediate neighbourhood there will be a number of completely orientated, firmly bound, molecules. Outside these there will be more molecules, not so firmly bound and perhaps not completely orientated. Still further from the ion there will be less bound, less orientated, molecules, and so on for some distance until we reach molecules that are only very slightly orientated and eventually molecules which do not feel the influence of the ion.

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It seems to us that only by some such scheme is it possible to imagine an ion with (say) 50 or 60 molecules of hydration. It is obvious that they cannot all be directly united to the ion, and yet it is very difficult to explain the results obtained from mobility experiments without assuming in some cases such a high *apparent* hydration.

But on the above assumption there will be no hard and fast line between bound and unbound molecules. It will be impossible, for example, to speak of the radius of the solvated ion. For this reason different methods of calculating the hydration will give quite different results for the number of "molecules of hydration".

We will therefore not concern ourselves with quantitative values for the hydration, but we may assume that for the cations the relative order of hydration is

$$Li > Na > K > Rb > Cs.$$

and that for the anions.

$$SO_4 > Cl > Br > NO_3 > I > CNS.$$

These series, as has already been said, are always to be found when we study the influence of the corresponding neutral salts on phenomena which involve an interaction between the molecules of a solute (or colloidal particle) and the molecules of a solvent. The position of the hydrogen ion in this series is more doubtful. Opinions on this differ so much that it is considered by some the most highly hydrated of the series and by others not to be hydrated at all. This later view is almost certainly wrong. As Freundlich [1] has pointed out, the hydrogen ion, which is simply a positive atomic nucleus whose diameter is about 10^{-13} cm, would have a velocity far greater than its actual velocity if it was truly not hydrated. An explanation from a quite different standpoint of its high mo-

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[1] Freundlich, Colloid and Capillary Chemistry, (Methuen 1922). p. 394.

bility was put forward by Ghosh[1] who suggested that $H^{\cdot}$ and OH' ions, being the ions which can originate from the solvent water, could be continually formed by alternate dissociation and recombination of the water molecules whereby a transference of charges would be brought about which would simulate an unusually large migration velocity.

The experiments with phenol, as will be pointed out in the next section, point to the hydration of the hydrogen ion being similar to that of the potassium ion.

EXPLANATION OF THE RAISING OF THE CRITICAL SOLUTION TEMPERATURE OF PHENOL-WATER MIXTURES

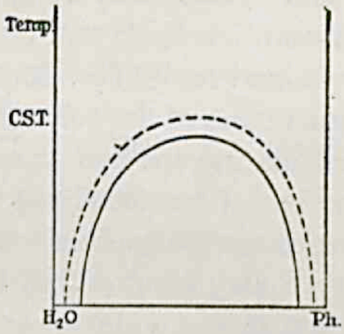

Fig. 2

The unbroken line in fig. 2 represents the temperature solubility curve for phenol in water. Below the critical solution temperature two phases are formed, the composition of these phases approaching one another more closely as the C.S.T. is approached. Eventually at the C.S.T. only one phase exists.

Let us now consider what happens if some KCl is dissolved in the phenol water mixture at a temperature below the C.S.T. The KCl will distribute itself between the two phases, the larger concentration being of course found in the water-rich phase. The ions of the KCl are, as we have already explained "hydrated" and consequently the orientation of the molecules of water will be different to what they were before the introduction of the salt. The water molecules which are orientated or bound by the potassium and

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[1] Ghosh, Journ. Chem. Soc. *113* 990 (1918).

chlorine ions will not be so free to take part in holding the phenol molecules in solution, and consequently the solubility of the phenol in this phase will be reduced and a certain amount of the phenol will be "salted out" into the phenol rich phase. At the same time owing to the affinity of the KCl for water, water will be drawn from the phenol-rich phase, the combined results of these two effects being to make the composition of the two phases more different. Similar results will also be brought about by the salt dissolved in the phenol-rich phase, but, owing to very low solubility, this will be of minor importance.

Consequently, since the composition of the two phases will be more different at all temperatures, the solubility curve will fall outside the solubility curve with no salt present, as shown by the dotted line in figure 2, and the critical solution temperature will be raised. (That the curve for an added salt does lie outside the curve for phenol-water has been shown by Timmermans) [1].

If instead of KCl we take an equal concentration of LiCl this "salting out" effect will be greater, since the lithium ions are more hydrated than the K ions, the composition of the two phases (at a temperature below the C.S.T.) will be made *more* different to one another than in the case of KCl and consequently the increase of the C.S.T. will be greater.

In this way we are able to explain all our results, namely, that the increase of the C.S.T. by a salt is an additive effect of the ions of the salt, and that the cations increase the C.S.T. in the following order:

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K}$$

and the anions in the order

$$\mathrm{SO_4} > \mathrm{Cl} > \mathrm{Br} > \mathrm{NO_3} > \mathrm{I} > \mathrm{CNS}$$

that is to say, the more hydrated the ion, the greater will be its influence in raising the C.S.T.

The effect of sodium hydroxide in lowering the C.S.T. is due to another cause. Here the electrolyte dissolves in the phenol to form sodium phenolate. The NaOH having dissolved in the phenol phase will attract water from the water-rich phase and make the two phases more alike so that the C.S.T. is lowered. In general, then,

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[1] J. Timmermans, Zeit. phys. Chem. *58* 129 (1907).

substances which dissolve in both phases tend to lower the C.S.T. This explanation is in accordance with the observation of Martin Fischer[1] that while the addition of NaOH caused the phenol-rich phase to swell in volume, the addition of neutral salts caused a contraction in the following order

$$KCNS < KNO_3 < KI < KClO_3 < KBr < KCl$$

and

$$KCl < NaCl$$

KCl and NaCl bringing about the greatest contraction, as we would expect from their greater hydration.

The results of these experiments can therefore be explained *qualitatively* on the assumption of the effect of the added salts being a simple "salting out" process, in which the ions of the salt reduce the solubility of the phenol according to their degree of hydration. In the following chapter we will show that in some cases the influence of salts in lowering the solubility of a non-electrolyte cannot be wholly explained on this assumption but that another influence must be postulated. It is therefore possible that in the case of the phenol-water mixture the second influence will also be present though not to an extent great enough to effect the results qualitatively.

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[1] M. Fischer „Theory of Lyophilic Colloids" 1st. Colloid Symposium (1923) p. 244.

II — THE INFLUENCE OF SALTS IN LOWERING THE SOLUBILITY OF NON-ELECTROLYTES

Although a great amount of solubility determinations of substances in the presence of salts have been made, there are very few data which give a complete cation and anion series for any one substance.

Rothmund[1] carried out solubility determinations of phenylthiourea in the presence of a number of electrolytes. He found the cation series to be (for nitrates):

$$Na > K > Li > Rb > Cs$$

where Na decreases the solubility most and Rb and Cs increase the solubility. The anion series was:

$$\tfrac{1}{2}SO_4 > Cl > Br > NO_3 > I.$$

His results are given on page 34.

A number of other results are summarised in a table given in Rothmund's book "Löslichkeit und Löslickkeitbeeinflussung". The substances whose solubilities in salt solutions are considered are however either gases or liquids. In the case of the gases there are not sufficient data to conclude that the lyotropic series hold for any particular gas and in the case of the liquid we are dealing with the rather different case of the separating of two liquid phases. In the older literature therefore phenylthiourea remains the one substance whose solubility has been studied in a sufficient number of electrolytes to show the lyotropic series.

Recently however a paper was published by Linderström-Lang[2] which contains some very interesting results. Linderström-Lang determined the solubility of hydroquinone and quinone respectively in various salt solutions. From his results it is apparent that the influence of the alkali chlorides upon the solubility of hydroquinone

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[1] Rothmund, Zeit. f. phys. Chem. *33* 401 (1900).

[2] Comptes-rendus du Lab. Carlsberg *15* No. 4 (1924).

varies greatly according to the particular cation — (thus lithium chloride reduces the solubility greatly and caesium chloride hardly at all) while for the solubility of quinone, the difference between the influences of the various alkali chlorides is much less marked. On the other hand he found that KI, KBr and KCl lower the solubility of hydroquinone to almost the same extent, while the solubility of quinone is lowered by KCl and actually raised by KBr. Here then we have a marked influence of the cations in the case of hydroquinone and, it would seem, a marked influence of the anions in the case of quinone. There is no evidence of a specific influence of either cation or anion in the other researches in solubility influence already referred to and so we considered these results of particular interest and worth extending, since with regard to the anions Linderström-Lang's results are, for our purposes, insufficient.

Linderström-Lang tries to connect the marked difference in the behaviour of quinone and hydroquinone with the fact that while quinone is an oxidising substance, hydroquinone is a reducing substance. He put forward a theory of "chemical polarisation" to explain the influence of the salts on these two substances, suggesting that an oxidising substance would not only have a tendency to attract electrons, but also a tendency (for the same reasons) to attract anions while a reducing substance would have a tendency to attract cations.

It seemed more probable to us that the real difference between the two substances lay in the basic and acid character of the quinone and hydroquinone respectively, especially as the results obtained by Linderström-Lang on the lowering of the solubility of succinic acid and of boric acid point to these two acids being of the hydroquinone type.

We therefore tried to find substances of the quinone type and turned our attention to basic substances. It was necessary to choose substances which were only slightly ionised, which had not too large a solubility and which could be estimated in the presence of the several salts used. We found it surprisingly difficult to find substances which would fulfil these conditions and eventually chose m- and p-nitro-aniline and p-phenylene diamine. We also used p-nitrophenol. Even for these substances it was necessary to develop special methods of analysis.

EXPERIMENTAL

About 30 ccs of the salt solution to be used were placed in a Jena glass bottle of about 45 ccs capacity (A, Fig. 3) fitted with a rubber stopper together with a suitable quantity of the substance whose solubility was be determined.The bottle was then shaken for about twenty hours in a thermostat the temperature of which did not vary by more than 0·02°C. The determinations were in all cases made in duplicate — the saturated solution being obtained from an unsaturated and also from a supersaturated solution. Agreement between two such determinations left no possible doubt that equilibrium had been reached. After shaking, the flask was removed from the shaker and placed in an upright position in the thermostat so that only its neck protruded from the water. The rubber stoppen was then removed and the glass T piece C attached to the neck by means of a piece of rubber tubing B. A glass tube D was passed through C as shown in the diagram and attached to C by rubber tubing. By blowing air through C the saturated solution could be blown out of the flask through D. The lower end of D contained a constriction, below which was placed a piece of cotton wool

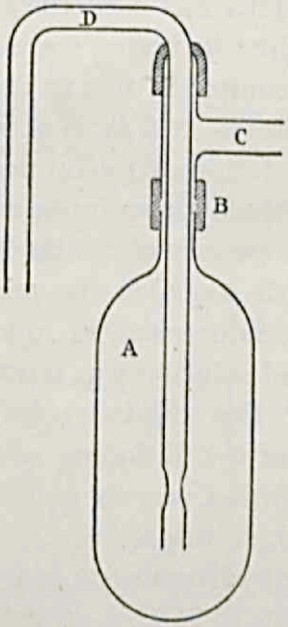

Fig. 3

through which the saturated solution was filtered. The first few cubic centimetres which passed through the filter were of course rejected, and then the remainder blown over into a clean dry flask. The quantity of the dissolved substance was then determined by a method of titration suitable for the particular substance.

HYDROQUINONE

The determinations of the solubility were carried out at 23·75°C so that Lindenström-Lang's result could be used for comparison. Owing to the instability of hydroquinone in neutral solution, a concentration of 0·01n HCl was used throughout. Thus, instead of determining the solubility in water we determined the solubility in 0·01n HCl and then compared this to the solubility in a solution which contained for example, 1·5 mols of KCl and 0·01n HCl. This was also the procedure followed by Lindenström-Lang.

The concentration of the hydroquinone was determined by adding a known quantity (an excess) of a standard iodine solution and titrating the excess with As_2O_3 in the presence of sodium bicarbonate. The actual procedure was as follows:

10ccs. of the saturated solution was made up with distilled water to 100 ccs. 10 ccs. of this diluted solution was then placed in a flask with 50 ccs. of 0·1 N iodine solution. 50 ccs. of a 5 % sodium bicarbonate solution was then added and the excess iodine titrated with 0·1n As_2O_3 solution.

The solubility of the hydroquinone in 0·01n HCl we found to be 0·6158 mols per litre at 23·75°C — a determination with a large excess of the hydroquinone in the solubility bottle and one with a small excess giving the same result which pointed to a high degree of purity. This compares to Linderström-Lang's figure 0.6180 mols per litre. Our results are summarised in Table 2 together with some of the results of Linderström-Lang, (the latter being marked with an asterisk). Owing to the different solubility for the hydroquinone found by him we have here only given his results expressed as a percentage of his figure for the solubility in water (third column). For LiCl and NaCl he only made determinations at 18°C, but as the percentage change in solubility does not vary much with temperature we may use these figures for comparison without introducing an (for our purposes) appreciable error. Also, as he employed different salt concentrations it was necessary to obtain the results given in the table by intrapolation.

QUINONE

The quinone was prepared from hydroquinone by oxidation with potassium dichromate and sulphuric acid. It was twice recrystallised from benzene and air dried. As in the case of hydroquinone, all the solubilities were made in 0·01n HCl.

The concentration of the saturated solution was determined by titrating with a solution of sodium thiosulphate.

TABLE 2

Solubility of Hydroquinone at 23·75°C.

Salt Solution	Solubility in grams per litre		Solubility as a percentage of that in water
Water	67·64	67·64	100·0
"	67·64		
1·5M KI.	50·62	50·62	74·8
	60·62		
1.5M KNO_3	53·98	54·09	80·0
	54·20		
1·5M KBr	47·91	47·91	70·8
	47·91		
* 1.5M KCl	—		67·0
† 0.5M K_2SO_4	52·62	52·72	($\frac{1}{2}$M = 78 or $\frac{1.5}{2}$ M = 67)
	52·82		
* LiCl.	—		56·6 (18°C)
* NaCl.	—		59·1 (18°C)
* CsCl.	—		95·0

* Results obtained from Linderström-Lang's work.

† On account of the comparatively low solubility of K_2SO_4. only determinations with 0.5 M K_2SO_4 were carried out. These gave a solubility of 52.72 grams per litre or 78 % of that in water, This gives by linear extrapolation a value of 67 % for $\frac{1.5}{2}$ M K_2SO_4.

To test the purity of the quinone, about 0·25 grams was weighed off and titrated. This gave 100·2 %. Further, solubility determinations were mady by (a) shaking 5 grams with 50 ccs. of water and (b) 1·5 grams with a similar quantity of water. This gave 13·98 and 13·97 grams per litre respectively, as shown in the table.

m-AND p-NITROANILINE, AND p-NITROPHENOL

To determine the solubilities of these substances it was necessary to find a method for their titration which would give sufficiently accurate results. In a method described by E. Knecht and

TABLE 3

Solubility of Quinone at 23·75°C.

Salt Solution	Solubility in grams per litre		Solubility as a percentage of that in water.
Water (1·5 gs. Quinone)	13·97 13·97	13·97	100·0
Water (5gs. Quinone)	13·98 13·98	13·98	—
0.15 M KCNS	23·75 23·78	23·77	170·1
,, KI.	20·86 20·92	20·89	149·6
“ KNO_3	18·44 18·47	18·46	132·1
,, KBr	15·12 15·18	15·15	108·5
,, KCl	12·61 12·64	12·63	90·4
$\frac{1\cdot5}{2}$ M K_2SO_4	8·89 8·91	8·90	63·7
* 1·5 M LiCl	—		77·3
* ,, NaCl	—		80·3
* ,, RbCl	—		93·8 (18°C)
* ,, CsCl.	—		97·6 (18°C)

* Results obtained from Linderström-Lang's work.

