

**Chemistry.**— "*On Lyotropy.*" By H. R. KRUYT and CONMAR ROBINSON.

(Communicated at the meeting of April 24, 1926)<sup>1</sup>).

The behaviour of electrolytes in solution is only partially explained by the osmotic theory. There are several properties of solutions of electrolytes which cannot be connected with the number of particles in solution. These properties are found for instance where one investigates the influence of electrolytes on the solubility of non-electrolytes, on reaction velocities, on the salting out of proteins, on the swelling of gels, on the surface tension of water and on the maximum density of water. In all these cases the effect of equimolecular solution is not the same and the influence which the salt exerts is a function of both the cation and the anion. The ions can be arranged in a series which gives the order in which they exert their influence.

A phenomenon not yet mentioned that shows this series is the electric mobility of the ions, which for the alkali metals is just in the reverse order to what we might expect from the size of the atoms. For a long time this has been accounted for by the property of the ions of binding water molecules. The sequence of the lyotropic series will therefore be that of the hydration of the ions. While not denying the truth of this explanation, it is certainly not complete; it can, however, suffice to explain most of the above mentioned phenomena. But to explain, for example, the influence of electrolytes on the surface tension of water one is inclined to turn to the influence of these substances or the molecular aggregation of the water.

Seeing that lyotropy plays so important a part in colloid chemistry, we have set out to investigate those phenomena which can be most easily controled. We first of all wished to show that LOEB's<sup>2</sup>) explanation that the lyotropic series is simply a consequence of alterations in the hydrogen ion concentration is wrong. For this purpose we investigated the influence of the addition of chlorides on the limited miscibility of phenol and water.

As in the meantime DUCKET and PATTERSON<sup>3</sup>) published a similar research, we shall not here quote our results except to say that they showed that KCl and HCl have exactly the same influence, which in itself is a complete refutation of LOEB's theory when extended to cover substances others than proteins.

Subsequently we investigated the solubility influence. We found that

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<sup>1</sup>) Published in this Academy's "Verslag der gewone vergaderingen", Vol. 35, p. 812, (meeting of September 25, 1926).

<sup>2</sup>) J. LOEB, *Proteins and the Theory of colloidal Behavior*, New-York 1922.

<sup>3</sup>) J. DUCKET and W. H. PATTERSON, *J. physic. chem.* **29**, 295 (1925).

systematic data were only available for one substance, namely phenylthiourea<sup>1)</sup>. In recent literature there is a very interesting investigation by LINDESTRÖM-LANG<sup>2)</sup> which prompted us to extend this research in order to establish for certainty certain conclusions which one is inclined to come to when considering his experiments. From his results combined with ours, one is able to draw the following noteworthy conclusions. The influence of salts on the solubility of quinone is only dependent on their anions. With what cation the anion is combined is almost immaterial. With hydroquinone the facts are just the reverse. Here one has a cation lyotropy while the anion plays a very subordinate role. In tables 1 and 2 are given the results of our experiments; those marked with a \* are taken from the work of LINDESTRÖM-LANG (interpolated from 1.5m). In the third column in these tables the solubility in water is given as equal to 100; as the solubility in water in our experiments was not exactly the same as in the experiments of LINDESTRÖM-LANG, we only brought these relative numbers into our tables. In fig. 1 and 2 the results are shown graphically, from which one may see directly the typical anion lyotropy for quinone and the cation lyotropy of hydroquinone.

From LINDESTRÖM-LANG's research it seems that succinic acid and boric acid belong to the hydroquinone type. We have tried to find other substances which belong to the quinone type. Firstly we chose substances which should have a more or less basic character, since the acids mentioned above belong to the type exhibiting cation lyotropy. In tables 3 and 4 are given the figures for meta and para nitroaniline respectively, in table 5 those for para phenylenediamine. In fig. 3 are given the results for salt additions of 0.2 m.

The analysis of the saturated solutions in the case of the nitroanilines was carried out by a specially developed method (potentiometric titration with  $TiCl_3$ ) which has already been published elsewhere<sup>3)</sup>. The solubility of the diamines was determined by precipitation of the diamine with picric acid, filtering off the picrate and back titrating with baryta using methyl red as indicator.

From the figure one sees directly that in all these three cases we have to do with anion lyotropy, exactly as in the case with quinone; there is a great influence of anions and a very limited influence of cations<sup>4)</sup>.

Finally in table 6 are given the results with nitrophenol (see also fig. 3). This gives the impression that here we are dealing with an intermediate case, as the influence of both anions and cations are quite marked.

