THE INFLUENCE OF A SECOND SOLUTE ON THE SOLUBILITY OF ORTHO-PHTHALIC ACID.

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That the solubility of a substance in water may be greatly affected by the presence of a second solute (particularly a salt), even when between the two there is no obvious possibility of chemical action, is a commonplace of laboratory and technical practice. It is perhaps difficult in specific cases to state that no chemical action whatever is occurring between two solutes, but numerous cases are on record in which the actual relations of apparent solubility are in the opposite direction from those which one might expect from any likely chemical reaction.

Extensive measurements have been made by various observers on the alterations of solubility brought about by both salts and non-electrolytes, in substances liquid, solid and gaseous when in contact with their solutions.* For the most part measurements with liquid solutes are of small value, since for adequate theoretical treatment the statement of experimental fact should include analyses of both layers (mainly solvent and mainly solute respectively) as they exist in saturation equilibrium. Such complete analyses have seldom been made, and the failure to carry them out has reduced the value of several considerable investigations such as those of Rothmund and Wilsmore† on the solubility of phenol in water, and of Euler‡ on that of ethyl acetate. On the basis of his results, which showed a decrease of solubility of the ester in presence of salts (with the effectiveness of the salts in roughly the same order as they appeared in experiments on gas solubilities), Euler concludes that the action of the salt is probably due rather to the ions than to the undissociated molecules.

Measurements on solids have been made by a number of observers, but little attempt has been made to obtain a quantitative expression for the salt influences exerted, though such is needed before the mode of action of the salt may be understood. The application of the theory of an altered internal pressure in the solution§ consequent on the presence of the salt does not give results consistent with experiment,|| while a simple hydrate theory attributing alterations in solubility to removal of solvent to form solvates gives inconsistent conclusions when applied to different systems.

* For a very full survey of the literature on this subject up to 1911, see J. Vargas Eyre, British Association Reports, "A Report on Solubility," Part I, 447 (1910) and Part II, 820 (1912). Also, up to 1906, Rothmund, *Löslichkeit und Löslichkeitsbeeinflussung* (Barth, Leipzig, 1907).

† Rothmund and Wilsmore, *Zeitschr. phys. Chem.*, **40**, 611 (1902).

‡ Euler, *ibid.*, **31**, 360 (1899).

§ Tammann, *Ueber die Beziehungen zwischen inneren Kräften und Eigenschaften der Lösungen*, 1907; Geffcken, *Zeitschr. phys. Chem.*, **49**, 257 (1904).

|| Levin, *ibid.*, **55**, 527 (1906).

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In a paper on the ionic solubility product of weak acids, Kendall* gives figures for the effect of acids of various ionic strengths on the solubilities of a number of weak organic acids. He comes to the conclusion that alterations effected by other acids in the solubilities of these are of two kinds: (1) A decrease in the dissociated portion consequent on the increased hydrogen ion concentration, together with (2) a decrease or increase of the undissociated portion according as this is more or less soluble in the added acid than in water. Such a possible variation in the so-called "constant undissociated value" was first maintained by Arrhenius.† (1) is governed by the law of mass action where weak acids only are concerned; while (2) is specific for any two solutes. If the second of these be a salt it is obvious that the effect corresponding to (1) will be an increase in apparent solubility owing to double decomposition, while (2) will be what is commonly called neutral salt action, and it should be possible to express it in terms of the concentrations of the ionic and unionized fractions of the salt. The constants in such an expression should be a quantitative measure of these salt actions for ions and molecules respectively. The difficulty is to get rid of the effect (1).

In order to obtain more extensive results than have been hitherto available on the solubility of a single substance in various aqueous solutions, and if possible to find some way of expressing the relative effects of salts and other solutes, measurements have been made on the solubility of ortho-phthalic acid in presence of several concentrations of each of some 26 solutes. A non-dissociated substance would have been preferable, but it is difficult to find a slightly soluble one which can be readily estimated with the necessary accuracy. In saturated solutions, the second dissociation of o-phthalic acid will be slight, and it may be regarded as a weak monobasic acid. For comparison of positive radicles the chlorides of Li, Na, K, Rb, Cs, NH_4 , H, Mg, Ca and Ba have been investigated, and for negative radicles the four halides, three halates, nitrate and sulphate of potassium. In addition there have been included the nitrate and sulphate of sodium, and also acetic acid, mercuric cyanide, ethyl alcohol, and cane sugar (pure and partly inverted). Measurements have been made at $25^\circ \pm 0.01$; with KCl and NaNO_3 at $35^\circ \pm 0.02$ also.