E. Hibbert[1] for the estimation of nitrogroups in aromatic compounds, the substance is boiled with an excess of titanous chloride and hydrochloric acid and the excess back titrated with a solution of a ferric salt. This method entails several disadvantages. Thus B. Diethelm and Foerster[2] from measurements of the reduction potentials of titanous solutions were able to conclude that the titanous ions may discharge hydrogen ions with the evolution of hydrogen. From the result of a careful investigation by C. F. van Duin[3] we may conclude that this decomposition may give rise to considerable errors when an acid titanous chloride solution is heated, even when every precaution is taken to exclude air from the solution. Van Duin was able to obtain concordant results when a correction was introduced obtained from a blank estimation in which the titanous chloride was heated for exactly the same time and in exactly the same manner as in the actual estimation. In our opinion even this method is not wholly satisfactory since the titanous chloride during the blank is under other conditions than that during the actual estimation. He also found it necessary to standardise the titanous chloride against a nitro compound. Similarly T. Callan and J. A. Russell Henderson[4] standardise against p- nitroaniline. In some cases they obtain low results when working with titanous chloride which they attribute to chlorination having taken place, and for this reason they prefer to use titanous sulphate.

For these reasons we set out to devise a method in which the decomposition of titanous chloride is eliminated and consequently the obtaining of theoretical results is not dependent on the choice of an arbitrary standard substance, and also in which the errors due to chlorination do not arise.

I. M. Kolthoff[5] has shown that the reduction potential of a titanous chloride solution is inversely proportional to the hydrogen ion concentration; that is that the reducing action of titanous chloride increases on decreasing the acidity of the solution. Hence we thought it of interest to investigate the estimation of nitrobodies with

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[1] "New reduction methods in volumetric analysis" (1918).

[2] Z. physik. Chem. *63* 138 (1908).

[3] Chem. Weekblad *16* 1111 (1919).

[4] J. Soc. Chem. Ind. *39* 86 T (1920) and *39* 157 T (1920).

[5] Rec. trav. chim. des Pays-Bas. *43* 268 (1924).

titanous chloride at low hydrogen ion concentration, as we may expect that the reduction will take place much more rapidly.

The addition of salts such as sodium bicarbonate or sodium acetate for lowering the acidity is not permissible as precipitation of $Ti(OH)_3$ and $Ti(OH)_4$ due to hydrolysis will take place. It is therefore necessary to use a substance such as Rochelle salt or sodium citrate which as well as having a buffer action also tends to form complexes and so keep the titanium in solution.

We made some experiments with Rochelle salt, but, as this gives a precipitate of potassium bitartrate while titrating with the strongly acid titanous chloride solution, we found it more convenient to use sodium citrate. In the presence of this salt we found that nitro compounds were rapidly reduced by titanous chloride at room temperature.

Method of Estimation

An approximately 0·05N solution of titanous chloride was made by boiling 80ccs. of the strongly acid 20 % titanous chloride solution, as supplied by Kahlbaum, with 100ccs. of concentrated hydrochloric acid for one minute and diluting with water to three litres. The solution was kept in a brown bottle in an atmosphere of hydrogen. The apparatus (see Fig. 4) is fully described by I. M. Kolthoff and O. Tomiček[1]. A potentiometric method of titration was employed. The titrations were carried out in a beaker fitted with a rubber stopper which was pierced with holes for the burette, the platinum electrode and the inlet and outlet of the carbon dioxide which was passed through before and during the titration. A clean platinum gauze electrode was used, the beaker being connected to a calomel electrode by means of a glass syphon filled with a saturated solution of potassium chloride. The readings were obtained by adjusting the pointer on a rolled slide wire until the galvanometer showed no deflection. The carbon dioxide was obtained from a cylinder and was freed from oxygen by passing through two wash bottles containing a mixture of 5 % titanous chloride and 20 % sodium citrate and a third wash bottle containing water.

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[1] I. M. Kolthoff and O. Tomiček, Rec. Trav. Chim. des Pays-Bas *43* 775 (1924).

We at first attempted a direct titration with titanous chloride, but the reduction took place so slowly in the neighbourhood of the end point, that, although results could be obtained in this way, from 40 to 50 minutes were necessary for the completion of a single titration even at 60° C.

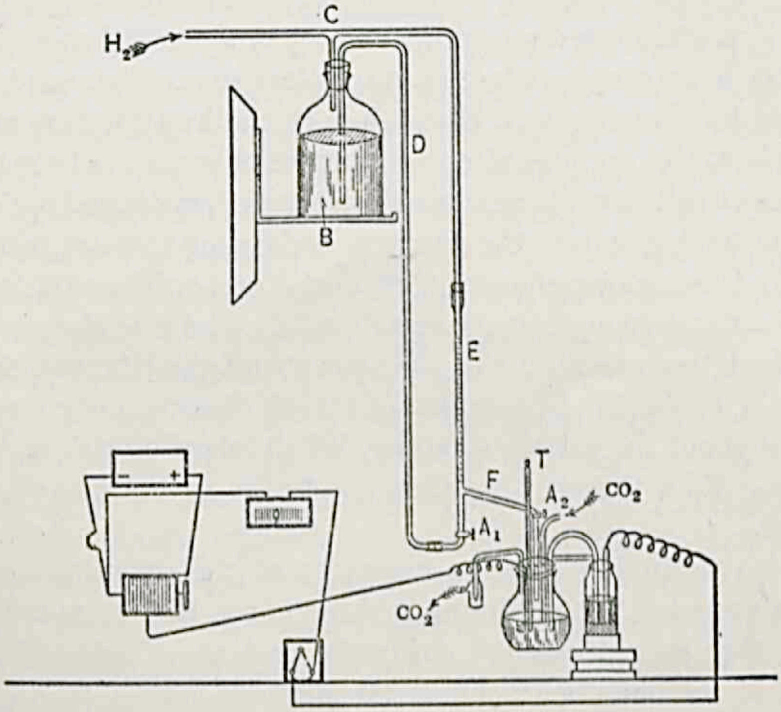

Fig. 4

We next tried adding a *small* excess of titanous chloride and back titrating with iron alum. In this way it was possible to carry out the whole estimation at room temperature in less than twenty minutes and obtain accurate results. Titrations at about 50° C were equally successful but the higher temperature is not necessary and might in fact be a disadvantage if the substance being titrated is very volatile. Finally the procedure was as follows:

25 ccs. of the solution of nitrobody were placed in the beaker together with 30 ccs. of a 20 % solution of sodium citrate. A little solid sodium bicarbonate (less than 0.25g.) was also added, this giving an evolution of carbon dioxide, so helping to remove the last traces of dissolved air from the solution. A steady stream of carbon dioxide (freed from air as already described) was passed

through the contents of the beaker for at least three minutes before the commencement of the titration. The titanous chloride was then run in slowly until the violet colour of the solution showed there was an excess of from 1 to 3 ccs. The violet colour of the titanous chloride is so much more intense in the presence of the citrate than the ordinary hydrochloric acid solution that an excess of 1 cc. was more than sufficient to give a marked colour, while with 2ccs. in excess the reduction takes place so rapidly even at room temperature that the back titration with the iron solution may be begun about two minutes after the titanous chloride has been added. The back titration with the iron solution was then carried out slowly until the sudden leap in the potential indicating the end point was reached. This sudden change in potential was sufficiently large to make the titration accurate to less than 0·1 cc. of iron alum solution when the latter was only half the strength of the titanous chloride solution (i. e. 0·025n). The stream of carbon dioxide is of course passed throughout the entire procedure. When following this procedure in no case did we meet with errors due to the air not being entirely removed.

The curves in Fig. 5. give examples of the magnitude of the jump in potential. The ordinate represents the E.M.F. as measured against the normal calomel electrode, and the abscissa 1 cc. of reagent in the neighbourhood of the jump.

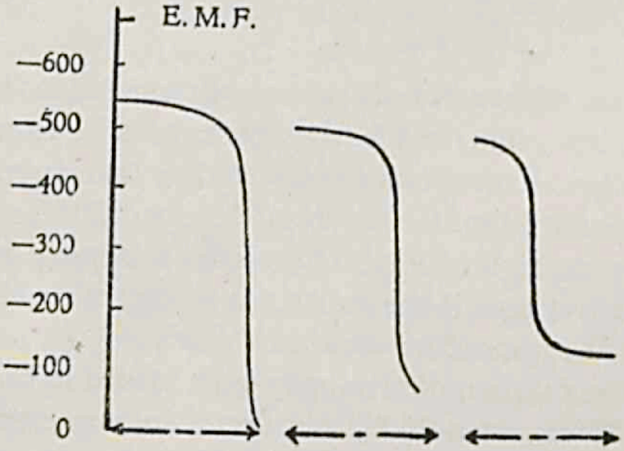

Fig. 5

Standardisation of titanous chloride solution.

The standardisation of the titanous chloride was carried out by titrating a 0·05n potassium bichromate solution at 50°C as described by Kolthoff and Tomiček[1]. Recently E. Zintl and A. Rauch[2] have raised objections to the use of potassium bichromate as a standardising substance. They claim that the titration is too slow and that when using the pure iron-free preparation of titanous chloride steady potential readings are not obtained and the method fails altogether to give a result. We went fully into this matter and although we worked with both the ordinary preparation containing iron as an impurity and the specially prepared iron-free titanous chloride supplied by Kahlbaum, in neither case did we find any difficulty in obtaining accurate results. The titration is, as Zintl and Rauch say, rather slow, but this is only a disadvantage in the first titration where even the approximate place of the end point is not known; the subsequent titrations may be carried out comparatively quickly since it is not necessary to take so many readings. Further we found the addition of a few drops of $CuSO_4$ solution greatly accelerated the reaction while not interfering with the results. On the other hand we found that the standardisation against a copper salt as recommended by Zintl and Rauch gave results which were always about 0·5 % to 1 % too high which is in agreement with the earlier results of Kolthoff and Tomiček. Details of these investigations are published elsewhere[1].

The influence of the amount of sodium citrate and sodium bicarbonate added

The sodium citrate we used was a commercial preparation twice recrystallised from water; it did not contain iron as an impurity. In order to know if the 30 ccs. of 20 % sodium citrate we used had any effect on the results, we standardised our titanous chloride against iron alum in the presence of this quantity of sodium citrate as well as in the ordinary acid medium. The results are set out below:

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[1] I. Kolthoff and O. Tomiček. Rec. Trav. Chim. des Pays-Bas *43* 775 (1924).

[2] E. Zintl & A. Rauch. Zeit. anorg. Chemie *146* 281 (1925).

[3] I. M. Kolthoff, O. Tomiček and C. Robinson, — Zeit. Anorg. Chemie. *150* 157 (1925).

TABLE 4

Substance titrated	ccs. of 20% sodium citrate added	ccs. of titanous chloride required. (about 0.05n)
25ccs. of iron alum (0·025n)	none	28·75
”	none	28.75
”	none	28·75
”	30	28·93
”	30	28·94
”	30	28·97
”	50	29·05
”	50	29·05

Thus in the presence of the sodium citrate the titre is 0·2cc. too high for 30ccs. of 20 % sodium citrate. Even after recrystallisation of the sodium citrate the result was still the same amount too high. The difference is proportional to the amount of citrate added as is shown in the table. We do not know whether this difference is due to the citrate itself or to some impurity present in it.

The following titrations involving smaller quantities of titanous chloride show that the error is a constant error of 0.20cc. of titanous chloride for 30ccs. of sodium citrate and not dependent on the amount of the titanous chloride used:

TABLE 5

Amount of $TiCl_3$ titrated	ccs. of sodium citrate added	ccs. of iron alum required
2·00 ccs.	none	1.15
”	none	1.15
”	30	1.00
”	30	1.05
	Mean difference = 0·12 cc.Fe = 0.21 cc. $TiCl_3$	

In the titration of nitrobodies this correction which is here also proportional to the amount of sodium citrate must be applied.

TABLE 6

Substance titrated	ccs. of sodium citrate added.	ccs. of $TiCl_3$ required	% nitrophenol	ccs. of $TiCl_3$ corrected by subtracting 0.2cc. for every 30ccs. of citrate used	% nitrophenol
25·00 ccs. of p. nitrophenol solution	30	23·78	101·0	23·58	100·1
,,	30	23·75	100·9	23·55	100·0
,,	60	24·01	102·0	23·61	100·2
,,	60	24·01	102·0	23·61	100·2

From these results we found that it was necessary to correct all our titration figures by subtracting 0·2cc from the figure obtained by subtracting the amount of the back titration from the quantity of titanous chloride added.

We also thought it advisable to see if the addition of the sodium bicarbonate could introduce any error:

TABLE 7

Substances titrated	Sodium bicarbonate added	Titanous chloride required
25·00 ccs. m-nitroaniline solution	0·50 grams	27·64 ccs.
,,	1·00 ,,	27·69 ,,
,,	4·00 ,,	27·74 ,,
,,	4·00 ,,	27·77 ,,
25·00 ccs. picric acid solution	none	21·95 ,,
,,	0.25 ,,	21·95 ,,
,,	5·00 ,,	22·07 ,,
,,	5·00 ,,	22·08 ,,

As in the actual titrations never more than 0·25g was used this could not affect results by more than 0·01 cc. and hence the error is negligible.

The addition of neutral salts was also found to have no influence.

Further details relating to the general application of this method are published elsewhere [1].

Purity of Substances used

The p-nitroaniline after two recrystallisations from alcohol gave a result about 1 % too high when analysed by the method described above. After two more recrystallisations the following results were obtained.

TABLE 8

Titanous chloride oxidised	Corrected for citrate error	Calculated titre (from bichromate standardisation)	Result obtained
23·27	23·07	22·95	100·5 %
23·19	22·99	22·95	100·2 %
23·19	22·99	22·95	100·2 %
23·27	23·07	22·95	100·5 %

The *m-nitroaniline* was recrystallised three times from alcohol and gave the following results on titration.

22·07	21·87	21·92	99·80 %
22·08	21·88	21·92	99·80 %
27·77	27·57	27·65	99·70 %

The p-nitrophenol was twice recrystallised from alcohol and gave on titration:

23·78 (30ccs. Sodium Citrate)	23·58	23·56	100·1 %
23·75 „ „ „	23·55	23·56	100·0 %
24·00 (60ccs. „ „	23·60	23·56	100·2 %
24·00 „ „ „	23·60	23·56	100·2 %

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[1] I. M. Kolthoff and Conmar Robinson — Rec. Trav. Chim. des Pays-Bas *46* 169 (1926).

The Solubility Determinations were carried out similarly to those with quinone and hydroquinone, the shaking being carried on for twenty hours. The temperature of the determination was 25°C. With the p- and m-nitroanilines the saturated solution was drawn off by the method already described and 10ccs. of the undiluted solution titrated; with p-nitrophenol 10ccs. of the saturated solution was made up to 100° and 25ccs. of this solution was titrated. Each titration given in the tables represents a titration on a separate solubility determination. For each substance solubility determinations in water were carried out with a large and small excess of the solid substance in the solubility, this being a further check on the purity of the substances. The salt solutions employed were 0·2 molar (0·1 molar in the case of K_2SO_4)

TABLE 9

Solubilities of p-nitroaniline at 25° C.

Solution	ccs. of $TiCl_3$ used (corrected for citrate error)		Solubility grams per litre	Solubility as a percentage of that in water
Water (with 0·40gs.)	21·87	21.83	0·5735	
Water (with 0·40gs.)	21·78			
Water (with 0·15gs.)	21·54	21·54	0·5657	100·0
	21·54			
0·2M KI	23·06	23.05	0·6053	105·5
0·2M KI	23·05			
0·2M KBr	22·14	22·21	0·5834	101·7
0·2M KBr	22·28			
0·2M KCl	21·38	21.34	0·5606	97·7
0·2M KCl	21·30			
$\frac{0{\cdot}2M\ K_2SO_4}{2}$	20·68	20.67	0·5430	94·7
	20·65			
0·2M NaCl	20·81	20·86	0·5480	95·5
0·2M NaCl	20·91			
0·2M LiCl	20·72	20.67	0·5430	94·7
0·2M LiCl	20·62			

TABLE 10

Solubilities of m-nitroaniline at 25° C.

