XCVI.—*Solubility Influences. Part IV. The Salting-out of Aniline from Aqueous Solutions.*

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IN continuation of previous work (Part I, J., 1925, **127**, 2660; Part II, J., 1926, 2935; Part III, *ibid.*, p. 2939) on the "salting-out effect," the influence of various salts on the solubility of aniline in water has now been systematically investigated. It has already been shown that substances which can dissolve in the solute the solubility of which is being determined give abnormal results, and consequently the first stage in the present work involved the examination of the solubilities of various salts and sugars in aniline. The following salts were found to be almost insoluble in aniline at 25° : sodium, potassium, and barium chlorides; sodium, potassium, barium, and strontium nitrates; potassium chlorate, chromate, ferrocyanide, fluoride, acetate, oxalate, carbonate, and hydroxide; sodium, potassium, and magnesium sulphates; ammonium oxalate; and sodium citrate. These substances were all used either alone or in pairs in the quantitative investigation of the "salting-out" of aniline from its aqueous solution. Salts which are hydrolysed to give appreciably acidic solutions could not be used. The following substances were found to be more or less soluble in aniline :

lævulose, glucose, sucrose, lactose; lithium, ammonium, cæsium, and rubidium halides (the fluorides were not examined); sodium and potassium bromides and iodides; ammonium and lead nitrates; copper, zinc, nickel, cobalt, chromium, and cerous sulphates. The last six substances all appear to form addition compounds with aniline; some of these compounds have already been isolated (Tombeck, *Compt. rend.*, 1898, **126**, 967) and the others are now being studied.

Experimental.

The aniline used was obtained by the fractionation of a pure commercial specimen until a portion of constant boiling point was obtained. The salts used were the best commercial products and were, in general, not further purified. The salt solutions were made up by weighing the salt and water; a small quantity of aniline was then added and the mixture was well shaken at a temperature a few degrees above that at which the solubility was being determined. The liquid was then placed in a thermostat at 25° or 50° and allowed to stand until it had become clear. (This procedure was found to be more satisfactory than shaking the mixture at the temperature of the thermostat.) The sample of saturated solution for analysis was removed in a warmed pipette, transferred to a stoppered bottle, and weighed. The amount of aniline present was either estimated directly by the bromine method (Sutton, " Volumetric Analysis," 1924, p. 367), or else the solution was first diluted with water and the aniline distilled in steam; the latter procedure was only adopted when the salts present were likely to interfere with the former method of estimating aniline. Preliminary experiments on the analytical method, in which known weights of pure aniline were used, gave very satisfactory results.

The method of calculating the results was the same as used in previous work (*loc. cit.*); m and w represent the number of g.-mols. of added salt and of water, respectively, required to make a solution which will be just saturated with 1 g.-mol. of aniline at the temperature of the experiment. The so-called " hydration number," n, which is a measure of the salting-out effect of a g.-mol. of the salt, is equal to $(w - w_0)/m$ where w_0, the value in pure water, is 135·7 at 25° and 117·2 at 50°. The hydration numbers have been extrapolated, as before, to infinite dilution of the salt, and the values so obtained, which are often only approximate, are given in parentheses at the bottom of each " n " column. A few results only are given for those alkali halides which were found to be soluble in aniline, in order to show the general tendency in these cases.

Lithium chloride.			Lithium bromide.			Lithium iodide.		
m.	w.	n.	m.	w.	n.	m.	w.	n.
				25°.				
1·27	145·2	7·5	0·54	128·2	—	0·34	125·7	—
32·29	342·4	6·0	6·90	133·1	—	1·69	113·3	—
232·7	843·4	3·0	36·61	118·8	—	4·80	70·9	—
				50°.				
1·10	125·4	7·5	0·48	114·0	—	0·30	110·2	—
31·59	297·6	5·7	6·35	122·7	0·9	1·52	101·5	—
200·1	725·2	3·0	34·37	111·4	—	4·61	68·0	—