Experimental.

As it is by no means easy to decide the most suitable method of representing concentration, densities have been determined for all solutions, so that the figures quoted on the basis of gram-mols per litre are available on any other basis of representation. Molar concentrations are used, unless otherwise stated, as they are more reasonable than equivalent concentrations when non-electrical properties in other than very dilute solution are concerned.

The method of obtaining saturation with phthalic acid was to shake an excess of twice crystallized acid with the solution under consideration in sealed glass tubes which had previously been steamed for from eight to ten hours. The tubes, eight to each salt, including, usually, one with pure water as a check, were shaken overnight in a modified Noyes apparatus, saturation being always attained in considerably less than this time. In some cases the solutions were heated before immersal in the bath, saturation being attained more rapidly from the side of supersaturation. Samples of about 30 c.c.

* Kendall, *Proc. Roy. Soc., A*, **85**, 200 (1911).

† Arrhenius, *Zeitschr. phys. Chem.*, **31**, 197 (1899).

were removed by a pipette carrying a cotton-wool filter, and duplicate titrations, against standard solutions of baryta with phenolphthalein as indicator, were made on each tube. These were carried out by weight: the bulk of the acid was neutralized by 0.1-equivalent normal baryta, and the end point determined with 0.02-normal. The differences between duplicate titrations of the same tube were seldom as great as 1 in 500. But completely different sets of measurements of the solubility in pure water showed differences as high as 1 in 200, which may be regarded as the possible experimental error of the work. Densities, determined with pycnometer or pipette, are correct to 1 in 5,000.

With potassium fluoride all tubes, pipettes, and beakers were coated internally with paraffin wax. With ammonium chloride difficulties in the way of titration made it necessary to adopt another method, namely, that of determining gravimetrically on a Gooch filter the phthalic acid remaining undissolved after shaking a known amount of solution with a known excess of acid. For the acids, hydrochloric and acetic, still another method was used, the estimation of a very small amount of phthalic acid in presence of a large excess of another acid not being accurate by titration. The form of tube used is shown in Fig. 1.

A rubber cap A fits on a narrow tube widened to a bulb B about $\frac{1}{8}$ inch in diameter. This bulb is crossed at its greatest diameter by a perforated platinum plate sealed all round its edge to the glass. A thick asbestos pad *b* almost fills the lower part of the bulb. C is the ordinary steamed tube, and is continued into a narrow tube carrying a tap D (lubricated with a mixture of rubber, paraffin wax, and oil) and turned upwards at the end. E is a rubber cap.

Solid phthalic acid is placed in C, slightly moist, before the filter tube B is sealed in position. The whole tube is then dried by immersion in a wide tube in a bath at 85°, while a current of dried air is drawn through it. When dry and cool it is weighed, and the solution to be examined is drawn in through D by suction at B. When sufficient has entered, the tap D is turned off and liquid in the tube beyond D removed with filter paper. The full tube is weighed and the weight of solution obtained. Caps A and E being fastened in position, the tube is shaken in the thermostat as long as necessary. The saturated solution is then drawn off (while the tube is still in the bath) through the filter *b*, the tube being drained as thoroughly as possible. It is then dried and weighed, and the difference between the first and last weighings gives the weight of acid dissolved. The method is fairly rapid, and though more accurate than a long evaporation of filtered solution, it is less so than the method used for the salts, and the worst error in reproducing results is 1 in 80.

Either Merck's guaranteed or Schuchardt's puriss. salts, twice or thrice crystallized, were used. The phthalic acid was Merck's, and was twice crystallized.

