

CCCXCI.—*Solubility Influences. Part II. The Effect of Various Salts on the Solubility of Ethyl Acetate in Water.*

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IN Part I of this series (J., 1925, 127, 2660), the influence of the alkali halides and of certain sugars on the solubility of ethyl acetate was described, and it was shown that when the added salt combined with or dissolved in the ethyl acetate the solubility measurements were of little value (compare Philip and Bramley, J., 1915, 107, 377). In continuing these investigations, therefore, only substances which are almost insoluble in the ester have been used, *viz.*, sodium, potassium, and ammonium nitrates; ammonium acetate and oxalate; potassium fluoride, chlorate, and chromate; calcium, strontium, barium, and lead nitrates; barium and cupric chlorides; sodium, potassium, magnesium, nickel, copper, and zinc sulphates; and potassium ferro- and ferri-cyanides.

EXPERIMENTAL.

The experimental details were as described in Part I (*loc. cit.*). Whenever a salt was likely to interfere in any way with the estimation of the ethyl acetate in the solution, the sample taken for analysis was diluted and the ester distilled off. A portion of the saturated solution was always examined to make sure that the hydrolysis of the salt had caused no appreciable decomposition of the ester. All the solubility measurements were made at 25°.

The results have been calculated in exactly the same way as before; m and w represent the number of g.-mols. of added salt and of water, respectively, required to make a solution which will be saturated with 1 g.-mol. of ethyl acetate at 25°. The so-called "hydration number," n , which really gives a measure of the salting-out effect of 1 mol. of salt, is equal to $(w - w_0)/m$, where w_0 , the value of w in pure water at 25°, is 66.15.

As before, the hydration numbers have been extrapolated to infinite dilution of the electrolyte; in some cases extrapolation is very uncertain, and so the values obtained are only approximate. The results of the extrapolation are given in brackets at the bottom of each " n " column.

The results recorded in the earlier paper indicate that the iodides either increase the solubility of ethyl acetate in water, or else reduce it to a small extent; it may be assumed, therefore, that the salting-out power of the iodine ion is negligible, and that it has a "hydration