Solution	ccs. of $TiCl_3$ used (corrected for citrate error)		Solubility In grams per litre	Solubility as a percentage of that in water
Water (with 0·15g.)	34·31	34·30	0·8929	100·0
Water (with 0·15g.)	34·29			
Water (with 0·60g.)	35·16	35·16	0·9151	
Water (with 0·60g.)	35·15			
0·2M KI	36·66	36·60	0·9527	106·7
0·2M KI	36·53			
0·2M KBr	33·94	34·02	0·8857	99·2
0·2M KBr	34·10			
0·2M KCl	33·03	33·11	0·8619	96·5
0·2M KCl	33·19			
$\frac{0\cdot2M}{2}$ K_2SO_4	32·17	32·08	0·8349	93·5
	31·98			
0·2M NaCl	32·72	32·71	0·8514	95·3
0·2M NaCl	32·70			
0·2M LiCl	32·33	32·46	0·8449	94·6
0·2M LiCl	32·58			

p-PHENYLENEDIAMINE

With this substance as with the nitrocompounds no sufficiently accurate method of estimating the concentration of the saturated solution could be found in the literature and it was necessary to develop a special method.

p-Phenylenediamine forms an insoluble compound with picric acid. Hence by adding a known quantity (an excess) of picric acid to a solution of p-phenylenediamine, filtering off the precipitate, and titrating the picric acid remaining in solution, it was possible to estimate the concentration of p-phenylenediamine solution. Preliminary experiments showed that the solubility of the picric acid coumpound was not high enough to introduce any appreciable error into our experiments. This was done by shaking some of the picric acid compound over night in picric acid solutions of similar concentrations to those used in the experiments, and then, after filtering, ascertaining if there had been any change in the concentration of the picric acid solution. In all cases no change was found within the limits of the experimental error of the titration. An addition of 0·2M KI solution (which might be expected to increase the solubility) also introduced no error.

The determination of the solubilities of the p-phenylenediamine was therefore carried out as follows: The p-phenylenediamine was shaken for 20 hours at 25° C in the particular salt solution in a

TABLE 11

Solubilities of p-nitrophenol at 25° C.

Solution	ccs. of $TiCl_3$ used (corrected for citrate error)		Solubility In grams per litre	Solubility as a percentage of that in water
Water (with small excess of solid)	45·25	45·23	11·82	100
"	45·20			
Water (with large excess of solid)	45·27	45·25	11·83	
"	45·23			
0·2M KI	47·52	47·62	12·45	105·3
0·2M KI	47·72			
0·2M KBr	45·62	45·59	11·91	100·8
0·2M KBr	45·55			
0·2M KCl	44·17	44·20	11·55	97·7
0·2M KCl	44·23			
$\frac{0{\cdot}2M}{2}$ K_2SO_4	43·96	44·00	11·50	97·3
	44·04			
0·2M NaCl	42·27	42·29	11·05	93·5
0·2M NaCl	42·31			
0·2M LiCl	41·69	41·71	10·90	92·2
0·2M LiCl	41·73			

thermostat, after which the saturated solution was drawn off in the manner already described for the other substances. 10ccs. of the saturated solution was made up to 100ccs.

To 25ccs. of this diluted solution was added 75ccs. of 0·05026 N picric acid solution (titrated against $Ba(OH)_2$ solution). This, after thorough mixing, was allowed to stand until the next morning. The supernatant liquid was then filtered. 50ccs. of the filtrate (the first portion coming through the filter having been, of course, rejected) was titrated with $Ba(OH)_2$, using methyl red as an indicator.

The solubility with a large excess of the solid present in the solubility bottle being higher than with a small excess (as shown in table 12), all the determinations were carried out with a small excess — about 2·5 grams being used for each determination. Here, as with the other substances, each titration corresponds to the solution obtained from a separate solubility determination.

TABLE 12

Solubilities of p-phenylenediamine at 25°C.

Solution	ccs. $Ba(OH)_2$	ccs. picirc acid combined (expressed in ccs. of $Ba(OH)_2$)		Solubility in grams per litre	Solubility as percentage of that in water.
Water (with 0·25g)	22·50	43·50	43·50	47·23	100·0
Water (with 0·25g)	22·50	43·50			
Water (with 0·5g.)	22·15	44·20	44·20	47·98	—
Water (with 0·5g.)	22·15	44·20			
0·2M KI	*20·60	47·60	47·60	51·68	109·4
0·2M KI	*20·70	47·60			
0·2M KBr	21·80	44·90	44·84	48·68	103·0
0·2M KBr	21·86	44·78			
0·2M KCl	*22·80	43·20	43·25	46·85	99·2
0·2M KCl	*22·75	43·30			
$\frac{0{\cdot}2}{2}$M K_2SO_4	24·40	39·70	39·80	43·21	91·5
	24·30	39·90			
0·2M NaCl	22·60	43·50	43·50	47·23	100·0
0·2M NaCl	22·40	43·50			
0·2M LiCl	*22·15	44·50	44·50	48·32	102·3
0·2M LiCl	*22·15	44·50			

TABLE 13

Solubilities of Boric Acid.

Solution	Temp.	Solubility in Water (mols per litre)	Solubility in 1 mol of salt.	Sol. in 1 mol. of salt as percentage of sol. in water
1M LiCl	17·85°	0·7219	0·6040	83·68
„ NaCl	17·85	0·7219	0·7090	98·23
„ KCl	17·85	0·7219	0·7694	106·6
„ RbCl	18·00	0·7319	0·7956	108·7
„ CsCl	18·00	0·7307	0·7923	108·4
„ KI	17·85	0·7219	0·7233	100·2

TABLE 14

Solubilities of Succinic Acid.

Solution	Temp.	Solubility in water (mols per litre)	Sol. in 1 mol. of salt	Sol. in 1 mol. of salt as percentage of sol. in water.
1M LiCl	18·00°	0·4974	0·3612	72·59
„ NaCl	18·00	0·4971	0·4085	82·17
„ KCl	18·00	0·4976	0·4788	96·20
„ RbCl	17·85	0·4914	0·4968	101·1
„ CsCl	17·85	0·4917	0·5208	105·9
„ KBr	17·85	0·4928	0·4902	99·47
„ KI	17·85	0·4928	0·5238	106·3

The picric acids solutions of different concentration were used in the determinations. In those determinations marked with an asterisk 75ccs. of picric acid equalled 88·80 ccs. of $Ba(OH)_2$, while in the other determinations 75ccs. of picric acid equalled 88·50 ccs. of $Ba(OH)_2$.

We may add to these six substances for which we have carried out solubility determinations the results of Linderström-Lang for boric acid and succinic acid. In order to make these results comparable to the other we have obtained the value of the solubilities in one molar salt solution by linear interpolation from the results which Linderström-Lang carried out at various salt concentrations, and expressed these results as a percentage of the solubility in water. Linderström-Lang's results were carried out at two slightly different temperatures, but the percentage figures may be compared. From his results it may be seen that the linear interpolation introduces no appreciable error for our purpose, the curve obtained by plotting the solubility against the salt concentration being very nearly a straight line.

Finally we may give some of the results of Rothmund and Biltz on the solubility of phenylthiourea in one molar salt solutions. The result for $CsNO_3$ is obtained by extrapolation from his results for a 0.5 molar solution.

The results of the nine substances whose solubilities in salt solutions have been studied are set out in Fig. 6 so that they may be readily compared. In this diagram the solubility of each substance in one molar salt solutions is given, these values being obtained when necessary from the value for the salt concentration at which the solubilities were actually determined by assuming that the increase or decrease of solubility is directly proportional

Table 15

Solubility of phenylthiourea at 20°C.

Solution	Solubility in grams per litre	Solubility as percentage of that in water
Water	2·12	100·0%
1M $LiNO_3$	2·10	99·1
" $NaNO_3$	1·92	90·6
" KNO_3	1·96	92·5
" $RbNO_3$	2·17	102·3
" $CsNO_3$	(2·54)	119·8
" KI	2·23	105·2
" KBr	1·79	84·5
" KCl	1·60	75·5
$\frac{1}{2}$M K_2SO_4	1·33	62·8

to the concentration of the salt. The error so introduced for the four substances dealt with by Linderström-Lang will be quite small as can be seen from his figures, and even if in the case of the other substances the error is somewhat greater it will certainly not be great enough to be of importance for our purpose — namely the comparison of the relative "spreading" of the cation and anion series. The temperatures at which the solubilities of the various substances were determined vary from 18°C to 25°C. However, as has been pointed out [1], the percentage change of solubility for a given concentration of salt does not vary appreciably with the temperature, and so here again no appreciable error is introduced.

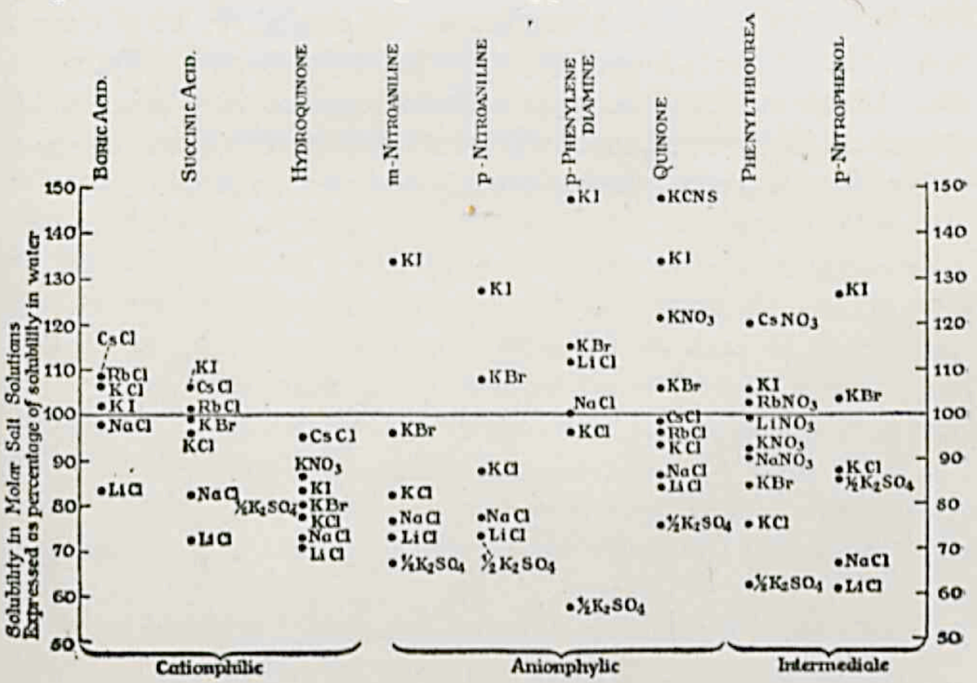

Fig. 6

If now we examine the figure, we see that there are four substances (quinone, m- and p-nitroaniline, and p-phenylenediamine) in which there is a very marked spreading of the anions and three substances (hydroquinone, boric acid and succinic acid) for which there is a marked cation spreading; the two remaining substances, (phenylthiourea and p-nitrophenol) seem to fall between these two

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[1] Rothmund, "Löslichkeit and Löslichkeitbeinflussung" p. 154 (Leipzig 1907).

extremes. The other remarkable point we notice is that for each substance (except hydroquinone) there are salts that actually increase the solubility of the substance, an increase of 50 % for a salt concentration of one mol being met with in some cases. The influence of the salts with like cation or anion is in the lyotropic series. Thus the lithium and sulphate ions (i.e. the most hydrated ions) cause the greatest decrease in solubility, while the caesium, iodine and sulphocyanate ions cause the greatest increase or least decrease in the solubility. There are, however, a few salts out of order. Thus for phenylthiourea, $LiNO_3$ is found *above* KNO_3 and in the case of p-phenylenediamine the cation series is actually found reversed with LiCl giving an increase of solubility. In the anion series, the nitrate is found above the iodide in the case of hydroquinone which exhibits the most extreme case of very small anion spreading. These exceptions will be referred to in the next section where we will try to give an explanation of the results.

III — THEORETICAL EXPLANATION

The influence of the cation or the anion in lowering the solubility of a non-electrolyte is, as we have seen, generally the greatest when the ion is most hydrated. For this reason it is frequently assumed that the influence of the ions is simply one of binding a certain proportion of the water molecules and so rendering them incapable of dissolving the substance which is "salted out". Debye [1] has more recently connected the lowering of the solubility of organic substances by addition of electrolytes with the fact that these organic substances lower the dielectric constant of water. We have however shown that cases of increased solubility frequently occur, and for this reason alone, this theory must be considered inadequate. Further we have shown that for some substances the anions seem to have a very great influence compared to that of the cations while other substances are influenced more by the cations than the anions. To explain these facts, therefore, it is necessary to assume that the solubility influence is brought about by more than one factor and in what follows we will show how such an explanation is to be found in the orientation of the dipoles of the water molecules.

Let us consider what happens when a substance dissolves in a liquid. As is well known, for a non-electrolyte to have more than an extremely low solubility in water, one or more polar groups must be present in the molecule [2], (witness the very low solubility of the inert gases, paraffins etc.). When therefore a substance containing such polar groups dissolves it may be considered the forces of attraction between the water molecules and the molecules of the solute overcome the forces holding the molecules of the crystal of the solute together ("lattice energy"). When the saturation point

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[1] P. Debye, Physik. Zeit. *26* 22 (1925).

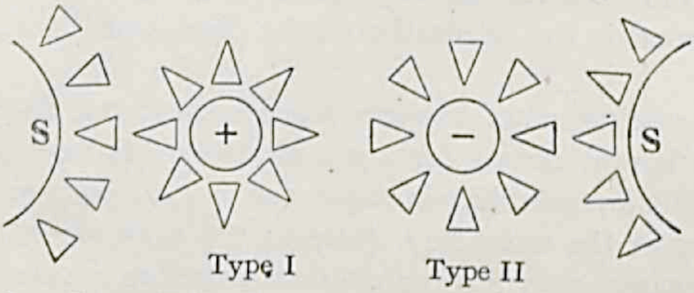
[2] W. D. Harkins, J. Am. Chem. Soc. *39* 354 (1917).

has been reached, these forces may be considered equal and we have a dynamic equilibrium. But as the molecules of the solute, although electrically neutral, contain one or more polar groups, the dipoles of the water molecules must be orientated around the solute molecules in a way similar to that we have described in dealing with the hydration of the ion. Thus if the polar group in question is negative (e.g. an hydroxyl group) the positive ends of the water molecules will be turned towards it. Further it will be seen that the forces of attraction between solute and solvent will be at their greatest when this orientation is complete, *and that anything that decreases this orientation will decrease the solubility ; similarly anything that increases the orientation will increase the solubility.*

Only the field strength round the polar group determines the orientation!

The solute molecules therefore may be considered to be surrounded by more or less orientated water molecules. These will not necessarily all be similarly orientated. Thus the molecule might have both positive and negative polar groups. In general however it may be assumed that there will be an excess of one kind of orientation over the other.

Similarly if a neutral salt is introduced into the solution there will be an attraction for one of the ions of the salt. Thus if there is an excess of the orientation of type I (Fig. 7) the substances will tend to attract cations, while if of type II it will attract anions. In general, the substance will tend to attract that ion which orientates molecules in the opposite direction, and repel the ion, which orientates water molecules in the same direction. We will therefore speak of cationphilic and anionphilic substances, according to whether the substance displays an attraction for the cation or the



S = Solute Molecule + = Cation — = Anion

Fig. 7

anion. These forces though not large will be sufficient to alter the mean distribution of the ions and a cationphilic substance will have in its immediate neighbourhood more cations than anions.