Sodium chloride.			Sodium bromide.			Sodium iodide.		
				25°.				
0·95	154·2	20·5	0·49	139·6	7·9	0·32	136·4	2·2
3·03	186·7	16·8	1·29	146·3	8·2	0·87	137·3	1·8
8·38	246·8	13·2	3·17	163·2	8·7	1·80	134·6	—
19·20	345·7	10·9	18·33	244·0	5·9	10·14	126·6	—
73·33	708·2	7·8	59·09	413·5	4·7	31·49	174·2	1·2
		(24)			(?)			(?)
				50°.				
2·66	163·7	17·5	0·44	123·8	15·0	0·28	120·0	9·9
7·44	219·0	13·7	2·80	143·9	9·6	0·76	120·6	4·5
31·82	411·8	7·8	17·15	228·1	6·5	25·52	141·2	0·9
					(18)			(13 ?)

Potassium chloride.			Potassium bromide.			Potassium iodide.		
				25°.				
0·74	148·4	17·2	0·43	140·4	10·9	0·30	137·2	4·9
2·11	166·6	14·6	1·16	146·8	9·5	0·77	134·5	—
5·33	199·4	11·9	2·63	156·8	8·0	1·59	132·1	—
10·43	245·1	10·5	6·88	174·8	5·7	3·62	132·3	—
30·89	383·5	8·0	27·57	273·7	5·0	22·68	139·7	0·2
		(22)						
				50°.				
0·64	129·2	18·7	0·37	121·5	11·5	0·27	119·9	10·1
1·91	150·9	17·6	2·35	140·2	9·8	0·69	119·9	3·9
4·93	184·4	13·6	6·25	162·6	7·3	3·07	112·4	—
16·85	278·9	9·6	25·28	251·0	5·3	20·80	128·0	0·5
					(14 ?)			(13 ?)

Rubidium chloride.			Rubidium bromide.			Rubidium iodide.		
				25°.				
1·13	143·2	6·7	0·75	132·6	—	0·55	124·2	—
7·20	194·6	8·2	3·80	140·6	1·3	2·30	107·6	—
39·96	326·8	4·8	19·58	181·5	2·3	5·82	83·7	—
				50°.				
1·00	126·7	9·5	0·66	116·1	—	0·49	109·5	—
6·61	179·1	9·5	3·52	130·2	3·6	2·12	99·2	—
38·17	312·8	5·1	18·51	171·5	3·2	5·58	80·2	—

Cæsium chloride.			Cæsium bromide.			Cæsium iodide.		
				25°.				
0·74	132·2	—	0·56	126·3	—	0·50	116·9	—
3·59	134·7	—	2·37	111·5	—	1·71	98·5	—
12·68	141·4	0·5	5·86	84·6	—	2·60	69·2	—
				50°.				
0·66	117·5	0·5	0·49	110·9	—	0·44	105·8	—
3·41	130·1	3·8	2·21	104·2	—	1·52	87·2	—
12·75	142·1	2·0	5·92	85·4	—	2·54	67·4	—

Ammonium chloride.			Ammonium bromide.			Ammonium iodide.		
				25°.				
1·05	140·9	4·9	0·49	*127·1*	—	0·34	*131·7*	—
5·82	155·1	3·3	5·23	*116·9*	—	2·82	*90·9*	—
13·94	162·2	1·9	11·93	*97·1*	—	7·31	*39·2*	—
				50°.				
0·95	127·6	10·9	0·43	*111·8*	—	0·30	*115·7*	—
5·42	144·3	5·0	4·76	*103·5*	—	2·41	*77·6*	—
13·72	163·1	3·3	11·15	*90·7*	—	6·25	*33·5*	—

The following results were all obtained at 25°.

Barium chloride.			Potassium nitrate.			Potassium chlorate.		
$m.$	$w.$	$n.$	$m.$	$w.$	$n.$	$m.$	$w.$	$n.$
0·26	142·8	28·2	0·50	138·0	4·6	0·20	137·3	7·9
0·48	148·8	27·1	1·34	142·9	5·4	0·42	139·4	8·8
0·59	151·7	27·3	3·04	153·4	5·8	0·63	140·3	7·2
1·37	169·6	24·8	5·33	169·4	6·3	0·86	141·8	7·1
3·88	218·6	21·3	8·3]	186·5	6·1	1·11	142·9	6·5
		(29)			(?)			(11·5 ?)