Table I contains a summary of the experimental results. The solubilities of phthalic acid are given in terms of the value in pure water determined in the same set or the preceding one. The value for this in gm.-mol per litre is 0.04185, this value being the mean of the following separate determinations, each the mean of two titrations (the figures are multiplied by 10⁴): 419, 418, 418, 418, 418, 418, 420, 417, 420, 419, 418, 418, 418, 418. Density of saturated solution is 1.0022.

FIG. 1.

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TABLE I.

Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
LiCl ...	0.0827	1.0043	0.985	0.984	- 0.1
	.1957	1.0072	.950	.944	- 0.6
	.3322	1.0104	.902	.898	- 0.4
	.5354	1.0152	.827	.831	+ 0.5
	.815	1.0217	.737	.745	+ 1.1
	1.250	1.0320	.616	.618	+ 0.3
	1.727	1.0430	.497	.490	- 1.4
NaCl ...	0.1271	1.0072	0.982	0.985	+ 0.3
	.2439	1.0119	.952	.952	0.0
	.4934	1.0219	.880	.883	+ 0.3
	.9697	1.0404	.751	.752	+ 0.2
	1.601	1.0652	.591	.586	- 0.8
	2.203	1.0868	.476	—	—
	2.978	1.1131	.363	—	—
KCl ...	0.0957	1.0067	1.013	1.0165	+ 0.35
	.2571	1.0139	.995	0.998	+ 0.3
	.5549	1.0279	.954	.954	0.0
	.8635	1.0415	.904	.905	+ 0.1
	1.299	1.0606	.830	.831	+ 0.1
	1.808	1.0823	.744	.744	0.0
	2.690	1.1195	.610	—	—
RbCl ...	0.0779	1.0088	1.016	—	—
	.2459	1.0232	1.023	—	—
	.4558	1.0420	1.009	—	—
	.772	1.0695	0.978	—	—
	1.142	1.1009	.937	—	—
	1.598	1.1370	.883	—	—
	2.085	1.1810	.821	—	—
CsCl ...	0.0692	1.0106	1.026	—	—
	.1961	1.0270	1.043	—	—
	.3444	1.0459	1.052	—	—
	.5653	1.0742	1.058	—	—
	.804	1.1043	1.058	—	—
	1.144	1.1473	1.050	—	—
	1.476	1.1881	1.032	—	—
NH ₄ Cl ...	0.0587	1.003	—	—	—
	.1403	1.005	0.99	—	—
	.286	1.007	.96	—	—
	.580	1.012	.92	—	—
	.888	1.016	.885	—	—
	1.350	1.023	.82	—	—
	1.895	1.031	.735	—	—
MgCl ₂ ...	0.0628	1.0073	0.988	0.986	- 0.3
	.1236	1.0117	.951	.945	- 0.7
	.2090	1.0229	.855	.855	0.0
	.4212	1.0344	.765	.767	+ 0.3
	.655	1.0532	.635	.636	+ 0.2
	.9215	1.0712	.507	(.498)	(- 2.0)
	1.317	1.0988	.365	—	—