Now the ions, as has already been explained, will also have orientated water molecules around them. The result will be that the cations will bring to the cationphilic substance water molecules orientated in a direction favourable to the solubility of the substance and so tending to *increase* its solubility. This may be represented as in Fig. 7. (Type I).

The anion, on the other hand, by its opposite orientation will tend to decrease the solubility, but its influence will be much less on account of it being repulsed instead of attracted by the cationphilic solute molecule. The net result of this "orientation influence" will therefore be an increase in the solubility. As well as this orientation influence there will of course also be a lowering of solubility due to the fact that the hydrated ions "bind" a certain proportion of the water molecules and so render them less free to take place in the solution of the substance, as described on P. 15 ("salting out" influence).

This influence, for an anionphilic substance, will also probably be greater for the anions than for the cations. For a highly hydrated ion, such as the SO_4 ion, the salting out influence will preponderate over the increase of solubility due to the orientation effect and consequently the ion will lower the solubility — but for a slightly hydrated ion such as the CNS, the orientation influence will preponderate and so there will be an increase of solubility.

Hence we will have a "spreading" of the anions as is the case with quinone. The cation influence will, as explained, be less marked, but will nevertheless show itself in the lyotropic order, due to the salting out influence.

If on the other hand we have an anionphilic substance (Fig. 7, Type II) an exactly corresponding argument holds — but in this case we will have a "spreading" of the anions instead of the cations.

If then we examine the results as set out in Fig. 6, we must conclude that quinone, the nitro anilines and p-phenylenediamine are anionphilic substances with positive polar groups which orientate water molecules with their negative ends towards them (type

II). On the other hand hydroquinone, succinic acid, boric acid and p-nitrophenol (the last to a less marked extent) must be considered cationphilic with negative polar groups.

The negative character of the acids may at first seem rather surprising, but we must remember that as we are dealing with weak acids, the solubility is really the solubility of the undissociated molecule. We find considerable evidence that this view of the polarity of these substances is correct in the recent work of Frumkin [1], from whose work it may be concluded that p-phenylenediamine and quinone are (for our purposes) positive (anionphilic) and that hydroquinone, boric acid and succinic acid are negative (cationphilic) substances. (See p. 42). That such direct experimental confirmation of the polarity of these substances is at hand is very fortunate as especially for quinone it would be difficult to arrive at any conclusion through a chemical *a priori* reasoning.

It will be seen from the figure that in the case of the nitro anilines we have been successful in finding substances which give a spreading similar to that for quinone — in fact the results for p-nitro aniline are almost identical with those for quinone; m-nitro aniline it would seem is definitely more anionphilic, since we find both a bigger spreading of the anion and a still smaller spreading of the cations.

With p-phenylenediamine we have a molecule similar to p-nitroaniline in every way except that the NO_2 group has been replaced by a second NH_2 group; and so we might expect a still greater anion spreading. This expectation was quite justified by the results, the anion spreading being the greatest found. Further it is extremely interesting to find that we have actually a reversal of the cation series. Apparently the "salting out" influence of the cation has been here so much reduced that lithium chloride actually increases the solubility. With the limited data available any detailed explanation of this cannot be put forward; the explanation must however rest in the factors already mentioned whose influence we do not know *quantitatively*.

Here, for instance, we do not know how much of orientation influence and of salting out influence is contributed by the lithium

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[1] Frumkin Zeit. phys. Chem. *109* 34 (1924), Ibid, *111* 190 (1924); Ibid, *116* 485 (1925); Ibid, *123* 321 (1926).

ion and the chlorine ion respectively; probably however the whole of the *increase* is due to the chlorine ion.

It may here be mentioned that if Linderström-Lang's theory that the different behaviour of quinone and hydroquinone rested in the fact that one was an oxidising agent and the other a reducing agent (p. 19) was correct, we would expect that p-phenylenediamine would show less anion spreading than p-nitro-aniline and that p-nitro-phenol would show more anion spreading. Exactly the reverse was however found.

p-Nitrophenol, as we expected, having no NH_2 group was found to be less anionphilic.

The most markedly cationphilic substance was hydroquinone (a benzene ring with two OH groups!) The anions are here extremely close together. None of the salts used, however increased the solubility. Probably CsI, would have done so.

Phenylthiourea seems to fall between the two types of substances. This being the one solid substance for which a satisfactory cation and anion series were formerly studied is then one reason why the existence of cationphilic and anionphilic substances has not previously been noticed. It is difficult to understand why $LiNO_3$ is here above KNO_3. The possibility of other factors taking part in the solubility influence must of course always be considered.

In spite however of these two or three irregularities in the series, the results for these nine substances seem quite in agreement with our main propositions:

That substances may be either "cationphilic" or anionphilic", according to how they orientate water molecules.

That the solubility influence of neutral salts consists of two parts (1) the "salting out" influence — which is greatest for the most hydrated ions — and (2) an "orientation influence" by which anions tend to increase the solubility of anionphilic substances and cations the solubility of cationphilic substances.

Frumkin's Experiments

Frumkin [1] in a recent series of papers has described experiments in which he has measured the potential difference at a water-air

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[1] P. 40. loc. cit.

interface when the interface is charged by the presence of various inorganic and organic compounds. In this way he was able to show that methyl alcohol or acetic acid, for instance, charged the surface positively, the more negative ends of the molecules (OH and COOH respectively) being below the surface and the CH_3 group above the surface.

On the other hand, if instead of acetic acid, trichloracetic acid is taken, the orientation remains the same, but now the negative Cl atoms give a negative charge to the surface. Succinic acid, in this way gave a positive charge. In this case the negative carboxyl groups are turned towards the water, as with acetic acid.

Aromatic compounds with a polar group charged the surface positively though very much less than the aliphatic substances. Thus nitrobenzene gave a positive charge. o-Nitrophenol gave a positive charge but m-nitrophenol gave a negative charge and p-nitrophenol still more negative. As the OH group of the phenols would certainly be turned towards the water, this shows that the NO_2 group is also negative and so p-nitrophenol is (for our purposes) a negative substance.

Hydroquinone gave a negative charge, but quinone a positive. These being both para compounds, it seems that the signs of their charges must be the same as those of their respective polar groups, which fits in with our explanation of hydroquinone being cationphilic and quinone anionphilic.

p-Phenylenediamine on the other hand gave a positive charge to the surface. The NH_2 groups are therefore positive, and so p-phenylenediamine was rightly considered anionphilic.

The nitro-anilines though not actually dealt with by Frumkin would of course come between p-phenylenediamine and nitrophenol, which is also in accordance with our results.

For more details of these experiments the original papers should be referred to. The evidence however seems quite convincing that the groups OH, COOH, NO_2 are negative while NH_2 is positive, and that quinone and hydroquinone have positive and negative polar groups respectively.

IV — THE INFLUENCE OF SALTS ON OTHER PHENOMENA

THE INFLUENCE OF SALTS ON THE SURFACE TENSION OF WATER

If a neutral inorganic salt is dissolved in water, the surface tension is increased. The surface tension of the solution may be expressed by the equation:

$$\sigma_s = \sigma_w \ (1 + mc)$$

where σ_s is the surface tension of the solution, σ_w the surface tension of pure water, c the concentration of the salt and m a constant. Actually, as was shown by Heydweiller[1] m is not strictly constant but passes through a minimum at about 1 mol. The action of the salt in increasing the surface tension is unmistakably an additive effect of the ions composing it, as was first pointed out by Valson[2]. The action of the different ions may be seen from the table given below which is taken from Freundlich's "Kapillarchemie", the results having been calculated from Heydweiller's[1] data:

TABLE 16

m Values of the Alkali Salts at 18°C.

	SO_4	Cl	Br	NO_3
Li	—	0·0286	0·0271	0·0192
Na	0·0357	0·0228	0·0184	0·0176
K	0·0418	0·0210	0·0151	0·0158
NH_4	0·0326	0·0195	—	0·0174

I[3] raises the surface tension even less than Nɔ pue εONS[4] hardly

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[1] Heydweiller Ann. d. Physik (4) *33* 154 (1910).

[2] Valson, Ann. de Chim. et de Phys. (4) *20* 361 (1870).

[3] Röntgen and Schneider, Wied. Ann. *29* 165 (1886).

[4] Freundlich and Seal, Kolloid Zeit. *11* 257 (1912).

at all. F on the other hand is found close to SO_4. The ions therefore influence the surface tension in the lyotropic series, the most hydrated ions causing the greatest increase of surface tension:

$$SO_4 > Cl > Br > NO_3 > I > CNS$$

and

$$Li > Na > K$$

Hiss[1] showed that the dynamic surface tension of water was considerably greater than its static surface tension. In his experiments the liquid under investigation was sucked into a capillary by means of a powerful air current to a height greater than that due to capillarity and atomised into spray. On stopping the air current at a definite time the liquid rapidly sank to the position determined by the surface tension. The position of the meniscus at very short intervals of time was now determined. With benzene and nitrobenzene the static surface tension was established in the shortest time measurable under the experimental conditions (less than 0.001 sec.). With pure water, however, the results are different, and an appreciable time elapses before the value of the static surface tension is reached.

TABLE 17

Transition from Dynamic to Static Surface Tension of Pure Water 16°C.

t_σ (in seconds)	σ
0·0000	81·8
0·0007	80·0
0·0040	77·2
0·0080	74·6
∞	73·8

Table 17 is from Freundlich's Kapillarchemie, the results having been recalculated from Hiss's data.

The explanation of this must be in the fact that water contains various kinds of molecules and that those having a lower surface

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[1] Hiss, „Über die zeitliche Änderung reiner Flüssigkeitsoberflächen" Diss. Heidelberg (1913).

tension are found to have a higher concentration at the surface than in the bulk of the solution.

The exceptional properties of water (i.e. [1] its extraordinarily high boiling point compared to its molecular weight [2], a specific heat nearly twice that of all other liquids [3], expansion instead of contraction on solidification, and [4], what is absolutely unique, a contraction on heating between 0° and 4°C.) led Röntgen [1] to put forward a theory that water consisted of a binary mixture of "water molecules" and "ice molecules", the latter of greater complexity but less density. This theory was developed by Sutherland [2] who suggested that steam consisted of molecules of H_2O, ice $(H_2O)_3$, and water a mixture of $(H_2O)_2$ and $(H_2O)_3$, the $(H_2O)_2$ being Röntgen's "water" molecules. Bousfield and Lowry [5] consider water a ternary mixture of $(H_2O)_3$, $(H_2O)_2$ and H_2O molecules, a theory which seems more in accordance with the facts. They also give reasons for thinking that water of hydration is in the form of $(H_2O)_2$ molecules. Our conception of water of hydration being orientated H_2O molecules tending to form chains is in some ways in agreement with this idea. We can, however, go further with our hypothesis and assume that the more complex "molecules" present in water are really chains of H_2O molecules, these having a smaller density than the single molecules. On lowering the temperature, more of these "chains" would tend to form (equivalent to more ice molecules). The single water molecules will be found in larger concentration in the surface of the liquid, and these having a lower surface tension (equivalent to steam molecules) would account for the static surface tension of pure water being lower than the dynamic surface tension as shown in the experiments of Hiss.

On the above hypothesis we may explain the influence of salts on the surface tension. If hydrated ions are introduced into the water a certain number of these will be present in or immediately below the surface, and will consequently introduce "water of hydration" into the surface. This having a higher surface tension than the simple molecules will increase the surface tension of the liquid,

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[1] Röntgen, Wied. Ann. *45* 91 (1891).

[2] Sutherland, Phil. Mag. (5) *50* 460 (1900).

[3] Bousfield and Lowry, Trans. Faraday Soc. *7* 85 (1910).

[5] See note 3 page 41.

the increase being greater the more hydrated are the ions. Consequently we find the ions increasing the surface tension in the lyotropic series.

It is therefore true to say that the influence of salts on the surface tension of water depends on the salts effecting the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$, (a suggestion which has been put forward more than once); this in its turn however ultimately depends on the orientation of the water molecules by the salts.

Superimposed on this purely "lyotropic" effect there may possibly be a second effect which is not due to the interaction of solute and solvent (i.e. a non-lyotropic effect).

THE INFLUENCE OF SALTS ON THE MAXIMUM DENSITY OF WATER

The fact that water shows a maximum in the temperature-density curve at 4°C. is intimately connected with the fact that water at ordinary temperatures is a mixture of single and complex hydrols as described in the previous section. The addition of inorganic salts to the water brings about a shift in this maximum. Coppet [1] has determined the lowering produced by a gram molecule of various salts per litre. Thus potassium chloride produces a lowering in the maximum density of 11·6°C. The following table shows some of his results:

TABLE 18

Molecular Lowering of the Temperature of Maximum Density of Salt Solutions

	Chloride	Bromide	Iodide
Rubidium	11·7	13·2	15·6
Potassium	11·6	12·8	15·4
Sodium	13·2	14·5	17·0
Lithium	6·0	7·0	8·3
Ammonium	7·2	8·7	11·1

Wright [2] also carried out a large number of determinations and was able to confirm the law of Despretz [3] that the lowering

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[1] Coppet, Ann. Chim. Phys. *3* 246 (1894); Compt. Rend. *125* 533 (1897); *128* 1559 (1899); *131* 178 (1900); 132 1218 (1901); *134* 1208 (1902).

[2] R. Wright, J. Chem. Soc. *115* 119 (1919).

[3] Despretz, Ann. Chim. Phys. *70* 49 (1839); *73* 296 (1840).

produced by the addition of a solute is directly proportional to the concentration of the solute. He also shows that the lowering produced by a highly ionised binary electrolyte is an additive effect of the cation and anion, and that the molecular lowering can be calculated by the addition of two moduli to the lowering produced by a molecular solution of a chosen standard substance (e.g. hydrochloric acid).

TABLE 19

Lowering of Temperature of Maximum Density of Salt Solutions (Wright)

	M/16	M/8	M/4	M/2	Molecular Lowering
HCl	—	0·7	1·3	2·6	5·2
$LiCl$	—	—	1·4	2·8	5·6
$NaCl$	—	1·6	3·1	6·2	12·4
KCl	—	1·4	2·8	5·5	11·0
NH_4Cl	—	1·0	1·8	3·6	7·2
HBr	—	0·9	1·8	3·7	7·4
$LiBr$	—	—	1·9	3·8	7·6
$NaBr$	—	1·8	3·7	7·4	14·8
KBr	—	1·6	3·2	6·5	13·0
NH_4Br	—	1·2	2·3	4·7	9·4
HI	—	1·2	2·2	—	8·8
LiI	—	1·2	2·3	—	9·2
NaI	1·0	2·0	4·0	—	16·4
KI	0·9	1·8	3·7	—	14·8
NH_4I	0·7	1·4	2·7	—	10·8
HNO_3	0·8	1·6	3·1	—	12·4
$LiNO_3$	—	1·6	3·1	—	12·4
$NaNO_3$	1·3	2·5	5·0	—	20·0
KNO_3	1·1	2·2	4·5	—	18·0
NH_4NO_3	0·9	1·8	3·6	—	14·4
Na_2SO_4	2·0	4·0	—	—	32·0

The experiments were made by means of a dilatometer, the readings being accurate to about 0·2°C. It will be seen that the molecular lowering is exactly proportional to the concentration for each particular substance, a result which is rather surprising. The results for those salts which he used are in fairly close agreement with those of Coppet, considering that different experimental methods were used.