<sup>1)</sup> V. ROTHMUND, Z. physik. Chem. **33**, 401 (1900); W. BILTZ, *ibidem* **43**, 41 (1903).

<sup>2)</sup> K. LINDESTRÖM-LANG, C. r. Lab. Carlsberg **15**, Nr. 4 (1924).

<sup>3)</sup> I. M. KOLTHOFF et C. ROBINSON, Rec. Trav. Chim. **46**, 169 (1926).

<sup>4)</sup> With phenylenediamine we have a reversal of the series K—Na—Li. We cannot say with certainty how this should be interpreted. There are other cases where Li is found out of its place (cf. V. ROTHMUND, Löslichkeit und Löslichkeitsbeeinflussung p. 153, Leipzig 1906).

TABLE 1.

Quinone		Temperature: 23.75°
Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	13.97	100.0
1.5 m KSCN	23.77	170.1
.. KI	20.89	149.6
.. KNO <sub>3</sub>	18.46	132.1
.. KBr	15.15	108.5
.. KCl	12.63	90.4
.. K <sub>2</sub> SO <sub>4</sub>	8.90	63.7
.. *LiCl	—	77.3
.. *NaCl	—	80.3
.. *RbCl	—	93.8 (18°)
.. CsCl	—	97.6 (18°)

TABLE 2.

Hydroquinone		Temperature: 23.75°
Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	67.64	100.0
1.5 m KI	50.62	74.8
.. KNO <sub>3</sub>	54.09	80.0
.. KBr	47.91	70.8
.. *KCl	—	67.0
1/2 m K <sub>2</sub> SO <sub>4</sub> <sup>1)</sup>	52.72	(1/2 m) = 78.0 of $\left(\frac{1.5 \text{ m}}{2}\right) = 68$
1.5 m *LiCl	—	56.6
.. *NaCl	—	59.1
.. *CsCl	—	95.0

<sup>1)</sup> On account of incomplete solution of the salt, only one determination with 1/2 m. K<sub>2</sub>SO<sub>4</sub> was made. This gave a solubility for hydroquinone of 52.72 grams per litre or 78%. This gives by linear extrapolation a value of 68% for  $\frac{1.5}{2}$  m. K<sub>2</sub>SO<sub>4</sub>.

TABLE 3.

<i>m</i> -Nitroaniline		Temperature 25°
Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	0.8929	100.0
0.2 m KI	0.9527	106.7
.. KBr	0.8857	99.2
.. KCl	0.8619	96.5
$\frac{0.2 \text{ m}}{2}$ K <sub>2</sub> SO <sub>4</sub>	0.8349	93.5
0.2 m LiCl	0.8449	94.6
.. NaCl	0.8514	95.3

TABLE 4.

<i>p</i> -Nitroaniline		Temperature 25°
Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	0.5735	100.0
0.2 m KI	0.6053	105.5
.. KBr	0.5834	101.7
.. KCl	0.5606	97.7
$\frac{0.2 \text{ m}}{2}$ K <sub>2</sub> SO <sub>4</sub>	0.5430	94.7
0.2 m LiCl	0.5430	94.7
.. NaCl	0.5480	95.5

TABLE 5.

<i>p</i> -Phenylenediamine		Temperature 25°
Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	47.23	100.0
0.2 m KI	51.68	109.4
.. KBr	48.68	103.0
.. KCl	46.85	99.2
$\frac{0.2 \text{ m}}{2}$ K <sub>2</sub> SO <sub>4</sub>	43.21	91.5
0.2 m LiCl	48.32	102.3
.. NaCl	47.23	100.0

TABLE 6.

p.-Nitrophenol,		Temperature 25°
Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	11.82	100.0
0.2 m KI	12.45	105.3
.. KBr	11.91	100.8
.. KCl	11.55	97.7
$\frac{0.2 \text{ m}}{2} \text{ K}_2\text{SO}_4$	11.50	97.3
0.2 m LiCl	10.90	92.2
.. NaCl	11.05	93.5

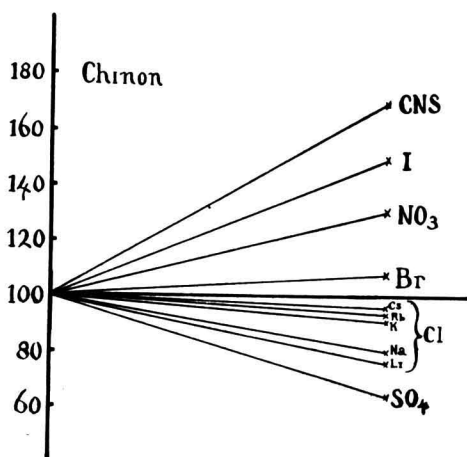


Fig. 1.