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Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
CaCl ₂ ...	0.0442	1.0065	1.005	1.001	-0.4
	.0877	1.0103	0.974	0.975	+0.1
	.2945	1.0287	.861	.857	-0.5
	.4576	1.0417	.768	.772	+0.7
	.6716	1.0608	.667	.659	-1.0
	.861	1.0766	.584	.585	+0.2
	.948	1.0843	.546	.547	+0.2
	1.461	1.1262	.374	—	—
	3.038	1.2500	.117	—	—
	4.299	1.3433	.0673	—	—
BaCl ₂ ...	0.0488	1.0110	0.997	0.999	+0.3
	.0956	1.0160	.971	.974	+0.3
	.1770	1.0359	.934	.933	-0.1
	.3103	1.0590	.877	.872	-0.6
	.4615	1.0854	.811	.810	-0.1
	.676	1.1250	.714	.729	(+2.1)
HCl ...	0.217	1.006	0.768	0.766	-0.3
	.639	1.013	.697	.698	+0.2
	1.175	1.020	.620	.613	-1.2
	1.915	1.034	.494	.494	0.0
	1.936	1.035	.486	.490	+1.0
KBr ...	0.0846	1.0095	1.013	(1.021)	(+0.8)
	.1760	1.0170	1.010	1.015	+0.5
	.3295	1.0300	0.996	1.000	+0.4
	.5586	1.0486	.971	0.973	+0.2
	.808	1.0693	.938	.944	+0.6
	1.828	1.1523	.785	.782	-0.3
KI ...	0.0963	1.0139	1.014	—	—
	.1893	1.0248	1.029	1.034	+0.5
	.3623	1.0451	1.021	1.023	+0.2
	.6713	1.0823	1.000	0.998	-0.2
	1.250	1.1502	0.947	.941	-0.7
	1.510	1.1800	.913	.912	-0.1
	1.981	1.2333	.851	.849	-0.2
NaNO ₃ ...	0.2518	1.0132	1.004	1.006	+0.2
	.487	1.0242	0.981	0.981	0.0
	.998	1.0469	.923	.922	-0.1
	1.488	1.0678	.861	.861	0.0
	1.962	1.0885	.795	.799	+0.6
	2.463	1.1097	.731	.729	-0.3
	2.981	1.1368	.667	.658	-1.4
Hg(CN) ₂ ...	0.0304	1.008	1.003	1.005	+0.2
	.0668	1.016	1.011	1.011	0.0
	.1733	1.036	1.030	1.030	0.0
	.2959	1.060	1.050	1.050	0.0
	.4000	1.080	1.069	1.068	-0.1
C ₂ H ₅ OH ... (Schuch. 99½ per cent.)	0.1015	1.0019	1.014	1.015	+0.1
	.1930	1.0008	1.027	1.028	+0.1
	.3723	0.9994	1.058	1.054	-0.4
	.646	.9970	1.097	1.094	-0.3
	.946	.9934	1.143	1.137	-0.5
	1.433	.9814	1.235	—	—
	2.026	.9829	1.366	—	—

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Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
Cane sugar	0'1547	1'0230	0'974	0'976	+ 0'2
	'2962	1'0413	'955	'956	+ 0'1
	'5199	1'0637	'909	'907	- 0'2
	'950	1'1245	'864	'857	- 0'7
	1'426	1'1860	'822	'786	(- 4'5)
Cane sugar partly in- verted.	0'0804	1'014	0'983		
	'1930	1'029	'957		
	'399	1'056	'914		
	'620	1'086	'862		
	1'255	1'172	'799		
	1'950	1'253	'578		
KF ...	0'1147	1'0108	2'448		
	'2925	1'0245	4'434		
	'5746*	1'0412	6'410		
K(C ₂ H ₃ O ₂)	0'0893	1'0110	3'040		
	'1984	1'0216	5'536		
	'3291	1'0280	7'04		
	'3384	1'0352	8'64		
	'547*	1'0453	11'9		
KNO ₃ ...	0'1058	1'0085	1'029		
	'1935	1'0140	1'042		
	'3353	1'0243	1'056		
	'5447	1'0355	1'058		
	'902	1'0567	1'056		
	1'100	1'0682	1'052		
	1'269	1'0788	1'042		
	1'622	1'0995	1'019		
	2'196	1'1321	0'977		
K ₂ SO ₄ ...	0'0265	1'0056	1'073		
	'0424	1'0079	1'102		
	'1063	1'0167	1'173		
	'2104	1'0310	1'231		
	'3721	1'0552	1'282		
	'6271	1'0854	1'312		
KClO ₃ ...	0'0282	1'0034	1'013		
	'1051	1'0095	1'023		
	'2085	1'0180	1'030		
	'3041	1'0252	1'029		
	'4055	1'0327	1'028		
	'5109	1'0406	1'026		
	'6126	1'0483	1'016		
KBrO ₃ ...	0'0192	1'0040	1'014		
	'0611	1'0099	1'023		
	'1312	1'0180	1'029		
	'2306	1'0300	1'033		
	'3902	1'0398	1'030		
	'4300	1'0432	1'027		

* At the next higher concentration, potassium hydrogen phthalate separated.

Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
KIO ₃ ...	0'0147	1'0043	1'011		
	'0317	1'0077	1'023		
	'0924	1'0186	1'061		
	'1525	1'0294	1'089		
	'2314	1'0433	1'125		
	'2901	1'0537	1'145		
	'3716	1'0678	1'176		
Na ₂ SO ₄ ...	0'0541	1'0088	1'048		
	'1428	1'0200	1'088		
	'567	1'0704	1'072		
	'898	1'1082	0'952		
	1'205	1'1418	'833		
	1'517	1'1750	'721		
H(C ₂ H ₃ O ₂)...	0'1905	1'003	1'034		
	'3484	1'004	1'063		
	'732	1'008	1'177		
	1'039	1'011	1'245		
	1'523	1'016	1'372		
	2'016	1'020	1'575		

The results are graphically shown in Figs. 2 and 3, where the order of effect of the various solutes is at once obvious. Molar concentration of solute is here plotted against relative solubility of phthalic acid in the solution, and each vertical division is a decrease of 0'1 in the latter. The general form of curve is the customary one of a more or less considerable initial rise followed by a more or less sharp fall.

Since phthalic acid is a weak electrolyte, some double decomposition with the salts is to be expected, and this is evidently represented in this initial rise. In those cases where a maximum (in some it is not very high) is reached and passed the decrease of solubility consequent on the so-called neutral salt effect has overcome the increase caused by double decomposition. The apparent increase will of course be greatest in the cases of salts of acids comparable in ionic strength with phthalic acid. Thus with potassium acetate and fluoride the immediate increase in solubility of the acid is very great, the rise being from 0'0418 to 0'45 molar normal, at which point potassium hydrogen phthalate begins to separate. This rise is too rapid to be shown in the figures.

When the curves are considered in order, it is apparent at once that in general it is the least electro-positive element which exerts the greatest depressing effect among the chlorides, both in the univalent and divalent metals. The curve for ammonium chloride is represented by dots to indicate that the experimental error in its determination is greater than that for the other salts. Among potassium salts, the order of effect among negative radicles is the same, that is to say, the most electro-negative or least electro-positive anion has the greatest depressing effect. Oxy-radicles give maximum points very high.

Comparing the pairs of salts of sodium and potassium in Fig. 3 (III) it is seen in each case that the sodium salt lessens the solubility more than the corresponding salt of potassium. Lundén* found the same thing in his work on ethyl acetate with salts of these two metals.

* Lundén, *Journ. Chem. Soc., Abst.*, **102**, ii. 911 (1912).

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To test whether there is a temperature coefficient to the effect of the salt upon the solubility of the acid, as is to be expected where chemical action in the ordinary sense is the main factor, measurements have been made with two salts at 35°, viz., KCl and NaNO₃. The results are detailed in Table II, and the relative lowerings at 25° and 35° are plotted in Fig. 4. It is clear that there is a temperature coefficient, but for part of their lengths the curves, especially those for KCl, run almost parallel. This is interesting, as it may

FIG. 2.†

be that in these latter portions of the curves a purely physical influence, without any considerable temperature coefficient, is concerned, while at the beginning of the curves the phenomenon is mainly chemical and with a coefficient. It will be seen that the lowering of solubility (value in pure water at the respective temperature = 1.000) is greater at the higher temperature than at the lower, as Hoffmann and Langbeck* found for other acids.

* Hoffmann and Langbeck, *Zeitschr. Phys. Chem.*, **51**, 385 (1905).

FIG. 3.

TABLE II.

Temperature 35°. Solubility of Acid in Pure Water = 0.0610 norm.

Salt.	Salt Conc.	Density.	Relative Solubility (Expt.).
KCl ...	0.0761	1.0063	1.006
	.1603	1.0097	0.989
	.339	1.0180	.972
	.674	1.0328	.917
	1.011	1.0480	.860
	1.541	1.0702	.766
	2.058	1.0925	.678
NaNO ₃ ...	0.0748	—	1.0024
	.1708	1.0066	0.998
	.396	1.0248	.964
	.745	1.0423	.912
	1.125	1.0629	.848
	1.727	1.0940	.754
	2.294	1.1226	.663

Further Discussion of Results.