When we consider in what order the ions exert their effect we find for the cations:

$$Na > Rb > K > Li > H$$

and for the anions:

$$NO_3 > I > \tfrac{1}{2}SO_4 > Br > Cl$$

This is not quite the lyotropic series. Na and SO_4 are quite out of their place, and NO_3 does not come between I and Br. On the whole however the less hydrated the ion, the greater seems to be its influence in lowering the maximum density of water. Probably we have here a lytropic effect superimposed on one or more other effects. The *purely* lyotropic effect (due to a change in the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ as already referred to under surface tension) would show itself in the density of the water of the solution (as distinct from the density of the solution) rather than in a shift of the *temperature* of maximum density. It is unfortunate that there are not sufficient data available for constructing the density-temperature curve for each salt solution. Such curves would probably be very interesting.

Bousfield and Lowry [1] showed that on the addition of 2 % NaOH the density maximum disappears; for 12 % solutions and upward the curve has a simple parabolic form, while 42·5 % NaOH makes the density temperature strictly linear from 0° to 100°C. A comparison of the minimum amount of such salts necessary to bring about such effects would no doubt also show the lyotropic series.

THE INFLUENCE OF SALTS ON THE VISCOSITY OF WATER

In table 20 are given the relative viscosities of various salt solutions of 1 normal concentration. In each case the viscosity of water at the temperature of the experiment has been taken as unity.

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[1] Bousfield and Lowry, Phil. Trans. A. *204* 282 (1905).

The increase in viscosity is almost directly proportional to the concentration of the salt for those salts which increase the viscosity.

To these figures may be added that sodium salts increase the viscosity in the order $NaOH > Na_2SO_4 > NaCl > NaBr > NaNO_3$

TABLE 20

Salt	Temperature	Viscosity	Investigator
LiCl	17·6°	1·147	Arrhenius
NaCl	17·6°	1·093	„
KCl	17·6°	0·987	„
RbCl.	25°	0·9846	Wagner
CsCl	25°	0·9775	„
K_2SO_4	17·6°	1·101	Arrhenius
KNO_3	17·6°	0·959	„
KI.	17·6°	0·912	„

and acids increase the viscosity in the order $NaCl > H_2SO_4 > HCl > HBr > HNO_3$. The alkaline earth chlorides increase the viscosity more than the alkali chlorides in the order Ca > Sr > Ba.

We see then that some salts increase the viscosity while others lower it, the greatest increase being caused by the most hydrated ion, the ionic series being

$$Li > Na > H > K > Rb > Cs$$

and

$$SO_4 > Cl > Br > NO_3 > I$$

in order of decreasing viscosity. We have then here again the lyotropic series. This is what we would expect if as a very rough first approximation we assume Einstein's[1] formula for the viscosity of a liquid in which spherical particles are suspended:

$$\eta_s = \eta_m \ (1 + 2{\cdot}5 \ \varphi)$$

where η_s is the viscosity of the suspension, η_m that of the pure liquid, and φ the volume of the particles in unit volume of the suspension. In other words if we assume that the greater the volume of the suspended particles (here hydrated solute) the

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[1] A. Einstein. Ann. d. Physik. (4) *19* 289 (1906); Kolloid. Zeit *27* 137 (1920).

greater will be the viscosity, we must expect the salts composed of the most hydrated ions to give the greatest viscosity. The results show however that as well as this there must be a second effect tending to decrease the viscosity only overcome by the first effects in the case of appreciably hydrated ions. A suggestion as to what hm. this other effect is cannot be made without taking up the whole theory of viscosity, which is outside the scope of this work.

THE INFLUENCE OF SALTS ON THE VELOCITY OF CHEMICAL REACTIONS

The velocity of chemical reactions is also influenced by the presence of salts in the solution, and here again we find the lyotropic series. With this phenomenon we find moreover that we get a *reversal* of the lyotropic series in some cases according to whether the action takes place in acid or alkaline medium. This was first pointed out by Höber [1]. Thus in acid catalysis of esters, and acid inversion of cane sugar, bromides favour the reaction more strongly than chlorides while sulphates inhibit it, the series being

$$\mathrm{Br} > \mathrm{Cl} > \mathrm{SO_4}$$

The cation series for the ester catalysis is (Höber)

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$$

On the other hand when we turn to the reactions in alkaline solutions we find that sulphates [2] assist basic saponification of esters while chlorides, bromides, nitrates and iodides inhibit to an increasing extent, the series thus being

$$\mathrm{SO_4} > \mathrm{Cl} > \mathrm{Br} > \mathrm{NO_3} > \mathrm{I}$$

for the anions, while Höber found for ester hydrolysis the cation series to be

$$\mathrm{Cs} > \mathrm{Rb} > \mathrm{K} > \mathrm{Li}$$

Cs inhibiting least and Li most.

The whole subject of reaction velocity cannot be discussed here. A possible explanation of the above facts however occured to us, and since it follows more or less logically from the assumptions al-

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[1] Höber, Beitr. z. chem. Physiol. u. Pathol. *9* 35 (1907); Zeit phys. Chem. 70 134 (1910).

[2] Spohr, Zeit. phys. Chem. *2* 194 (1888); Arrhenius, Zeit phys. Chem. *4* 226 (1889).

ready made to explain the solubility influence it is perhaps worth while putting forward, especially as up to the present no other explanation has been suggested.

The velocity of the above mentioned reactions is governed by the catalytic action of either hydrogen or hydroxyl ions as the case may be. Lapworth [1] has put forward the theory that the hydrated hydrogen ion has much less catalytic activity than the unhydrated hydrogen ions. He examined widely differing examples of hydrogen ion catalysis in organic solvents and showed that small quantities of water produced a marked retardation in all cases. Those reactions which occurred in both water and alcohol were found to go enormously faster in alcohol. Lapworth accounts for this by supposing that the water causes a reduction in the number of nonhydrated hydrogen ions, which he supposes to be the active catalytic agent. Dawson [2] from experiments on the reaction between acetone and iodine also supports this view. Lapworth assumes the hydrated hydrogen ions are complex ions probably of the form $(H_2O.H)^+$, the theory however may be easily adapted to fit in with our somewhat different views on hydration. The chief point is that anything tending to increase the hydration of the hydrogen ions will decrease the velocity of the reaction while anything decreasing the hydration will increase the velocity of the reaction. A similar line of reasoning to that used in explaining the "orientation effect" which gives rise to an increase in the solubility will lead us to conclude that the anions will tend to increase the hydration of the hydrogen ions while cations will dehydrate. Consequently we find that the most hydrated anion, SO_4, has the greatest inhibiting action, while the most hydrated cation (lithium) tends most to increase the velocity of reaction. This will be the case for all reactions catalysed by hydrogen ions, but for a reaction dependent on the catalytic influence of hydroxyl ions the two series will be reversed, since the cations will hydrate while the anions will dehydrate, which is in accordance with the experimental data. This will probably not be the only action of the salts, and there may

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[1] Fitzgerald and Lapworth J. Chem. Soc. *93* 2163 (1908); Lapworth J. Chem. Soc. *93* 2187 (1908); see also H. S. Taylor „A Treatise of Physical Chemistry" (Macmillan) (1924), p. 915 et seq.

[2] J. Chem. Soc. *99* 1 (1911); Dawson and Powis, ibid., *105* 1093 (1914).

be a tendency for the salts to increase the "active mass" of the reacting substances, (corresponding to "salting out" in solubility) so accelerating the reactions, but this will not be so important as the first influence and will not prevent the complete reversal of the series.

The suggestion that the neutral salt effect in accelerating the velocity of hydrogen ion catalysed reactions is due to the dehydration of hydrogen ions is put forward by H. S. Taylor[1], who points out that this theory is in accordance with the fact that the neutral salt action is independent of the substrat[2]. The possibility of certain ions "hydrating" arises as a consequence of the assumptions made in accounting for the increase of solubility in solubility influences.

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[1] H. S. Taylor, „A Treatise of Physical Chemistry", P. 917.

[2] Taylor, Medd. K. Vetensk. Nobelinst. *2* No. 34 (1913).

V — SUMMARY

The cases we have described do not exhaust the phenomena taking place in true solution in which the lyotropic influence of salts is found. The adsorption of salts under certain conditions may be cited as yet another example. Thus Odén [1] found that the adsorption of nitrates on charcoal took place in the following order.

$$Cs > Rb > K > Na > Li$$

and for potassium salts:

$$CNS > I > Br > Cl > SO_4$$

i.e.: 't grootste ion is 't makkelijkst polariseerbaar. CNS: dipool!

thus the least hydrated ion is most easily adsorbed. This is because more work is necessary to withdraw the more hydrated ions from the bulk of the solution, owing to their greater affinity for the water and also because the protecting "sheath" of hydration makes the adsorption more difficult. The adsorption is of course often complicated by other influences. The experiments of Kruyt and van der Made [2] and Kruyt and van der Spek [3] show that lyotropic influences play a part in the neutral salt influence in dyeing. Such phenomena are however often too complicated to be easily interpreted and will not be dealt with here.

We see therefore that there are a number of phenomena on which the influence of neutral salts is due to the independent effects of the cation and anion which exert their influence in the following order.

$$Li > Na > K > Rb > Cs$$

and $$SO_4 > Cl > Br > NO_3 > I > CNS$$

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[1] Odén and Anderson, J. Phys. Chem. *25* 311 (1911); Oden and Langelius. J. Phys. Chem. *25* 385 (1921).

[2] H. R. Kruyt and Miss J. E. M. van der Made, Proc. Kon. Akad. v. Wetensch. Amst. *20* 636 (1917).

[3] H. R. Kruyt and van der Spek, Verslag. Kon. Akad. v. Wetensch. Amst. *27* 109 (1918).

These are also the series obtained if we arrange the ions in order of decreasing hydration. In the case of the solubility influence we have shown that the lyotropic influence of the ions is due to two reasons, firstly the hydration of the ions (giving rise to "salting out") and secondly the orientation of water molecules (which sometimes gives rise to increased solubility). The second reason accounts for the occurence of a specific influence of either cation or anion. Sometimes these two effects act in opposition to one another, which may give rise to an irregularity or reversal of one of the series. These properties of the ions also account for their influence on other lyotropic phenomena. In some cases, (e.g. influence on surface tension of water) we have seen that the salts influence the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ but this influence is really dependent on the "orientation" influence of the ions.

Note. The conception that ions orientate water molecules is of course not new. Thus Fajans [1] postulates a similar "polarisation" of the water molecules by the ions to account for the solubility of alkaline halides being least when the cation and anion are about equally hydrated.

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[1] Fajans, Naturwiss. *37* 729 (1921).

PART II

THE LYOTROPIC SERIES IN COLLOIDAL PHENOMENA

I — FLOCCULATION VALUES

If we determine the minimum concentration of a number of salts necessary to bring about the flocculation of a typically lyophobic sol we find, as is well known, that this minimum concentration (hereafter referred to as the flocculation value or F.V.) varies very considerably with the valency of the ion of opposite sign to that of the charge on the sol particles. Thus for the As_2S_3 sol we find the following flocculation values as determined by Freundlich[1]

KCl	49·5	millimols per litre
$CaCl_2$	0·65	,, ,, ,,
$AlCl_3$	0·093	,, ,, ,,

The dependence of the flocculation value on the valency of the ion is fully dealt with in text books on colloid chemistry[2] and will not be considered here. If however, instead of taking cations of various valency we take cations of the same valency, we find again differences for the F.V.s. though certainly very much less marked[1]:

LiCl	58	millimols per litre
NaCl	51	,, ,, ,,
KCl	49.5	,, ,, ,,

Here again we have the lyotropic series. The stability of lyophobic sols is governed by the charge of the particles. The stability of lyophilic sols depends partly on the charge of the particles but also

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[1] Freundlich, Z. phys. Chem. *44* 129 (1903), Ibid *73* 385 (1910).

[2] Freundlich, "Kapillarchemie"; H. R. Kruyt, "Colloids": etc.

on the hydration of the particles, as has been shown by Kruyt and de Jong[1].

We might therefore expect that the lyotropic influence of salts would be more marked in the case of lyophilic sols, and this in fact is the case. Thus with the agar sol (which may be considered the typical lyophilic sol as de Jong[1] has pointed out) we find that it can be "salted out" by NH_4F, K_2SO_4 Na_2SO_4 but not by NH_4Cl, KCNS and KI although more concentrated solutions of the latter can be prepared. This "salting out" is undoubtedly closely related to the "salting out" influence of salts on the solubility of substances and involves a dehydration of the hydrated particles. De Jong has shown this to be the case by means of viscosity measurements with the agar sol, additions of $MgSO_4$ in concentrations just less than that required to salt out bringing about a marked drop in the viscosity. In general then, we find that the more hydrated the ions of the salt, the more easily will that salt "salt out" a lyophilic sol. In this phenomenon it should be remembered, quite large concentrations of salt are necessary to bring about flocculation, the phenomenon being in fact quite different to that of the flocculation of lyophobic sols where very small quantities of salt can bring about complete flocculation — in the case of the lyophilic sol not only has the charge of the particles to be removed but also their hydration.

There are however, a number of sols which in a sense stand between the lyophilic and lyophobic. Though not truly lyophilic sols they are without doubt to some extent hydrated. Amongst these may be mentioned the ferric hydroxide sol and the aluminium hydroxide sol (both positively charged) and the vanadium pentoxide sol (negatively charged). Flocculation values for all these sols (as will be shown later) show a much more marked lyotropic influence than is to be found from the flocculation values of typically lyophilic sols.

Scarpa[2] has shown that a lyophilic sol (such as agar or gelatin) can be dehydrated by adding a sufficiently large concentration of alcohol, the resulting alcoholic sol having all the properties of a

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[1] H. R. Kruyt and H. G. Bungenberg de Jong, Zeit. phys. Chem. *100* 250. (1922); Koll. Beihefte *28* 1 (1928).

[2] O. Scarpa, Kolloid Zeit. *15* 8 (1914).

lyophobic sol — low viscosity, sensitivity to electrolytes, particles visible in ultramicroscope etc. If then the appearance of a strongly marked lyotropic influence of salts on a sol, as shown by the relative values of the F. V. for different salts, is connected with the hydration of the colloidal particles, dehydrating such sols with alcohol should remove the influence. We therefore thought that the determination of the F. V.s for various salts in various concentrations of alcohol should throw some light on the mechanism of this lyotropic influence. The results of such experiments are given in the following sections.

EXPERIMENTS WITH VANADIUM PENTOXIDE SOL

Freundlich and Leonhardt[1] have made a study of the V_2O_5 and the Mo_2O_5 sol and the influence of electrolytes upon them. Instead of determining flocculation values they determined turbidity values, that is the amount of salt required to bring about a marked turbidity within a definite time. The following are their results for the V_2O_5 sol prepared according to the method of Biltz.

LiCl	130	millimols	per	litre
NaCl	50	,,	,,	,,
NH_4Cl	25	,,	,,	,,
KCl	17	,,	,,	,,
RbCl	7·7	,,	,,	,,

A similar remarkable spreading of the lyotropic series is shown in their results for the Mo_2O_5 sol.

$\frac{LiSO_4}{2}$	$>$ 500	millimols	per	litre
NaCl	60	,,	,,	,,
NH_4Cl	26	,,	,,	,,
KCl	12	,,	,,	,,
RbCl	5.0	,,	,,	,,
$CsNO_3$	2.6	,,	,,	,,

The fact that both of these sols give gelatinous precipitates and that the V_2O_5 sol readily sets to a gel may be taken as suggesting that the sols are to some extent hydrated and this is borne out by the results of our experiments.

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[1] Freundlich and Leonhardt, Kolloid. Beihefte 7 172 (1915).

Preparation of Sol

The sol was prepared from ammonium vanadate according to the method of Biltz [1] slightly modified. The ammonium vanadate was rubbed up with dilute hydrochloric acid in a mortar, a red powder separating out from the mixture. This was washed several times by repeatedly mixing with water, allowing to settle in a glass cylinder and decanting. After this had been repeated seven times a point was reached where there was no longer settling. The whole was then transferred to a large flask, made up to four litres with distilled water and shaken up vigorously until thoroughly peptised. A very small amount of thymol was added to protect the sol against bacterial contamination. It was also found that the sol lasted longer if kept in the dark.

