CCCXCII.—*Solubility Influences. Part III. The Salting-out Effect of Mixtures on Aqueous Solutions of Ethyl Acetate.*

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THE present investigation on the influence of a mixture of two substances on the solubility of ethyl acetate in water was undertaken not only with the object of contributing to the general problem, but also in order to study a possible method for the detection of complex-ion formation in solution. In the formation of a complex ion, in general, one molecule of undissociated salt and one or more simple ions are removed; hence it appeared possible that the salting-out power of the complex ion might differ appreciably from that of the constituents. By comparing the solubility influence of a mixture of salts which do not appreciably form complex ions (*e.g.*, sodium and potassium chlorides) with the behaviour in a case in which complexes are probably formed (*e.g.*, potassium and cupric chlorides), it was hoped that some light would be thrown on this subject; the results obtained hitherto, however, have given no positive information.

The salting-out effects of the following mixtures, of varying composition, have been examined : Dextrose and sucrose, lævulose and sucrose, sucrose and sodium chloride, sodium and potassium chlorides, ammonium and sodium chlorides, ammonium and potassium chlorides, lithium and sodium chlorides, sodium and barium chlorides, potassium and cupric chlorides, and sodium and potassium nitrates. By a special method of calculation the salting-out effect of a mixture of substances is compared with the sum of the salting-out effects of the two constituents, making use of the results for single substances obtained previously (J., 1925, **127**, 2660; preceding paper).

EXPERIMENTAL.

The experimental method was exactly the same as that already described (*locc. cit.*). All the substances used had been examined earlier in these investigations. The solutions of the mixed substances were prepared by weighing the two separate amounts of the constituents and dissolving them in a known weight of water. The experimental temperature was 25·0° throughout. The columns headed M_1 and M_2 give the number of g.-mols. of each of the substances in the mixture in the order named at the head of each table of results, and w represents the number of g.-mols. of water required to make a solution which will just dissolve one g.-mol. of ethyl acetate at 25°. In pure water, the value of w, *i.e.*, w_0, is equal to 66·15, and $w - w_0$ is a measure of the salting-out power of the $M_1 + M_2$ g.-mols. of the two added substances; for convenience, the quantity $w - w_0$ is regarded as the number of g.-mols. of water "removed" or "fixed" by the mixture of substances. In order to compare the results obtained for the mixtures with those given by the separate constituents, the following method was adopted. From the results given in previous papers (*loc. cit.*), w was plotted against the concentration of added substance, m/w, for all the single substances involved in the present work. From the appropriate curves, the values of w_1 and w_2 corresponding to the concentrations M_1/w and M_2/w were read off; $w_1 - w_0$ and $w_2 - w_0$ then give the number of g.-mols. of water "fixed" by m_1 and m_2 g.-mols., respectively, of the two substances, where m_1/w_1 is equal to M_1/w, and m_2/w_2 to M_2/w. The number of g.-mols. of water "fixed" by M_1 and M_2 g.-mols., respectively, of the two added substances when each is present in solution alone at the same concentration, relative to water, as it exists in the mixed solution will then be given by the expressions $(w_1 - w_0)M_1/m_1$ and $(w_2 - w_0)M_2/m_2$; these two quantities represent the separate salting-out effects of the two constituents of the mixture, and their sum, in the columns headed "$w - w_0$ calc." in Table I, is compared with the experimentally determined value.

TABLE I.

			$w - w_0$.	
M_1.	M_2.	w.	(obs.).	(calc.).
	Dextrose and sucrose.			
0·44	0·48	78·2	12·0	12·2
0·45	0·25	79·0	12·8	11·0
1·05	0·27	85·2	19·0	17·2
1·07	0·57	86·0	19·8	20·3
2·35	0·35	92·0	25·8	28·0
1·36	1·46	95·4	29·2	34·0
0·63	1·39	95·6	29·4	26·3
0·77	2·42	98·4	32·2	37·2
2·84	0·74	101·3	35·1	37·4
1·03	4·38	113·2	47·0	56·1
	Sodium and potassium chlorides.			
2·08	0·77	118·0	51·8	53·4
1·77	1·60	119·5	53·3	62·0
3·34	0·83	123·3	57·1	75·4
2·95	4·58	160·0	93·8	116·9
	Lævulose and sucrose.			
0·48	0·55	81·7	15·5	18·4
0·57	1·22	84·8	18·6	23·3
0·65	2·12	87·6	21·4	31·5
1·12	4·82	126·0	59·8	62·3
	Sucrose and sodium chloride.			
0·27	1·69	104·2	38·0	34·7
0·62	1·85	110·0	43·8	38·5
1·42	1·93	118·1	51·9	50·5
2·88	2·02	128·6	62·4	67·4
2·16	2·11	131·7	65·5	60·1
0·41	4·74	146·0	79·8	79·7
0·85	5·03	153·6	87·4	86·1
0·43	7·90	169·2	103·0	108·4
2·80	8·36	187·4	121·2	143·9
0·97	29·8	333·8	267·6	307·6