In terms of any simple theory of solutions, it is not possible to explain fully such results as are here given, but it is worth while to bring forward certain points of interest in the curves.

Any attempt to differentiate between the action of ions and undissociated salt molecules in these solubility phenomena brings one at once to the difficulty of finding a proper expression for the degree of dissociation of the salt. Calculations based on conductivity measurements are to be suspected because nothing certain is known as to the relations between ionic mobility and solution viscosity. Values deduced from freezing-point measurements are probably worse. All that can be done is to admit the possibility of error and take the least objectionable course of using degrees of dissociation calculated from conductivity data in the ordinary way.

A further difficulty in discussing the curves of Figs. 2 and 3 is presented in the initial portion. The rise is doubtless due in part to chemical double decomposition, but since salts do not dissociate in accordance with the simple law of mass action it is not possible to obtain an accurate expression for it. Some of it may be due to increased dissociation of the acid.* But it will be noticed that in a number of cases this initial rise is comparatively slight, the influences tending in the direction of lessened solubility soon exceeding those

FIG. 4.

giving an increase in apparent solubility. As salt concentration increases, the latter will not increase proportionately and at a sufficiently high concentration it will be slight compared with the decrease due to the so-called neutral salt action. In fact, the form of the latter part of the curve will be determined mainly by the direct action (of whatever kind) of salt ions and molecules on the solubility, but not double decomposition, of the acid. If then this curve be extrapolated to cut the relative solubility axis, a value S_0 will be obtained, representing approximately what the concentration of phthalic acid would be in pure water if those conditions alone ruled in approaching it which determine the latter part of the curve, beyond the initial maximum. Putting S as the calculated solubility we should have—

$$S = S_0 \{ 1 + kaC + k'(1 - \alpha)C \}$$

where α is the degree of dissociation of the salt at concentration C , calculated from the best figures quoted in Abegg's *Handbuch*. Here it is assumed that the salt action is exerted on all the dissolved acid, not merely on the undissociated fraction: for the testing of a relation between salt concentration

* Bohdan von Syzskowsky, *Zeitschr. phys. Chem.*, **58**, 420 (1907); **63**, 421 (1908); **73**, 269 (1910).

and undissociated acid, as suggested by Kendall,* more information is required than is available regarding the dissociation of phthalic acid in presence of salts, especially if it is possible that the extent of this dissociation is greatly affected by the salts.

Choosing suitable values for k and k' , which we may call the ionic and molecular constants of "neutral salt action" respectively, the values in column 5 of Table I (here expressed in relative figures) are obtained, and in the 6th column are the percentage differences between these and the figures obtained by experiment. It is possible to calculate for those salts only where the initial rise of the curve is slight, but in the list of those examined there are ten available for such calculation, as is hydrogen chloride also. k is calculated as the constant for a single chlorine ion plus its positive partner, that is, concentrations are calculated in equivalents. For convenience equivalents have been used also for k' , though where molecules only are concerned, the molar concentration is the more reasonable. The values of S_0 , k , and k' are summarized in Table III.

TABLE III.
Ionic and Molecular Constants of "Neutral Salt Action."

Salt.	S_0 .	k .	k' .
HCl	0.0330	-0.20	-0.20
LiCl	.0425	-0.41	-0.16
NaCl	.0428	-0.30	-0.21
KCl	.0431	-0.057	-0.415
$\frac{1}{2}$ MgCl ₂	.0430	-0.395	-0.18
$\frac{1}{2}$ CaCl ₂	.04325	-0.40	-0.096
$\frac{1}{2}$ BaCl ₂	.0430	-0.395	-0.00
KCl	.0431	-0.057	-0.415
KBr	.0427	+0.115	-0.85
KI	.0433	+0.102	-0.71
NaNO ₃	.0430	-0.072	-0.16
Hg(CN) ₂	.0420	—	+0.085
C ₆ H ₅ OH	.0418	—	+0.145
C ₁₂ H ₂₂ O ₁₁	.0420	—	-0.15

Looking at the figures in column 6 of Table I, it is seen that except in the stronger salt solutions, where the calculation of the degree of dissociation is very uncertain by reason of ignorance of the relation between ionic mobility and solution fluidity, the percentage error in the calculated relative solubility as compared with the found fluctuates irregularly, and seldom reaches the limit of error of the determinations. In fact, one is able to express with considerable accuracy the decrease of saturation concentration of phthalic acid in terms of the concentrations of the added ions and molecules.