On analysis the sol was found to contain 0·184 grams of V_2O_5 per litre.

This sol was not precipitated on the addition of an equal volume of 96 % alcohol even after standing for two or three days. The colour of the sol with alcohol added was however, much browner than the original sol which was more of a reddish colour. This colour did not appear immediately after adding the alcohol but developed slowly over a period of about five hours. The browner alcoholic sol exhibited a brighter cone when viewed through the slit ultramicroscope. A higher concentration of alcohol (15 ccs. of alcohol added to 10ccs. of sol) brought about complete precipitation after the three and a half hours.

Determination of Flocculation Values

The flocculations were carried out in flat bottomed glass tubes (2 cms. in diameter and 10 cms. high). The tubes were tightly closed by corks covered with pure tin foil.

Flocculation values for lithium, sodium and potassium chlorides were first determined without the addition of alcohol. For this purpose the sol was diluted with an equal volume of water. 10ccs. of this diluted sol was pipetted into one of the glasses and 5ccs. of the salt solution of three times the required final concentration was added by means of another pipette and the contents of the glass

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[1] Biltz, Berichte d. deutsch. chem. Ges. *37* 1098 (1904).

thoroughly mixed by shaking. The figures given for the salt concentration in the tables in all cases refer to the concentration in the final mixture of sol plus salt solution. Several glasses were thus filled with increasing concentrations of salt and allowed to stand for two hours, at the end of which time the concentration just sufficient to bring about flocculation was noted. The sol was considered to be flocculated when a clear zone was visible between the meniscus and the dark red brown precipitate. The flocculation value having been thus roughly determined another series was made giving a more accurate value and so on until the correct value was reached as accurately as the experimental error would allow. The F.V.s could be determined correct to about 4 %; with the alcohol mixtures the error was slightly more, due to the settling of the flocculation in the presence of alcohol not taking place so uniformly (in some cases a precipitate would float at the top instead of sinking). The results were however in all cases sufficiently accurate to leave no doubt about the phenomena here described. The flocculation values in the presence of the alcohol were carried out so that the concentration of the V_2O_5 was the same in the final mixtures as in the flocculation values without alcohol. Thus for the addition of $33\frac{1}{3}$ % by volume of alcohol, $33\frac{1}{3}$ ccs. of alcohol and $16\frac{2}{3}$ ccs. of water were added to 50ccs. of the original sol. 10ccs of this mixture was then placed in the glass. A salt solution was then made up containing the *same* concentration of alcohol, and three times the concentration of salt required in the final mixture. 5ccs. of this alcoholic salt solution were then pipetted into the glass as before.

By this means, all the flocculations were carried out on a sol of the same concentration of vanadium pentoxide and the addition of the salt solution was not accompanied by the disturbing effects which would arise on mixing if a salt solution was added of different alcohol content to the sol.

The results for LiCl, NaCl and KCl for the aqueous V_2O_5 sol and the sol plus two different concentrations of alcohol are shown in the table. The experiments were carried out as quickly as possible so that the error due to the change of flocculation values with time would not be appreciable. The final determinations for all salts at each particular concentration of alcohol were carried out simultaneously.

TABLE 21

Flocculation values of Vanadium Pentoxide Sol (in millimols)

Salt	50 % by volume water added	$33^{1}/_{3}$ % by vol. alcohol $16^{2}/_{3}$ % by vol. water added.	50 % by volume alcohol added
LiCl	410	8·0	3·6
NaCl.	70	6·0	3·0
KCl	20	3·4	2·1

The flocculation values are given in millimols per litre. It will be seen then that for the aqueous solution we obtained results similar to those obtained by Freundlich and Leonhardt. The addition of alcohol however as well as making the solution very much more sensitive to all three salts (as might be expected if the stability of the solution is to some extent due to its hydration) brings the flocculation values *relatively* as well as absolutely, much closer together. Thus while for the ordinary sol the F.V. for LiCl is over twenty times that for KCl, the addition of an equal volume of alcohol makes the F.V. for LiCl only 1·7 times that of KCl.

The precipitate formed in the alcoholic sols differed in appearance for the different salts. Thus the precipitate with KCl was much more voluminous than the precipitate given with NaCl, and that with NaCl more voluminous than that given with LiCl. The colours also differed, the LiCl precipitate being brownish like the colour of the alcoholic sol while the KCl precipitate was more reddish. On shaking up the precipitates and allowing them to settle again the LiCl precipitates settled rapidly in about three minutes The NaCl precipitates took about twenty five minutes and the KCl ones over an hour.

EXPERIMENTS WITH FERRIC HYDROXIDE SOL

The ferric hydroxide sol was chosen as an example of a positively charged sol exhibiting somewhat lyophilic properties.

Preparation of Sol

10 grams. of ferric chloride (Kahlbaum's "zur Analyse") were

dissolved in 1 litre of water. A solution of ammonium carbonate was added slowly to this while stirring continuously until the point was reached where there was just no remaining precipitate. The solution was then dialysed on a Zsigmondy-Heyer star dialyser for three days, a freshly prepared collodion membrane being used. At the end of this time the water showed no reaction for chlorine ions with silver nitrate. At the end of the dialysis the volume of the solution had increased to about one and a half litres.

Analysis showed the solution to contain 0·148 grams of Fe_2O_3 per 100ccs.

Determination of Limit Values

These were carried out similarly to the determinations with the vanadium pentoxide solution.

2ccs. of the sol diluted with water or alcohol were placed in the flocculation glass and then 1cc. of the salt solution of the same alcohol content as the sol was added to this and the whole well mixed. The tubes were tightly closed with corks covered with tin foil and allowed to stand for 24 hours, after which the salt concentration which was just enough to bring about flocculation was noted. The sol was considered to be flocculated when there was a clear zone of liquid between the meniscus and the precipitate. The longer period (24 hours) before reading was found more suitable for these experiments since the precipitate formed in alcoholic sols settled much more slowly than in the aqueous solution, and consequently if the reading were made after a shorter time (one or two hours) it was impossible to compare the limit values for the two sols.

Experiments were made with KCNS, KI, KNO_3 and KCl and the results are shown in the table.

It will be seen that the alcoholic sol is much more sensitive to all the salts in the presence of alcohol. On the other hand, the relative values for KI, KNO_3 and KCl are not much changed.

Unlike the vanadium pentoxide sol, the ferric hydroxide sol was not precipitated by alcohol alone, even when added in very large quantities, e.g. ten volumes.

The two F.V.s for KCNS for the aqueous solution were obtained at the beginning and end of the experiments respectively and show that the solution had not changed appreciably during this time.

TABLE 22

Flocculation Values of Ferric Hydroxide Sol (in millimols)

	1 vol. of sol. 3 vols of water	1 vol. of sol. 3 vols. of alcohol.
KCNS	16	3·65
KI	54	5·0
KNO_3	44	3·60
KCl	29	2·20
KCNS (repeated)	17	

EXPERIMENTS WITH ALUMINIUM HYDROXIDE SOL

This was chosen as another example of a positively charged sol.

Preparation of Sol

The sol prepared by the method of Gann[1] is said to gelate on addition of electrolytes instead of flocculating and consequently a sol was prepared by another method described by Müller[2]:

A preparation of crystalline aluminium chloride of the "Onderlinge Groothandel" was used. This was found to have only a trace of iron present as shown when treated with potassium thiocyanate. 100 gs. of the aluminium chloride were dissolved in about 750 ccs. of water. 75ccs. of this was diluted to about 250 ccs. and precipitated by adding dilute ammonium hydroxide to the boiling solution until there was a slight excess. The solution was then filtered and the precipitate washed three or four times as quickly as possible with hot distilled water. The precipitate was then transferred to a beaker with about 600 ccs. of water and boiled. O.1N HCL was added, 2 ccs. at a time, the contents of the flask being boiled for a few minutes after each addition, this being continued until the amount of hydrochloric acid necessary to peptise the sol had been added. The last two or three cubic centimetres of the acid was added in still smaller portions.

In this way an opalescent, rather opaque sol was obtained. Analysis showed it to contain 0·424 grams of Al_2O_3 per litre. A slight

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[1] Gann, Kolloid Chem. Beihefte *8* 64 (1916).

[2] Zeit. anorg. Chem. *57* 310 (1908).

precipitate was formed from the sol during the next forty eight hours. The sol was consequently decanted before being used for the following experiments.

Determination of Flocculation Values

The sol was found not to be flocculated even on the addition of very large quantities of ethyl alcohol (seven volumes of alcohol to one of sol). On the other hand acetone flocculated the sol on the addition of three volumes.

The flocculation values were carried out exactly as in the case of the ferric hydroxide sol. The readings were made after twenty four hours, the sol being considered flocculated if any precipitate had formed at the bottom of the glass. This was found to be the most suitable end point as in some cases the flocculation was not complete.

Flocculation values were determined for KCNS, KI, KBr and KCl. The corresponding determinations for KNO_3 could not be made owing to the small solubility of this salt in alcohol being too low.

The results are given in the accompanying table.

TABLE 23

Flocculation Values of Aluminium Hydroxide Sol (in millimols).

	1 vol. sol. 3 vols. H_2O	1 vol. sol. 1 vol. H_2O 2 vols. alcohol	1 vol. sol. 3 vols. alcohol	1 vol. sol. 4 vols. alcohol
KCNS . . .	500	500	> 850	> 680
KI	440	525	> 500	
KBr	470	360	> 300	
KCl	380	180	95	70
KCl (8 days later) . . .	360		100	

When a figure such as "> 850" is given this means that this was the highest concentration of salt tried and that at this concentration there was no flocculation, it being impossible to reach the flocculation value on account of the limited solubility of the salt in the alcohol concentration used. The figures given in the last column are not strictly comparable as the concentration of the sol is here somewhat different.

The check determinations made with KCl at the end of the experiments (after eight days) show that there was no appreciable experimental error due to the change in the stability of this with time.

Before offering an explanation of the phenomena described for these three sols of the somewhat lyophilic type we will first describe some similar experiments carried out with both a negative and a positive typically lyophilic sol — namely the gelatin sol. In these experiments it will be seen we obtained direct evidence that an ion of opposite charge to the charge of the sol can under certain circumstances actually stabilise the sol by means of its water of hydration, a fact of primary importance in explaining these results.

EXPERIMENTS WITH GELATIN SOL

Preparation of the Gelatin Sols

For this method isoelectric ash free gelatin ($P_H = 4{\cdot}7$) was prepared by Loeb's method from the best quality photographic gelatin produced by the "Lijm en Gelatinefabriek" of Delft.

A 1 % gelatin sol was made up. For this purpose the weighed quantity of gelatin was allowed to swell for one hour in cold water. It was then heated on a water bath to 60°—65° until dissolved and subsequently filtered hot through a thoroughly washed ash free filter, the temperature not being allowed to fall below 40°. So as to preserve the solution a very small crystal of thymol was added just after the gelatin was completely dissolved but before filtering.

A positively charged acid sol was prepared by adding 1.5 ccs. 0·1N HCl to 100ccs. of the isoelectric sol. This gave a sol with a $P_H = 4{\cdot}2$. (determined with indicators).

Similarly a negative sol was prepared by adding 1·5ccs. 0·1nNaOH, this giving a $P_H = 5{\cdot}4$.

To prevent gelation, all the gelatin sols were kept in a thermostat at 37° C.

Addition of Alcohol to the Isoelectric Sol

On adding a large quantity of alcohol to the isoelectric sol, the gelatin was immediately precipitated as an amorphous white mass. To find exactly the least quantity of alcohol which would bring about precipitation it was necessary to set out a series of mixtures containing various quantities of alcohol but the same concentration of gelatin. Thus a 75 % (by volume) alcohol mixture was prepared by adding 30ccs. of 96 % alcohol to 10ccs. of the 1 % gelatin sol (the mixture thus containing 0·25 % gelatin) and a 30 % alcohol sol was prepared by adding 18ccs. of water and 12ccs. of alcohol to 10ccs. of gelatin sol. Intermediate concentrations were obtained similarly. 5 ccs.of these various mixtures were placed in flocculation glasses and examined after having stood all night:

35 40	42	44 45 50	75	(percentage by volume of 96 % alcohol)
no precipitation	some precipitation	complete precipitation	precipitated immediately	

Thus 42 % alcohol was the smallest concentration to bring about a precipitation. 75 % alcohol brought about immediate precipitation. Concentrations between these values brought about opalescence which was followed by precipitation on standing. 40 % alcohol and below gave no opalescense and no precipitate.

Experiments with the Positive Sol

The addition of alcohol even in very large quantities (e.g. ten volumes of alcohol (96 %) to one of sol) did not cause a precipitate. Mixtures containing increasing quantities of alcohol were set out in flocculation tubes exactly as with the isoelectric sol, the gelatin concentration (0·25 %) being the same in all of them.

The following concentrations were tried

50 52·5 53·75 55·0 57·5 60·0 75·0 (percentage by volume of 96 % alcohol)

53·75 % alcohol or over caused the sol to become opalescent, 50 % alcohol or even somewhat less caused a slight opalescence after standing for some hours. In no case was there a precipitate formed. It was therefore expected that the sol with about 50 % alcohol would be sufficiently sensitive to electrolytes for the purpose of our experiments.

Determination of Flocculation Values

The flocculation values for the various salts were determined in a similar way to the methods already described for the other sols. In every case the sol was diluted four times, by adding to one volume of sol 3 volumes of a mixture of alcohol and water so that the final mixture contained 0·25 % gelatin and the required percentage of alcohol. 2ccs. of this mixture were pipetted into a number of flocculation glasses and to each glass was added 2ccs. of a mixture of electrolyte solution and alcohol containing the same percentage of alcohol and twice the concentration of electrolyte required in the final mixture of 4ccs. The glasses were well shaken immediately after the addition of the electrolyte and allowed to stand for about 18 hours, being well corked with corks covered with pure tin foil. After this time it was noted which concentrations of salt had caused a precipitation and which had not.

If the influence of alcohol on gelatin was similar to that on the vanadium pentoxide sol it would be expected that high concentrations of alcohol would give flocculation values for KCNS, KBr and KCl which did not differ from one another by much. Some preliminary experiments were therefore made with 75 % alcohol which gave the following results.

KCNS	2·50	millimols
KBr	2·20	,,
KCl	1·80	,,

These were as expected.

The Existence of an upper limit to the salt concentration necessary to flocculate

With 60 % alcohol however some results which had not been expected were obtained. Here it was found that not only was there a limiting value for the electrolyte *below* which no precipitate was formed, but that there was also a second limiting value *above* which no precipitate was obtained. This will be seen in the widely spaced series for KCNS (60 % alcohol) shown in table 24.

TABLE 24

Flocculation of (positive) alcoholic gelatin sol (60 % alcohol)

KCNS in millimols . . .	1360	680	136	68	34	13·6	6·8	3·4
flocculation . .	—	—	—	+	+	+	—	—
appearance . .	perfectly clear, not opalescent		cloudy, no ppte.	precipitate			slightly opalescent	

It will be noticed that for the higher concentrations where no precipitation was obtained, the opalescence on the other hand actually disappeared. This at once made us think that there might be some connection between the existence of this hitherto unexpected upper limit value and some observations made by Scarpa [1]. Scarpa found that for a gelatin-water-alcohol system containing 48·7 % alcohol by weight, some electrolytes caused precipation while others brought about no precipitation and actually caused the opalescence of the sol to disappear. He also found that the addition of solid sodium chloride did away with the opalescence. De Jong found that, if after the addition of the solid sodium chloride some more alcohol was added, the opalescence returned. He therefore put forward the suggestion that this was a lyotropic phenomenon in which the viscosity maximum of the binary system alcohol-water was displaced.