Sodium nitrate.			Lead nitrate.			Ammonium nitrate.		
<i>m.</i>	<i>w.</i>	<i>n.</i>	<i>m.</i>	<i>w.</i>	<i>n.</i>	<i>m.</i>	<i>w.</i>	<i>n.</i>
0.29	67.3	3.8	0.072	65.9	—	0.32	70.3	12.8
0.82	74.9	10.6	0.20	71.1	24.5	0.87	71.2	5.7
1.86	79.2	7.0	0.49	81.2	30.6	1.83	73.3	3.9
5.58	105.9	7.1	1.04	78.4	11.7	4.41	78.4	2.8
14.25	157.0	6.4	1.92	82.9	8.7	8.29	87.1	2.5
27.25	219.3	5.6			(38 ?)	17.52	117.9	2.9
		(15)						(14)
Ammonium acetate.			Potassium chromate.			Calcium nitrate.		
0.42	71.6	12.9	0.14	71.7	39.3	0.15	66.0	—
1.04	86.7	19.7	0.42	86.4	48.1	0.37	65.9	—
3.03	118.7	17.3	1.25	124.0	46.2	0.83	69.0	3.4
16.04	274.1	12.9	6.70	288.6	33.2	2.08	80.9	7.1
56.53	567.0	8.8	56.16	1436.0	24.4	4.73	101.7	7.5
		(24)			(52)			(?)
Strontium nitrate.			Barium nitrate.			Potassium nitrate.		
0.11	62.4	—	0.047	67.8	34.0	0.25	68.7	10.0
0.30	67.7	5.0	0.098	71.1	50.0	0.68	72.8	9.7
0.74	78.3	16.3	0.20	69.9	18.5	1.51	76.8	7.0
1.74	83.4	9.9	0.41	69.6	8.3	3.69	83.0	4.6
		(40 ?)			(45 ?)			(13)
Barium chloride.			Cupric chloride.			Nickel sulphate.		
0.051	66.7	9.8	0.078	73.0	87.8	0.094	73.0	72.3
0.10	68.1	19.0	0.15	72.9	45.0	0.27	80.1	51.5
0.31	75.6	30.3	0.29	76.0	33.9	0.68	100.4	50.3
0.73	89.7	32.2	0.45	83.3	38.1	2.13	147.4	38.1
1.19	91.6	21.4	0.76	89.0	30.0	6.62	281.2	32.5
3.36	136.8	21.0	1.14	99.4	30.0	17.73	531.5	26.2
		(50 ?)			(110)			(90 ?)
Potassium sulphate.			Ammonium oxalate.			Magnesium sulphate.		
0.073	71.1	67.1	0.097	74.3	83.5	0.11	77.8	101.8
0.16	73.6	46.3	0.20	79.6	67.0	0.33	87.8	64.2
0.49	93.4	55.5	0.35	88.0	62.3	0.78	102.2	46.1
1.04	115.8	47.7	0.52	98.9	62.9	2.86	178.2	39.2
		(75)			(85)			(120)
Sodium sulphate.			Copper sulphate.			Zinc sulphate.		
0.078	69.7	44.9	0.11	78.1	108.2	0.089	71.0	54.0
0.24	83.0	70.0	0.30	81.2	50.0	0.27	83.1	62.6
0.54	98.5	59.8	0.78	102.7	46.8	0.68	103.4	54.7
1.11	124.6	52.6	1.59	132.7	41.8	2.01	142.2	37.8
		(82)			(150)			(72)
Potassium ferricyanide.			Potassium ferrocyanide.			Potassium chlorate.		
0.077	72.0	75.3	0.074	85.0	259.5	0.098	65.4	—
0.22	77.1	49.5	0.21	93.5	130.0	0.20	67.2	5.0
0.53	87.8	40.8	0.52	110.7	85.6	0.32	71.6	17.0
1.44	106.4	27.9	2.04	199.5	65.3	0.41	70.1	9.5
3.34	145.5	23.7			(350)	0.53	69.7	6.6
		(105)						(20 ?)
Potassium fluoride.								
0.53	80.4	26.8						
1.95	119.4	27.3						
8.83	258.3	21.7						
		(29)						

number" of zero. Combining this assumption with the results given here and in Part I, the "hydration numbers" *per equivalent* of various ions at infinite dilution may be readily deduced:

"Hydration" of Ions at Infinite Dilution.

Cations.			Anions.			
Cu ⁺⁺ 44	Ni ⁺⁺ 17	NH ₄ ⁺ 11	Fe(CN) ₆ ^{'''} 75	F ['] 17	ClO ₃ ['] 9	
Mg ⁺⁺ 33	Li ⁺ 17	Rb ⁺ 10	C ₂ O ₄ ^{''} 31	CrO ₄ ^{''} 14	Br ['] 5	
Sr ⁺⁺ 18?	Na ⁺ 14	Zn ⁺⁺ 10	SO ₄ ^{''} 26	C ₂ H ₃ O ₂ ['] 13	NO ₃ ['] 2	
Ba ⁺⁺ 17?	K ⁺ 12	Cs ⁺ 9	Fe(CN) ₆ ^{'''} 23	Cl ['] 10	I ['] 0	
Pb ⁺⁺ 17						

These results indicate that in general the greater the valency of an ion the greater is the salting-out power of one equivalent. A large or complex ion, such as the ferricyanide ion, may, however, have only the same salting-out power as a smaller ion of lower valency.

Discussion.