Potassium acetate.			Potassium carbonate.			Potassium hydroxide.		
0·55	146·1	19·0	0·42	157·5	52·2	1·06	159·8	22·8
1·54	160·1	15·8	1·45	211·1	52·0	3·69	218·1	22·4
3·90	191·3	14·2	4·90	338·7	41·4	13·10	367·2	17·7
11·84	257·7	10·3	35·26	1084	26·9	78·28	975·0	10·7
30·04	250·6	3·8	502·9	7199	14·2	1055	6098	5·6
83·14	452·7	3·8				4083	12730	3·1
		(23)			(72 ?)			(29 ?)

Potassium chromate.			Sodium nitrate.			Barium nitrate.		
0·29	150·5	51·7	0·62	143·1	12·5	0·09	*133·8*	—
0·88	176·4	46·3	1·67	150·0	8·5	0·19	136·5	4·2
2·33	225·7	38·7	3·98	167·2	8·1	0·29	138·1	8·1
8·37	380·7	29·3	11·94	225·9	7·6	0·40	139·3	9·0
30·35	764·5	20·7	73·35	519·7	5·2	0·51	140·0	8·5
		(60)			(15 ?)			(?)

Strontium nitrate.			Sodium sulphate.			Sodium citrate.		
0·24	136·2	2·1	0·42	162·4	63·9	0·22	156·9	94·8
0·62	138·4	4·3	1·45	216·3	55·6	0·71	192·2	80·0
1·35	142·7	5·2	4·81	345·8	43·7	2·09	270·2	64·4
3·30	155·0	5·9	13·31	599·4	34·8	9·70	555·6	43·3
11·83	208·4	6·1			(74)	18·99	821·4	36·1
		(?)						(115)

Potassium sulphate.			Potassium ferrocyanide.			Potassium oxalate.		
0·15	145·3	63·1	0·19	183·7	250·2	0·35	155·9	58·2
0·33	155·0	59·0	0·40	171·9	91·0	1·08	189·4	49·7
0·76	177·3	54·5	1·04	213·7	74·8	2·92	245·4	37·6
2·09	232·6	46·3	3·58	334·8	55·6	9·14	422·0	31·3
		(72)			(350)			(70)

Magnesium sulphate.			Ammonium oxalate.			Potassium fluoride.		
0·47	158·0	47·1	0·21	144·5	41·7	1·07	168·9	31·1
1·62	201·7	40·7	0·44	153·4	39·9	3·84	235·7	25·6
5·00	300·2	32·9	0·73	162·3	36·5	14·12	410·6	19·5
30·29	1282	37·8	4·04	171·3	34·3			(35)
		(53 ?)			(46)			

The values of w are given in italics in those cases in which the salt causes the solubility of aniline in water to *increase*, hence it is seen that substances which are soluble in aniline (see p. 636) do not salt it out from its aqueous solution. This behaviour, as was the case with ethyl acetate (see Parts I and II), is most marked with iodides and nitrates, and, in fact, at 25° aniline is miscible in all proportions with a 60% solution of lithium iodide in water (compare Part I, p. 2665). We may assume, as before (Part II, p. 2935), that the " hydration number " of the iodide ion is zero, and so we may calculate the following values for the " hydration numbers " *per equivalent* of various ions at infinite dilution :

" Hydration " of Ions at Infinite Dilution.