The approximate agreement between the observed and calculated values of $w - w_0$ in the results quoted above indicates that for small concentrations the salting-out effect of a mixture of two substances, which do not form complexes, is almost equal to the sum of the separate effects; this is in agreement with the conclusions of Linde (*Arkiv Kemi, Min., Geol.*, 1917, **6**, No. 20, 1) who investigated the salting-out influence of mixtures of sodium sulphate and sulphuric acid (total conc., $N/2$), sodium sulphate and hydroxide (total conc., $N/2$), and sodium chloride and acetate (total conc., N) on an aqueous solution of ether. In more concentrated solutions, however, particularly when dealing with a mixture of two electrolytes, the salting-out influence is seen to be much less than would be expected if each salt exerted its own salting-out power at its particular concentration independent of the presence of the other. This is probably due to an electrical interaction between the two substances, and corresponds with the fact that the salting-out power per molecule of a single substance, in general, decreases with increasing concentration (see previous papers). In order to correct for the mutual interaction of the ions in the mixture, the calculations described above have been slightly altered; in determining the salting-out power of each constituent of the mixture separately, it is assumed that its concentration is equal to the total concentration of the two salts, that is $(M_1 + M_2)/w$, instead of M_1/w or M_2/w. The values of w_1 and w_2 corresponding with this new concentration are then read off from the appropriate curves; from these m_1 and m_2 are determined, where m_1/w_1 and m_2/w_2 are each equal to $(M_1 + M_2)/w$. The number of g.-mols. of water " fixed " by each constituent is then given by the same expressions as used previously. By comparing the results thus obtained for mixtures of sodium and potassium chlorides with those given by the first method, it is seen that there is probably some justification for the assumption of mutual interaction of the ions of the substances in the mixture. The agreement between the observed and calculated values for the salting-out power, even in concentrated solutions, is noteworthy (Table II).

TABLE II.

			$w - w_0$	
M_1.	M_2.	w.	(obs.).	(calc.).
Sodium and potassium chlorides.				
2·08	0·77	118·0	51·8	47·8
1·77	1·60	119·5	53·3	52·6
3·34	0·83	123·3	57·1	63·7
2·95	4·58	160·0	93·8	96·2
7·47	2·70	190·0	123·8	126·9
16·34	4·36	274·2	208·0	214·6
5·57	17·63	274·7	208·5	219·2
13·55	11·12	308·6	242·4	254
36·68	7·16	448·6	382·4	387
Sodium and barium chlorides.				
0·71	0·16	84·3	18·1	19·0
0·92	0·38	93·6	27·4	28·9
0·83	0·60	97·2	31·0	34·6
1·74	0·21	104·9	38·7	37·8
0·88	0·83	105·9	39·7	43·0
3·19	0·25	123·9	57·7	59·5
Potassium and cupric chlorides.				
0·59	0·50	89·9	23·7	25·2
0·57	0·25	92·7	26·5	17·5 ?
1·27	0·27	96·0	29·8	30·9
0·68	0·85	99·0	32·8	36·7
0·73	1·22	104·2	38·0	47·3 ?
3·01	0·43	124·2	58·0	58·5
4·56	0·52	138·5	72·3	76·8
Sodium and ammonium chlorides.				
0·92	0·86	96·3	30·1	29·2
1·98	1·07	116·2	50·0	44·8
Potassium and ammonium chlorides.				
0·59	0·83	91·7	25·5	23·9
1·37	0·93	102·1	35·9	35·0
Lithium and sodium chlorides.				
1·13	0·84	95·4	29·2	30·9
1·38	2·13	119·3	53·1	50·3
Sodium and potassium nitrates.				
0·39	0·34	70·6	4·4	7·5
0·43	0·76	76·3	10·1	8·8
0·46	1·27	77·7	11·5	12·2
0·47	1·64	79·4	13·2	14·6
0·94	0·80	80·5	14·3	13·0
1·46	0·47	82·9	16·7	13·3
1·13	1·91	91·3	25·1	16·5
7·39	1·55	131·9	65·7	53·1

The results obtained for other mixtures show that the salting-out power of a mixture is roughly equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of the ions. In the case of the mixed nitrates, the results appear to be erratic; this is probably due to the fact that these salts do not behave normally when salting-out ethyl acetate. A number of observations have also been made with mixtures of lead and sodium nitrates, lead and potassium nitrates, and lead and barium nitrates; owing to the same uncertainty, the detailed results are not given, but they tend to show, again, that the salting-out effect is additive.

The results obtained for the mixtures of potassium and cupric chlorides, in which complex-ion formation probably occurs, show that the salting-out property of ions cannot be utilised for the detection of complexes in solution. It has been shown (preceding paper) that an ion of high valency has, in general, a larger salting-out power per equivalent than one of lower valency. In the case under discussion, if the cuprichloride complex is bivalent then its salting-out power might be as great as the sum of the salting-out powers of the undissociated chloride and the two chlorine ions from which it is formed; the solubility influence of the mixture of potassium and cupric chlorides would then be the same as it would have been had no complex ion been formed. Although instances may subsequently be found in which abnormal solubility influences correspond with complex-ion formation, yet it is clear that normal results do not indicate an absence of such complexes.

The above results throw no light on the cause of the salting-out effect, because it is obvious that they may be explained equally well by the " hydration of ions " theory (Rothmund, *Z. physikal. Chem.*, 1900, **33**, 401) or by the " electrical stress " theory discussed in the preceding paper.

Summary.

(1) The influence of the following mixtures on the solubility of ethyl acetate in water at 25° has been investigated. Dextrose and sucrose, lævulose and sucrose, sucrose and sodium chloride, sodium and potassium chlorides, sodium and ammonium chlorides, potassium and ammonium chlorides, lithium and sodium chlorides, barium and sodium chlorides, potassium and cupric chlorides, and sodium and potassium nitrates.

(2) The salting-out power of a mixture is, in general, equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of ions.

(3) The salting-out effect cannot be utilised for the detection of complex-ion formation.

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