It is generally accepted that a highly polar liquid will readily dissolve other polar liquids, but not those which are only slightly polar or non-polar (Hildebrand, "Solubility," 1924, p. 85); the greater the difference in polarity the less is the mutual solubility of the liquids. The molecules of water are highly polar and consequently in the liquid state they are held together in a strong electrostatic field; water is therefore said to be "associated." Such a liquid will naturally have a high cohesive power and a large internal pressure, and only a comparatively small solvent power for a non-polar substance like ethyl acetate. When a salt is added to the water the resultant ions will intensify the electrical field and so increase the polarity and the internal pressure (Hildebrand, *op. cit.*, pp. 97, 139; Lewis, *J. Amer. Chem. Soc.*, 1913, **35**, 1448; 1916, **38**, 762), with the result that the solvent power for a feebly polar substance is decreased. The more intense the electrical field produced by the ions of the added salt the greater should be the salting-out power of those ions. If we consider a series of univalent ions (*e.g.*, those of the alkali metals), the electrical field will be most intense in the vicinity of the smallest ion, *viz.*, the lithium ion, and hence the salting-out powers of the ions in the series should follow the order Li > Na > K > Rb > Cs. This order is in agreement with that actually found, and it should also hold good independently of the nature of the non-polar substance being salted out, provided that the salt does not combine with or dissolve in it. If the valency of the ion is increased the salting-out power per equivalent is generally increased too, and this suggests that owing to the concentration of several charges on one ion the electrical field per unit

charge is intensified; this appears to be quite reasonable. If the ion of higher valency is of large bulk, however, the effect of the increased number of charges may be counteracted; this seems to be the case with the ferricyanide ion.

The so-called "hydration number," which represents the magnitude of the salting-out power, is really a measure of the intensity of the electrostatic field surrounding an ion, on the basis of the views outlined above. If we adopt the physical interpretation of ionic hydration, according to which molecules are attracted electrostatically by the charged ion (Born, *Z. Elektrochem.*, 1920, **26**, 401; *Z. Physik*, 1920, **1**, 221; Debye and Hückel, *Physikal. Z.*, 1923, **24**, 305), then the number "*n*," although not representing stoichiometrically the number of water molecules attached to each ion, is still a measure of what might be termed the "hydration effect."

The factors described above cannot, however, be the only ones at work in the process of salting-out. Apart from the difficulty of accounting simply for the "salting-out" power of the sugars (see Part I), we have to explain the abnormal results given by certain substances, *e.g.*, the nitrates. The hydration number of these salts, instead of decreasing with increasing concentration of salt, may be at first negative, then increase to a maximum, and finally decrease gradually. This suggests that two factors are at work; one, responsible for the salting-out effect, is opposed, particularly in dilute solution, by the second, which tends to increase the solubility of the neutral substance. Sugden (this vol., p. 174) has suggested that anions do not salt out at all, but exert to a varying extent a depolymerising effect on the associated water molecules, thus increasing their solvent power for a non-polar substance. A comparison of the salting-out powers of potassium nitrate and potassium ferrocyanide shows that this view is improbable, and that anions actually have a salting-out effect, although it is probably very small for the nitrate and iodine ions. An alternative suggestion is that the reduction of the dielectric constant of water in dilute solutions of electrolytes (Lattey, *Phil. Mag.*, 1921, **41**, 829; Ulich, *Z. Elektrochem.*, 1925, **31**, 413) may have some influence on the intensity of the electrical field in the liquid and so affect the power of dissolving neutral substances.

It is often suggested that there may be some connexion between the hydration of a salt in solution and its tendency to form stable solid hydrates. No such connexion could be detected when the hydration effect of sodium sulphate was determined both below and above the transition temperature between the decahydrate and the unhydrated salt, by measuring the solubility of ethyl acetate in a 7.5% solution of the salt. The results were as follows :

Temperature	10°	25°	38.5°	50°
Hydration number	47.6	54.4	52.0	53.0

These observations should have been made with a saturated solution of the salt, because it is from such a solution that the solid separates, but they show that it is very unlikely that the hydration effect is appreciably less at temperatures well above the transition point than it is below this temperature.

Summary.

(1) The solubility of ethyl acetate has been determined at 25° in solutions of a number of salts at various concentrations. The "hydration number" of each salt has been calculated and, where possible, extrapolated to give the value in a solution of infinite dilution.

(2) In general, the hydration effect of an ion is greater the greater its valency and the smaller its size.

(3) It is shown that the hydration of an ion and its salting-out power may both be due to the electrostatic field existing in the vicinity of the ion.

(4) The iodine and nitrate ions have a negligible salting-out power and frequently cause an increase in the solubility of neutral substances in water.

(5) The salting-out power of sodium sulphate in 7.5% solution appears to be the same below and above the transition temperature of the decahydrate.