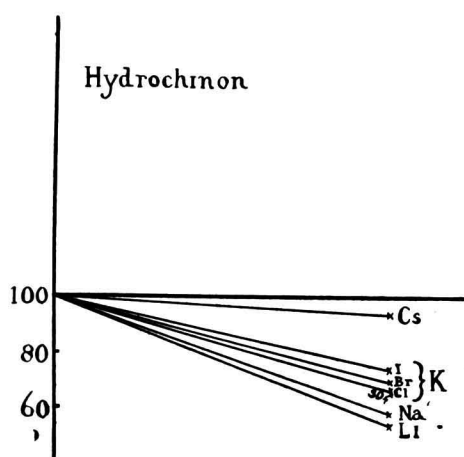


Fig. 2.

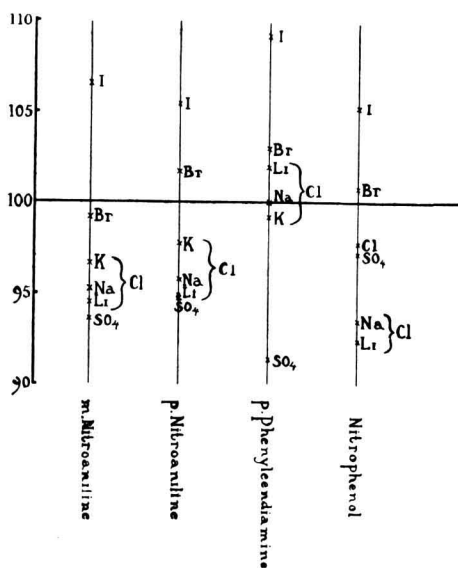
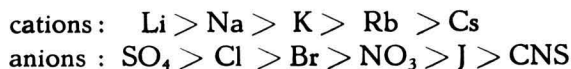


Fig. 3.

The investigations described above are of interest in the understanding of lyotropy. Thus while one usually bases theories of lyotropy on the "neutral salt influence" and the „salting out effect", here we have a marked specific influence of both cation and anion and also the frequent occurrence of an increase of solubility by the added salt.

DEBIJE <sup>1)</sup> has 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. Increase of solubility is not so easily accounted for by this theory and it does not lead us to expect a specific influence of the ions. It seems to us that an explanation may more easily be found in the orientation of the dipoles of the water in the immediate neighbourhood of the ions, that is to say the orientation of the water of hydration, although at present one can only make surmises.

We have already stated that various physico-chemical phenomena show that hydration decrease in the following order :



This in general will be the sequence for the salting out effect, Li and  $\text{SO}_4$  having a strong, and Cs and CNS a weak salting out effect. Hence we always find this series.

The solution of a substance implies an attractive force between the molecules of the substance and those of the solvent. As we may consider this attraction electrical in origin, the water molecules will not only be attracted, but in consequence of their dipolar character they will be orientated. Two kinds of orientation are of course possible: either the positive end or the negative end of the water molecule may be turned towards the solute molecules. Assuming a polar character of the dissolved organic substance, one of these two orientations must preponderate. At the same time however there will be an attraction for one of the ions of the dissolved salt. But also there will be orientated water molecules round these ions.

Now if for example the molecule is anionphilic (we assume that quinone and the amines investigated belong to this class) then the orientation of the dipoles round the anions will favour the orientation round the organic molecules and hence increase their solubility. Cations on the other hand will bring about a decrease in the solubility but their influence will be small since their concentration will be less in the neighbourhood of the organic molecules.

Thus, as well as the ordinary salting out effect there is an increase of solubility brought about (in this case) by the anions. The CNS lowers the solubility very little on account of its low hydration and the increase in solubility will therefore preponderate. The sulphate ion has a strong

<sup>1)</sup> P. DEBIJE, Physik. Z. **26**, 22 (1925).

lowering influence and its lowering influence will therefore preponderate. The influence of the cations is quite subordinate since they are kept further from the molecule. What small influence they do exert will be in the order of their salting out effect. In fact here we have the behaviour of quinone and the nitroanilines investigated. For cationphilic substances (hydroquinone and the acids) an exactly corresponding argument holds.

Seeing the present hypothetical character of these considerations we are at present further developing the theory. We hope later to return to the subject when we will publish our investigations on colloidal systems.

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