Kations.				Anions.						
Na·	14	NH₄·	3	Fe(CN)₆''''	75	C₂O₄''	23	C₂H₃O₂'	11	NO₃' 0
K·	12	Sr··	3·0	Citrate'''	24	F'	23	Cl'	10	I' 0
Ba··	4·5	Mg··	2·5	SO₄''	24	CrO₄''	18	Br'	5	
				CO₂''	24	OH'	17	ClO₃'	0	

The " hydration numbers " for most of the kations are distinctly unusual even when determined from experiments on salts which are insoluble in aniline; the abnormality may be connected with the basic nature of the aniline, or it may be due to the hydrolysis of the salts, but further discussion is unprofitable in the absence of sufficient information. For anions, however, the values given above bear a striking resemblance to those obtained from the experiments on the salting-out of ethyl acetate from its aqueous solution. It is again seen that, as a rule, high valency and small size tend to increase the salting-out power of an ion. Rothmund (" Löslichkeit," 1907, p. 152) has observed that, in general, the effect of a salt in reducing the solubility of a neutral substance is independent of the nature of the solute, and the results given above, calculated by a different method, show that this generalisation holds good, in a modified form, for the salting-out of ethyl acetate and aniline.

The Salting-out Effect of Mixtures.—The influence on the solubility of aniline of the following mixtures has been examined at 25° : sodium and potassium chlorides, sodium and barium chlorides, sodium and potassium nitrates, sodium and barium nitrates, potassium and barium nitrates, potassium chloride and nitrate, and sodium chloride and potassium nitrate. The results are given in terms of M_1 and M_2, representing 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) which, when dissolved in w g.-mols. of water, form a saturated solution with 1 g.-mol. of aniline. The

values of $w - w_0$ determined experimentally, given in the columns headed " obs.," are compared with those calculated by the *second* method described in Part III of this series (*loc. cit.*). The agreement

M_1.	M_2.	$w - w_0$. obs.	calc.	M_1.	M_2.	$w - w_0$. obs.	calc.
Sodium and potassium chlorides.				Sodium and barium chlorides.			
1·41	1·10	37·6	40·9	1·36	0·38	32·2	33·8
1·59	2·51	55·8	59·3	1·49	0·84	43·8	46·1
3·35	1·33	65·3	67·5	3·25	0·46	59·3	61·7
3·77	2·96	84·7	86·8	3·60	1·01	74·3	75·4
4·94	7·74	136·6	138·2	4·45	2·50	109·5	108·0
10·99	4·31	167·7	169·2	10·53	1·48	154·5	154·5
14·49	11·36	241·1	243·5	13·28	3·73	208·8	203·0
Sodium and potassium nitrates.				Sodium and barium nitrates.			
0·80	0·68	9·6	9·5	0·80	0·26	8·4	8·6
0·87	1·48	16·4	13·7	0·86	0·61	13·1	11·3
1·77	0·75	18·8	17·9	1·75	0·28	16·9	16·4
1·89	1·59	24·7	24·1	Potassium and barium nitrates.			
2·20	3·70	40·7	40·2				
4·48	1·88	46·3	46·9	0·66	0·27	5·8	5·4
5·36	4·51	66·8	67·1	0·70	0·57	9·6	7·8
				1·42	0·28	11·6	9·9
Potassium chloride and nitrate.				Sodium chloride and potassium nitrate.			
0·98	0·74	18·8	18·6				
1·04	1·54	23·8	23·5	1·32	0·78	27·1	27·5
2·20	0·81	33·0	34·7	1·41	1·66	33·4	32·5
2·33	1·72	38·7	39·2	3·15	0·91	53·1	53·6
2·71	4·00	55·3	55·2	3·36	1·94	60·3	59·9
6·12	2·26	79·9	79·8	3·90	4·51	79·6	76·6
7·25	5·35	104·2	103·5	9·89	2·86	137·3	136·8
				11·7	6·76	167·7	164·9

between the observed and the calculated values of the salting-out powers ($w - w_0$) of various mixtures confirms the conclusion therein reached, that " 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 the ions."

Owing to the fact that so many common salts are soluble in aniline, it was not found possible to investigate the salting-out power of a complex ion, in order to compare the value with that of its constituents.

Summary.

(1) The solubility of aniline has been determined in aqueous solutions of a number of single salts, and of mixtures of salts.

(2) The results obtained confirm the conclusions reached as the result of previous work on the salting-out of ethyl acetate.

(3) The salting-out effect of anions on the solubility of aniline is almost identical with that on the solubility of ethyl acetate, but the results obtained with some kations are quite different.