The constants involved are nearly all negative, and for the three ions of potassium, sodium, and lithium (each with chlorine) k increases, while for the chloride molecules k' decreases arithmetically as positivity decreases. For the second group metals the opposite holds for k' , while the ionic constants are practically identical for all three, having a slightly lower value than that of the lithium and chlorine ion pair.

* Kendall, *loc. cit.*

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Comparing the three halides of potassium, it is seen that the order of constants is not that of the anion atomic weights, and for the bromide and iodide the ionic constants are positive. This latter fact is rather unexpected, though there would seem to be no reason why positive ionic constants should be considered unlikely. It is not possible to separate the effects of any two oppositely charged ions, but it would seem probable, when one considers the ionic constants for the various chlorides, that the value is strongly negative for the ions of chlorine, lithium, sodium, barium, calcium, and magnesium, and possibly positive for potassium and nitrate ions (and possibly the anions of sulphate and oxyhalides). In the case of hydrochloric acid (Fig. 3, II), for which the ionic and molecular constants of the later part of the curve are equal, there is at the initial portion of the curve a rapid drop due to the common hydrogen ion. But in the case of the other acid examined, acetic, either the small amount of acetate ion present, or, more likely, the acid molecules, exert so strong a positive effect as completely to overwhelm any decrease in solubility due to the common ion. The formation of a soluble compound between the two acids, acetic and phthalic, naturally suggests itself to account for this, but any such formation would probably be due to the oxygen in the molecules, and therefore one would expect to find in aqueous solution a considerable hydration of acetic acid. But judged by freezing-point measurements this does not seem to be the case to any considerable extent, as the lowerings in acetic solutions are not greatly different from those calculated on simple theory. A positive action, possibly not chemical in the ordinary sense, therefore seems likely, and in that case it is not improbable that ions and salt molecules may also have positive effects.

Undissociated solutes can possess but one constant—that is, the curves of relative solubility of phthalic acid should be straight lines. To about 1 in 200 this is the case in solutions of ethyl alcohol and cane-sugar up to 1-normal, the constants being here positive and negative respectively. The case of mercuric cyanide is probably accounted for by double decomposition; it gives a very good straight line with k' positive.

Whatever may be the mechanism of the action which shows itself in the altered solubility in presence of salts, of such a solute as phthalic acid, whether it be hydrate formation and consequent removal of water from its solvent rôle or “secondary” influences not properly regarded as chemical, some connection may be expected between the degree of reduction of solubility and the amounts of the various new constituents present as the result of salt addition. Possibly the number of these (ions and molecules, variously complex and hydrated) is so great that so many constants become necessary as to make the resulting equation worthless when applied to results liable to experimental error. But it is at any rate of interest to see, as may be done to some extent in the present case, how far a relation can be applied which takes account of the two main portions of the dissolved salt.

A comparison of various forms of so-called neutral salt action such as are shown in freezing-point lowerings,* solubility alterations, changes in reaction velocity,† and in rate of diffusion,‡ seems to show that the order of effect of the salts is not such as to justify a supposition that a specific salt property is the common and sole cause in all cases. The sequence of salt effect may be different in these different cases, or even in the same case, such as that of freezing-point lowering, with different second solutes. Any constants, therefore, which connect salt concentration with the modified

* Rivett, *Zeitschr. phys. Chem.*, **80**, 537 (1912).

† *Idem*, *ibid.*, **85**, 113 (1913).

‡ Abegg, *ibid.*, **11**, 248 (1893).

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property of a second solute would seem to depend, not only on the nature of the salt, but also on that of the particular second solute (possibly with varying temperature coefficients in either case). Until the latter factors can be allowed for, it does not seem probable that a *prima facie* likely common cause can be quantitatively demonstrated in the various phenomena grouped together loosely as examples of neutral salt action.

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