To return to our own experiments, we found that the addition of more alcohol to the mixture containing 1360 mm. of KCNS caused the opalescence to return. We also found, on adding solid sodium chloride to the original 60 % alcohol gelatin sol, that, as found by Scarpa, the opalescence disappeared and no precipitation was brought about even by dissolving quite a considerable quantity of the sodium chloride. Further, solid potassium thiocyanate was found to have the same effect.

Some very interesting results were obtained by placing the dry crystals of the salt at the bottom of a flocculation tube, carefully pouring the alcoholic gelatin sol over the crystals and allowing the salt to diffuse upwards through the sol. As the salt diffused upwards through the opalescent sol, there first appeared a zone of quite clear sol immediately above the crystals, sharply defined from the still opalescent sol above it. As diffusion proceeded this zone extended upwards. Later a second clear zone (corresponding to the higher concentrating of electrolyte above the higher limit value already mentioned) appeared and extended downwards. This upper zone was separated from the opalescent zone by a jagged edge formed by the precipitate from the upper part which floated

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[1] Scarpa — Koll. Zeit. *15* 8 (1914). cf. also de Jong Diss., Utrecht (1921) p. 85.

on the opalescent sol. The bottom clear zone on the other hand continued to be sharply defined by a horizontal line of demarcation. If not too great a quantity of salt was used, it was eventually all dissolved, and it could then be clearly seen that there was no precipitation whatever in the bottom zone. Here then we have the various stages of the irregular series (p. 66) already described present in one test tube: at the bottom, (highest concentration of electrolyte) no precipitate and opalescence destroyed, i.e. a zone where the sol is actually stabilised and seems to be more lyophilic, in the middle a zone where there is no precipitation but the opalescence remains (lower concentrations of electrolytes), and at the top a zone where precipitation has taken place leaving a clear liquid (still lower concentrations). The concentrations which are too low to bring about a precipitate are present at the top of the tube earlier in the experiment before diffusion has gone far enough to allow a zone of precipitation to form.

We found these phenomena could be repeated with more or less ease for any combination of electrolyte and alcoholic concentration which give a lower and higher limit value (see later).

We may here give a description of two actual experiments.

A gelatin sol containing 55 % alcohol was used. This sol which had been mixed 24 hours previously was strongly opalescent. Two flocculation tubes were used, in (1) more sodium chloride crystals were placed than could dissolve in the sol under the conditions described, while the bottom of (2) was only just covered with crystals. 20ccs. of the sol was then run in slowly from a pipette. This gave a column of liquid 75mms. high. A millimeter scale was placed behind each of the tubes and they were allowed to stand untouched for a couple of days, care being taken that they were well corked so that there could be no evaporation of alcohol. The results are given in Table 25.

In each case the top clear zone was separated from the middle opaque zone by a jagged line, not horizontal, which showed clearly the presence of an actual precipitate floating on the sol below. This is shown in Fig. 8.

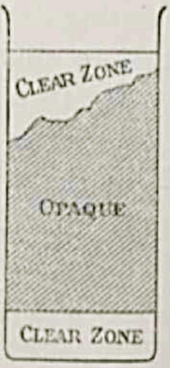

Fig. 8

Similar results were obtained with KCl and KCNS The KCNS dissolved too rapidly to give sharp results.

TABLE 25

(1)	Time	(2)
Opaque throughout	0 hrs.	Opaque throughout
Top 3mm. clear. Bottom 3mm. clear.	0·75 hrs.	No change at top. Bottom 2mm. clear.
Top 6mm. clear. Bottom 4mm. clear.	3·25 hrs.	No change at top. Bottom 2mm. clear.
Top 15mm. clear. Bottom 5mm. clear.	12 hrs.	Almost clear zone at top. Bottom 8mm. clear (the whole clearing slightly).
Top 17mm. clear. Bottom 7mm. clear. (about 75 % of the salt dissolved.)	24 hrs.	Bottom 9mm. clear, above this a band of thick precipitate 7mm. wide, and above that clear liquid. (all salt dissolved).

As an explanation of these facts we put forward the following hypothesis.

Let us consider a gelatin sol containing sufficient alcohol to make it opalescent and having the properties of a lyophobic sol as described by de Jong, the gelatin particles being "dehydrated" by the alcohol. If now some electrolyte is added, the ions of the electrolyte of opposite charge to the particles will be attracted to the surface of the particle, in a quantity depending on the concentration of electrolyte. If sufficient electrolyte is added, eventually a point is arrived at where the critical potential of the sol is reached and the sol flocculates (the first limit value of our irregular series). The flocculation only takes place after the sol has been allowed to stand for some time. If instead more electrolyte is added, a further increase in the quantity of ions in the vicinity of the particles will take place.

Why: alcohol dipoles have nearly the same electric moment as water dipoles!

These ions, hydrated in aqueous solution, will be surrounded by a larger concentration of water molecules than exists in the bulk of the alcohol-water system. Consequently by concentrating round the gelatin particle they will increase the percentage of water in its immediate neighbourhood, and so, if the quantity of alcohol present is not too much they will bring about a "rehydration" of the gelatin. When this rehydration has taken place, the sol, although no longer stable on account of its charge, will not flocculate owing to the stabilising influence of the hydration of the particles. This explains the second limit value *above* which no concentration of electrolyte will bring about flocculation.

We now prepared a new gelatin sol and investigated *both* these limit values at various concentrations of alcohol. The results are summarised in the table. The first figure in the brackets is the highest concentration in millimols of the particular electrolyte which would give a precipitate, the second figure being the lowest concentration to give a precipitate. The "end point" for the determination of the limit values was in every case taken as the concentration which would bring about *any* precipitate, irrespective of size, in some cases the flocculation being incomplete.

TABLE 26

Flocculation Values of Positively Charged Gelatin

Percentage alcohol	55 %	50 %	45 %	40 %
KCl	(60—2·0)	(27—2·9)	(18—4·5)	(9—5)
KBr	(70—2·6)	(30—3·3)	(20—4·0)	(10—4·5)
KCNS.	(80—3·0)	(35—4·0)	(22—3·5)	(10—4·0)
LiCl.	(60—2·0)	—	(18—4·7)	—

The experiments with the 40 % alcohol mixture were not so accurate as the other, it not being possible to find the limit value so sharply.

The significance of these figures will be more appreciated by studying the graph (Fig. 9) in which percentage of alcohol is the ordinate and concentration of electrolyte the abscissa. If we first consider the points for the higher and lower limit values for KCl and KCNS at 55 % alcohol, we will see that if the curves for the limit values (both higher and lower) of KCl and KCNS respectively are to be continuous they must cut at some point. This is found to be the case for the lower limit values between 45 % and 50 % alcohol. In the table this is shown by the reversal of the series for the lower values between these two concentrations of alcohol.

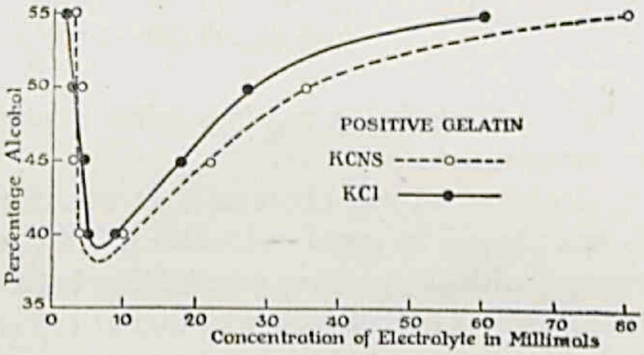

Fig. 9

We see then that in the figure we have an area of precipitation corresponding to certain concentrations of alcohol and of salts. Outside this area no precipitation can take place. To the right of this area is the area where, although the concentration of alcohol is high enough (about 39 %) to make precipitation possible, the concentration of the salt is sufficiently high to bring about stabilisation by rehydration at the particular concentration of alcohol. The most highly hydrated salt (KCl), it will be noticed, brings about this rehydration most easily. In the lower flocculation values it will be noticed that the sol is most sensitive to the most highly hydrated anion, as are the aluminium hydroxide and the ferric hydroxide sols.

We now prepared a new negative gelatin sol (as described on page 77) and carried out similar experiments. The results are given in the accompanying table.

TABLE 27

Flocculation Values for Negatively Charged Gelatin

Percentage Alcohol	65 %	70 %	75 %	over 75 %
LiCl	No precipitate	(55—7·0)	(110—2·8)	Too Sensitive
NaCl	,,	(60—5·2)	(110—2·35)	,,
KCl	,,	(65—3·0)	(120—2·00)	,,
KCNS	,,	(65—3·0)	(120—1·85)	,,

With less than 70 % alcohol it was impossible to obtain precipitates at any concentration.

With 55 % alcohol a sol was obtained that was distinctly opalescent. This was allowed to stand over solid KCl for two days, as in the experiments with the positive gelatin. The bottom 7cms became quite clear, but no flocculation appeared at top of tube, suggesting that no flocculation would take place at any concentration of KCl. This was further confirmed by the following series:

120	45	22.5	11.25	5.13	2.25	1.125	m. mols KCl.
All became as clear as water.					Opalescent and no precipitate		

Results with 65 % alcohol were similar:

175	87.5	44	35	17.5	8.25	5.8	3.5	1.75	1.20	m. mols KCl.
All became as clear as water.						Slightly cloudy				

similarly with LiCl:

180	90	45	36	18	9	5.6	3.6	1.8	1.0	m. mols LiCl.
All became as clear as water						Slightly cloudy				

With 70 % and 75 % alcohol higher and lower limit values were obtained as already shown in Table 27. For both these mixtures, standing over NaCl gave the clear zone at bottom of tube as well as flocculation at the top of the tube, leaving a cloudy zone in the middle, as already described for the experiments with positive gelatin.

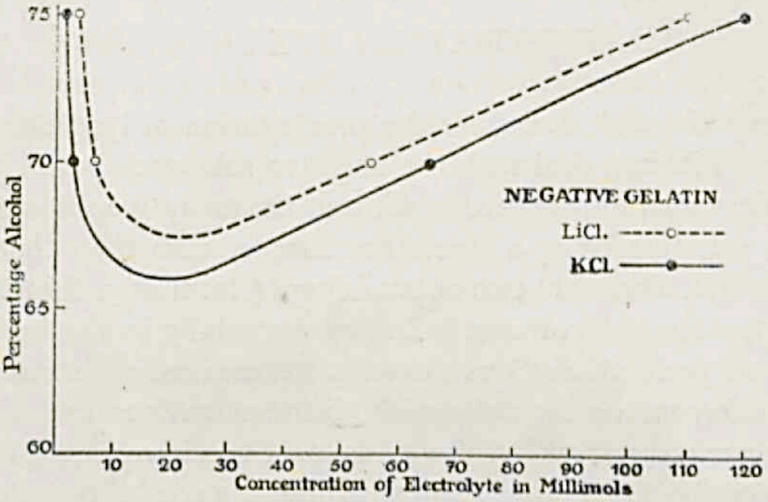

Fig. 10

If we examine the results as they appear when set out in the graph (fig. 10), we see that as in the case of the positive gelatin sol, there is an area within which precipitation takes place and outside which precipitation cannot take place. The curves for LiCl and KCl do not cut as do the curves for KCl and KCNS in the case of the positive sol. For the lower flocculation values the partially dehydrated sol is most sensitive to the least hydrated salt (KCl) as is the case with the negatively charged vanadium pentoxide sol but not with the positively charged sols. These and other facts will be dealt with in the explanation which follows.

II — THEORETICAL EXPLANATION

To explain these series for the precipitation of lyophilic sols by salts, we will first deal with the negative sols, such as the partially lyophilic vanadium pentoxide sol and the truly lyophilic negative gelatin sol; this being a somewhat simpler case than that of the positive sols. There are two outstanding facts: firstly, that there is a very considerable lyotropic influence (especially in the case of the vanadium pentoxide sol) as shown in the marked differences in the flocculation values for salts with different cations and the same anions, and secondly that the sol is most sensitive to the least hydrated cation (potassium). In explaining the solubility influence of salts we showed that an ion might make its influence felt in two ways, firstly by a stabilisation effect due to its power to orientate water molecules and secondly, due to a "salting out" effect. If we consider the mechanism by which a crystalloid is held in solution in a saturated solution, we see that every molecule of the solvent plays its part in keeping this quantity of crystalloid in solution; and consequently if any of the water molecules are used for another purpose, as is the case in salting out, some of the crystalloid must come out of solution — in other words there is a decrease in the solubility. In the case of a sol, however, every molecule of the water present does not play a direct part in keeping the disperse phase in suspension — consequently a considerable quantity of a salt can be added (especially if the sol is not greatly hydrated) without any "salting out" taking place. In some cases (e.g. the agar sol) where a neutralisation of the charge is not in itself sufficient to bring about flocculation, eventually a point will be reached (if the solubility of the salt is high enough) where "salting out" of the sol will actually take place. This case will be referred to again on page 79. But in the case of a sol which, though to some extent hydrated, owes its stability chiefly to its charge, no salting out effect will make itself felt at the low salt concentrations which is sufficient to bring about flocculation. The other effect, stabilisation, due to the favourable orientation of the water molecules by the ion of opposite charge, will, however, appear. That is to say, the negatively charged vanadium pentoxide particle will tend to have its hydration increased by the cations which neutralise its charge, the degree of this hydration depending, of course, on the degree of hydration of the cation. Consequently the hydration will be increased by the lithium ion, and the critical potential at which flocculation takes place will be lower for LiCl than for KCl. Consequently, the highest flocculation value is for lithium chloride, the series being:

$$Li > Na > K > Rb > Cs$$

instead of the other way round as would be the case if the salting out effect played any appreciable part.

Evidence that this theory is correct is obtained from the experiments with the partially dehydrated gelatin. Here it was shown that the addition of sufficient electrolyte, considerably in excess of the minimum amount necessary to bring about flocculation, actually re-hydrated the sol, this re-hydration being manifested by the sol remaining stable with the higher concentrations of electrolytes and actually becoming water clear although the alcoholic sol without the addition of the electrolyte was opalescent or opaque.

This, then, is the explanation of why we find that all negative sols, such as the lyophobic sols of gold, platinum, As_2S_3, the semi-lyophilic solutions of V_2O_5, Mo_2O_5, Sulphur (Sven Oden's) and the truly lyophilic sols such as agar and negative gelatin (the two latter) when partially dehydrated by alcohol) are least sensitive to the most highly hydrated cation, the series for the flocculation values being:

$$Li > Na > K > Rb > Cs$$

(The aqueous sols of agar and negative gelatin are so highly hydrated as to be stable even when sufficient electrolyte has been added to entirely neutralise the charge; and consequently precipitation is only brought about by salting out following on neutralisation of charge, which means that they will be most sensitive to the most highly hydrated salt).

Provided flocculation can be brought about by the lowering of the potential ζ to a critical potential, and that the hydration is not in itself sufficient to leave the sol stable, this lyotropic influence will be more evident the greater the hydration. Thus in the lyophobic sol and the dehydrated V_2O_5 sol it is quite small, but for the aqueous V_2O_5 sol the hydration of which seems to be considerable the difference between the F.V.'s for the various monovalent cations is very large.

We will not here go into the question of what determines whether a sol is by nature lyophilic or lyophobic, but we may assume that a truly lyophobic sol is incapable of appreciable hydration even when in contact with highly hydrated ions of opposite charge, so that the lyotropic influence is always small. On the other hand, a sol such as V_2O_5 or the partially dehydrated gelatin sol will, on account of the peculiar structure of the particle and the peculiar surface forces characteristic of this particle, tend to have its hydration increased when in contact with highly hydrated ions of opposite charge and this the more readily the greater the hydration of the particle under ordinary conditions; so that lyotropic influence will here be evident.

It should be remembered that the decreased lyotropic influence with the alcoholic vanadium pentoxide may be due not only to the sol being made more lyophobic by the alcohol but also to the influence of the alcohol in dehydrating the ions of the added salts. This dehydration of the salts by the alcohol may be the reason why the lyotropic influence was never so marked with gelatin as with vanadium pentoxide, as alcohol had to be added in a concentration which was no doubt sufficiently high to appreciably dehydrate the ions of the salts before the gelatin became sufficiently sensitive to enable flocculation values to be obtained.

The case of the positive sol is somewhat different. Here we see that the sol instead of being most sensitive to the least hydrated ion of opposite charge (CNS), is more sensitive to the more hydrated ions, the flocculation values being in the order:

$$CNS > I > Br > NO_3 > Cl$$

On first sight it might be thought that this was evidence that the "salting out" influence of the ions in some way came into play much more than in the case of the flocculation of negative sols by cations of the alkali metals. The lithium ion, for example is certainly more hydrated and not less hydrated than the chlorine ion and further not only is there no evidence that positively charged sols are more easily dehydrated than negatively charged sols but on the contrary all the evidence goes to suggest that positively charged sols are more difficult to dehydrate (for example the positive ceric hydroxide sol)[1].

We must then look for the explanation in some other factor. Is this factor to be found in the properties of the positive sols or in the properties of anions as distinct from cations? No factor is to be found in the properties of the sols themselves that does not have its counterpart in the negative sols. If on the other hand we consider the properties of the salts of the anion series we notice one distinct difference from the cation series. While for the cation series

$$LiCl > NaCl > KCl > RbCl > CsCl$$

solubility *decreases* with decreasing hydration of the cation, for the anion series

$$KCl > KBr > KNO_3 > KI > KCNS$$

solubility *increases* with decreasing hydration of the anion. We have then in this anion series an increasing tendency to go into solution running antibatic with the hydration of the anions. Thus, as we go from the chlorine ion to the thiocyanate ion we find an increasing "freedom" of the ion which can increase the solubility of the salt in spite of the decreasing hydration. This same "freedom" of the ion will, when the ion is adsorbed on the surface of the colloid particle, increase the stability of the sol by imparting to the particle a kind of buoyancy — in other words this is a peptising effect which is a minimum with the chlorine ion and reaches a maximum with the thiocyanate ion. Such a tendency exists no doubt also with cations, but would not make itself seen as it would run in the same direction (synbatic) with the increasing hydration of the cations. With the anions, as we have shown, however, it runs antibatic to the hydration and is sufficiently great to bring about the reversal of the series with the flocculation of positive solutions. The preponderance of this effect is no doubt also partly due to the anions being less hydrated than the cations with which they are compared in the experiments.

In this connection it should be remembered that the marked peptising influence of iodine and thiocyanate ions is well known.

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[1] H. R. Kruyt and Miss van der Made, Rec. Trav. Chim. des Pays-Bas 42 277 (1923).

Thus von Weimarn [1] has found that LiCNS and LiI are most active in peptising cellulose (see p. 81).

This then may be taken as the explanation of why the flocculation values for the aqueous positive sols (ferric hydroxide, aluminium hydroxide, dehydrated gelatin) exhibit the lyotropic series in the reverse order to the negative sols. The fact that the lyotropic influence does not become less marked in these sols on the addition of alcohol (in the case of aluminium hydroxide it actually increases) may be assumed to be caused by complications arising out of the superimposing of this additional factor on those already mentioned. As long as we are ignorant of the relative part played by these factors an exact explanation must be impossible.

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[1] P. P. von Weimarn, Kolloid Zeit *11* 41 (1912), *40* 120, 360 (1926).

III — OTHER COLLOIDAL PHENOMENA IN WHICH THE LYOTROPIC SERIES APPEARS

Osmotic Pressure

Lillie[1] describes the strong lowering of the osmotic pressure of protein sols by electrolytes and finds an unmistakable connection with the lyotropic series of the anions. This effect of the electrolyte may be due to its bringing about an aggregation of the protein particles into larger groups as well as its influence on the apparent osmotic pressure through the effect on the membrane equilibrium. There seems however to be no direct evidence to show that this change in osmotic pressure is actually connected with a change in particle size.

Salting Out of Lyophilic Sols

The appearance of the lyotropic series in the salting out of lyophilic sols was first shown by Hofmeister and his pupils[2] who determined the lower limit of concentration at which a sol of white of egg was immediately rendered turbid. The greatest effect was brought about by the most hydrated ion in the series.

Citrate > Tartrate > Sulphate > Acetate > Chloride >
Nitrate > Chlorate

while iodides and thiocyanates do not produce a turbidity in attainable concentrations.

The above series holds for neutral or weakly alkaline sols. In weakly acid sols however (as were first pointed out by Posternak[3] and Pauli[4] in experiments on white of egg sols) the anion series is reversed, being:

$$CNS > NO_3 > Br > Cl > SO_4$$

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[1] Am. Journ. of Physiol. *20* 127 (1907).

[2] Lewith, Arch. experim. Pathol v. Phermakol *24* 1 (1888); Hofmeister ibid *24* 247 (1888).

[3] Ann. de l'Institut Pasteur *15* 85 (1901).

[4] Wo Pauli, Beitr. z. chem. Physiol. u Pathol. *5* 27 (1904).

In the theory we have put forward this might be explained as being due to the hydration of the ion being imparted to the particle. Somewhat similar facts are found for the salting out and increase of solubility of amino acids, the same ionic series varying in the same way when neutral and acid amino acids are compared[1].

Swelling of Gels

It has been stated by numerous workers that for the swelling of gels in salt solutions the lyotropic influence makes itself felt. The $H^\cdot$ ion concentration, however, has a very great influence on the degree of swelling and as no measurements are available in which the swelling in the different salt solutions has been compared at constant $H^\cdot$ ion concentration, the results must be accepted with caution. The lyotropic influence is most marked with anion series. Gels seem to swell more strongly in thiocyanate[2] and iodide solutions than in chloride solutions, while the swelling in chloride solutions is more marked than in sulphates. From Hofmeister's experiments[3] and also Wo. Ostwald's[4] experiments it appears that sulphates hinder swelling while chlorides, nitrates and bromides assist.

The lyotropic series of the cations appears to be less pronounced.

As has already been mentioned the swelling depends greatly on the $H^\cdot$ ion concentration. From the earlier work it would appear that for swelling with different acids the lyotropic series appears. According to Loeb[5] however this difference disappears when allowance is made for the difference in the $H^\cdot$ ion concentration.

Optical Rotation of Proteins

Carpenter[6] carried out measurements of the influence of salts on the optical rotation of gelatin. Although the experiments were

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[1] P. Pfeifer and Würgler, Zeit f. physiol. Chemie *97* 128 (1916).

[2] Meusel, „Ueber die Quellkraft der Rhodanate und die Quellung als Ursache fermentartiger Reaktionen" Gera (1886).

[3] Hofmeister, Arch. f. exp. Pathol. v. Pharmakol. *28* 210 (1891); *27* 395 (1890).

[4] Wo Ostwald, Pflüg. Archiv. *108* 563 (1905); *111* 581 (1906).

[5] J. Loeb, J. of Gen. Physiol. *3* 247 (1920).

[6] D. C. Carpenter, J. Phys. Chem. *31* 1873 (1927).

carried out at a constant hydrogen ion concentration ($P_H = 6.0$) a marked lyotropic series was found. The greatest lowering of the optical activity was brought about by KI, the effect of KBr being less, and that of KCl still less. This is in direct opposition to the view of Loeb. According to Loeb we should expect under these circumstances no specific anion influence, the cation alone exerting an influence on the alkali side of the isoelectric point.

Peptisation of Proteins

Gortner, Hoffmann and Sinclair[1] found a lyotropic series for the peptisation of proteins of wheat flour by equal concentrations of different salt solutions. Thus they found that for normal solutions of the salts KF peptised 13 %, KCl 23 %, KBr 36 %, and KI 64 % of the protein, the anion series being:

$$F < SO_4 < Cl < \text{Tartrate} < Br < I$$

A distinct cation series was also found although this was not so marked.

$$Na < K < Li < Ba < Sr < Mg < Ca$$

(Here again we meet with the Na and K ions in unexpected order).

Measurements of the hydrogen ion concentration showed that the series did not arise from differences in this. The results show in a striking way how inadequate is the usual definition of "globulins".

Similar results were obtained by von Weimarn[2] for the peptisation of cellulose, fibroin, chitin, casein, fibrin and keratin by salt solutions for all of which he found the dispersing power of the salts was as follows:

$$LiCNS > LiI > LiBr > LiCl$$
$$NaCNS > NaI$$
$$Ca(CNS)_2 > CaI_2 > CaBr_2 > CaCl_2$$

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[1] R. A. Gortner, W. F. Hoffmann, and W. B. Sinclair, Kolloid Zeit. *44* 97 (1928).

[2] P. P. von Weimarn, Kolloid Zeit. *11* 41 1912, *40* 120 300 (1926).

IV — CONCLUSION

We have seen then that the same lyotropic series occur for phenomena taking place in colloidal solution as for those taking place in true solution. The spreading of these series, as shown in the flocculation values of various sols is dependent on the hydration of the colloidal particles. This in the case of the vanadium pentoxide sol the spreading is greatly diminished on the addition of alcohol. The well known example of the sulphur sol of Sven Oden (lyophilic) where a large lyotropic influence is found and that of von Weimarn (lyophobic) where the lyotropic influence is small may be cited as another example [1].

In a case of true flocculation of a solution (as distinct from the "salting out" of a sol such as agar by the addition of a *large* quantity of salt) we find that for a negative sol the least hydrated cation has the greatest influence (where monovalent ions are considered). We have shown that the reason for this is that hydrated oppositely charged ions can *hydrate* the particle to some extent and so add to its stability with the result that a larger quantity of salt is required to bring about flocculation. Evidence that this view is correct is obtained from the experiments which show the rehydrating of a dehydrated gelatin sol by the addition of sufficient electrolyte, resulting in a "zone" of flocculation, and also from the relative size and appearance of the precipitates obtained by flocculating a vanadium pentoxide sol with lithium, sodium and potassium chlorides respectively.

The case of the positive sol is different. Here the anion series shows that the most hydrated ion has the greatest effect. Though it naturally occurs to one that this might be due to the hydrated ions exerting a salting out effect, we do not believe this to be the explanation. If the salting out influence of the ions made itself apparent,

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[1] H. Freundlich, „Colloid & Capillary Chemistry" (London 1926) p. 619.

there seems every reason to expect that this would be more apparent in the case of the cation influence on negative sols than in the case of the anion influence on positive sols — so that the series would be just the reverse to what we find.

Consequently we have put forward the suggestion that the sequence of the anions for positive sols depends on another property of the ion, its tendency to go into solution, which for the anion increases with decreasing hydration — this, we suggest exerts a kind of buoyancy to the colloidal particle, and so by counteracting the hydrating effect of the ion brings about a reversal of the series. A similar influence of the cations on negative sols would in this case exist, but as here it would be greatest for the most hydrated ion, it would act in the same direction as the hydration effect and so not bring about a reversal of the series.

Thus for positive sols we have two opposing lyotropic influences. The result of adding alcohol will therefore be more difficult to foretell than in the case of the negative sol. Thus for instance if the influence of the alcohol was to reduce the hydrating effect of the ion without reducing the peptising effect (or reducing this to a lesser degree) we would get a spreading of the lyotropic series in the flocculation values instead of the flocculation values approaching one another. As a matter of fact we found a spreading of the series in the case of the aluminium hydroxyde sol, and no change in the case of the ferric hydroxide sol.

A true salting out effect (taking place in the bulk of the solution) is to be found in the salting out of a lyophilic sol and here also the lyotropic series appears. This however is quite distinct from the lyotropic influence (which is exerted at the surface of the colloidal particle) for the flocculation values of the less lyophilic sols.

Similar lyotropic influences of electrolytes are exerted on other colloidal phenomena. These however need further investigation before conclusions can be drawn. The results at present available are however sufficient to show that a lyotropic series frequently appears which cannot be accounted for by differences in hydrogen ion concentration as Loeb believed.

SUMMARY

(1) The lyotropic series:

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$$

and

$$SO_4 > \mathrm{Cl} > \mathrm{Br} > NO_3 > \mathrm{I} > \mathrm{CNS}$$

have been found to exist for a number of phenomena both in true and colloidal solutions. In none of these is its occurence due to changes in hydrogen ion concentration.

(2) In the case of the solubility influence and allied phenomena the primary cause of the series is the salting out influence brought about by the hydration of the ions.

(3) In solubility influences we find however a specific cation or anion influence for certain substances which cannot be explained in this way. At the extreme end of the series (corresponding to low hydration of ions) even an increase in solubility sometimes occurs.

(4) This has been shown to be due to the fact that ions orientate water molecules and can, under certain circumstances, by bringing about a favourable orientation actually increase the solubility of a nonelectrolyte. This effect is superimposed on the true salting out influence.

(5) The presence of a hydrated ion also influences the equilibrium $nH_2O \rightleftharpoons (H_2O)_n$. From this probably arises the lyotropic influence of the ions in displacing the maximum density of water.

(6) The salting out of a typically lyophilic sol by a large quantity of salt is a dehydrating effect closely connected with the solubility influence in true solution. The lyotropic influence occurs however not only in this phenomenon but in the flocculation values of lyophobic and slightly lyophilic colloids, where precipitation is brought about by a comparatively small quantity of electrolyte — in this case the lyotropic influence is more marked the more hydrated the sol.

(7) Dehydrating the sol with alcohol in some cases reduces the lyotropic influence.

(8) For negative sols the more hydrated the cation, the less its influence in bringing about flocculation. This is because the oppositely charged hydrated ions by introducing favourably orientated water molecules, increase the hydration of the colloidal particles.

(9) For positive sols the more hydrated the anion the greater its influence in bringing about flocculation. We suggest that this is because there is a peptising influence of the anion which is greatest for the least hydrated ion. A similar influence exists for the cations and negative sols, but as here it increases with increasing hydration of the ion it does not reverse the series.

(10) A number of other colloidal phenomena where the lyotropic series occurs are briefly considered. Differences in hydrogen ion concentration are not the cause of the series occurring, as Loeb believed.

STELLINGEN

I

Krishnamurti claims that during the formation of a gel from a gelatin sol, the colloid particles grow in size at the expense of molecularly dispersed gelatin in the intermicellar liquid. He has not shown this to be the case.

Krishnamurti, Proc. Roy. Soc. (A) *122* 76 (1929).

II

The impression given by Hatschek in his book „the Viscosity of Liquids" that the viscosity of lyophilic sols, as a class, depends on the rate of shear is entirely misleading.

Hatschek, „The Viscosity of Liquids" (G. Bell & Sons London 1928).

III

The Budde effect in chlorine is not dependent on the presence of moisture.

Martin, Cole and Lent, J. Phys. Chem. *33* 148 (1929)

IV

The experiments of Stringfellow show conclusively that Baly and Duncan are not justified in assuming that two molecular types of gaseous ammonia exist.

Baly and Duncan, J. Chem. Soc. *121* 1008 (1922).
Stringfellow, J. Chem. Soc. *131* 1 (1929).

V

The theory put forward by Sugden that cations are hydrated and that anions are not hydrated is untenable.

Sugden, J. Chem. Soc. *128* 174 (1926).

VI

Sugden's calculations of the parachors of organic substances have shown that Lowry's statement that most double bonds are semi-polar, and that in organic chemistry a double bond usually reacts as if it contained one co-valency and one electro-valency, is inaccurate.

Lowry, J. Chem. Soc. *123* 822 (1923).
Sugden J. Chem. Soc. *127* 1525 (1925).

VII

Nitrogen can be chemically active and yet show no visible luminosity.

Willey, J. Chem. Soc. *129* 2831 (1927).