THE ACTIVITY COEFFICIENT OF NON-ELECTROLYTES IN AQUEOUS SALT SOLUTIONS FROM SOLUBILITY MEASUREMENTS. THE SALTING-OUT ORDER OF THE IONS

MERLE RANDALL AND CRAWFORD FAIRBANKS FAILEY
University of California, Berkeley, California

In the preceding paper we studied the activity coefficient of gases dissolved in aqueous salt solutions. It was found that the quotient of the logarithm of the activity coefficient of the dissolved gas by the ionic strength, μ, of the salt was approximately a constant.

If the activity of the non-electrolyte is determined by having a solid phase in equilibrium, rather than by the pressure of a gas, the accuracy of the results should be greater. In the present paper we study the activity coefficient of iodine, phenylthiourea, and *o*-nitrobenzaldehyde.

The solubility of these substances in water is small and we may take the activity, a, of the non-electrolyte in its saturated aqueous solution equal to its molality, m°, and its activity coefficient, γ_u, is, therefore, unity. In the presence of the salt, since the solid phase is present, $a_2 = m\gamma =$ constant. Hence, the activity coefficient in any salt solution is given by the expression, $\gamma_u = m^\circ/m$, where m is the molality of the non-electrolyte in the salt solution.

Linderström-Lang (1) in a recent paper has investigated the effect of a large number of salts on the solubilities of hydroquinone, quinone, succinic acid, and boric acid. He calculated the quantity $(\log(S^\circ/S))/c$ where S° is the solubility in pure water of the substance investigated, expressed as mols per liter, S its solubility in the salt solution, and c the equivalent concentration of the salt. This quantity $(\log(S^\circ/S))/c$ was found to be approximately constant for a given saturating substance and a single salt at different concentrations, increasing with concentrations of salt in some cases, in others decreasing. We do not have the necessary density determinations to enable us to calculate (log γ_u)/μ. From approximate densities we estimate that this quantity will also be approximately constant, its variation being in some cases greater, in some less, than Linderström-Lang's expression.

TABLE 1

Activity coefficient of iodine[2] *in aqueous salt solutions*[1]

Solubility in water = 0.001321 M at 25°—0.001815 M at 35°

SALT	μ	γ_u	$\frac{\log \gamma_u}{\mu}$	SALT	μ	γ_u	$\frac{\log \gamma_u}{\mu}$
Na_2SO_4, 25°	1.267	1.376	0.1094	$NaNO_3$, 25°	6.455	2.204	0.0532
	1.997	1.653	0.1093		7.787	2.613	0.0536
	4.095	2.784	0.1086		9.302	3.161	0.0537
	5.166	3.628	0.1083				
				$NaNO_3$, 35°	0.2376	1.000	0.0000
Na_2SO_4, 35°	0.224	1.028	0.0535		0.4241	1.022	0.0223
	0.499	1.116	0.0955		0.8651	1.083	0.0400
	1.095	1.298	0.1034		2.222	1.220	0.0389
	2.122	1.619	0.0986		4.818	1.627	0.0439
	3.666	2.459	0.1066		7.898	2.287	0.0455
	5.646	3.897	0.1046		11.81	3.270	0.0436
	7.155	5.657	0.1052				
	9.843	10.72	0.1047	NaH_2PO_4, 25°	0.5897	1.227	0.1507
	10.45	12.67	0.1056		1.218	1.478	0.1393
					1.883	1.763	0.1308
$NaNO_3$, 25°	0.736	1.072	0.0410		2.597	2.036	0.1189
	1.469	1.178	0.0484		3.355	2.665	0.1269
	2.120	1.287	0.0517		5.044	5.535	0.1473
	4.063	1.641	0.0529		5.987	13.22	0.1873
	4.991	1.904	0.0560				

[1] The numerical citations in these tables are to the corresponding references.

The measurements of Carter (2) on the solubility of iodine, of Biltz (3) and of Rothmund (4) on the solubility of phenylthiourea, and of Goldschmidt and Sunde (5) on the solubility of *o*-nitrobenzaldehyde, have been converted to molalities, and the activity coefficients calculated are given in tables 1 to 3. The first columns give the salt, the second the ionic strength of the salt, the third the ratio of the solubility in pure water to that in

TABLE 2

Activity coefficient of phenylthiourea in aqueous salt solutions at 20°

Solubility in water = 0.01394 M at 20°

SALT	μ	γ_u	$(\log \gamma_u)/\mu$
$AlCl_3$[3]	0.250	1.076	0.1272
	0.500	1.087	0.0724
	1.003	1.155	0.0624
	2.014	1.296	0.0559
$MgSO_4$[4]	0.250	1.040	0.0680
	0.500	1.091	0.0756
	1.000	1.208	0.0821
	2.000	1.478	0.0849
$BaCl_2$[3]	0.189	1.062	0.1381
	0.376	1.076	0.0845
	0.756	1.132	0.0712
	1.523	1.315	0.0780
	3.093	1.591	0.0652
$LiNO_3$[4]	0.125	0.996	−0.0136
	0.252	0.991	−0.0154
	0.507	0.986	−0.0120
	1.031	0.984	−0.0067
$NaCl$[3]	0.125	1.048	0.1632
	0.251	1.082	0.1362
	0.505	1.161	0.1283
	1.018	1.367	0.1333
$NaClO_3$[3]	0.126	1.009	0.0309
	0.252	1.012	0.0206
	0.510	1.047	0.0392
	1.039	1.098	0.0391
$NaClO_4$[3]	0.126	0.980	−0.0698
	0.253	0.980	−0.0347
	0.512	1.002	0.0017
	1.048	1.059	0.0237
NaI[3]	0.126	0.992	−0.0277
	0.253	0.981	−0.0328
	0.510	0.956	−0.0382
	1.041	0.959	−0.0174

SALT	μ	γ_u	$(\log \gamma_u)/\mu$
Na_2SO_4[4]	0.189	1.054	0.1204
	0.378	1.123	0.1333
	0.758	1.272	0.1378
	1.532	1.646	0.1412
$NaNO_3$[4]	0.126	0.996	−0.0134
	0.252	1.004	0.0067
	0.508	1.030	0.0251
	1.032	1.074	0.0300
KCl[3]	0.125	1.036	0.1232
	0.252	1.087	0.1436
	0.508	1.127	0.1021
	1.031	1.282	0.1046
$KClO_3$[3]	0.126	1.000	0.0000
	0.253	1.012	0.0205
	0.513	1.036	0.0300
KBr[3]	0.126	1.027	0.0921
	0.253	1.034	0.0573
	0.510	1.067	0.0552
	1.041	1.139	0.0542
KI[3]	0.126	0.982	−0.0626
	0.253	0.952	−0.0845
	0.513	0.950	−0.0434
	1.050	0.909	−0.0394
K_2SO_4[4]	0.189	1.049	0.1100
	0.377	1.111	0.1212
	0.758	1.242	0.1241
	1.532	1.565	0.1269
KNO_3[4]	0.126	0.999	−0.0038
	0.253	0.996	−0.0067
	0.511	1.010	0.0084
	1.043	1.043	0.0175

TABLE 2—*Continued*

SALT	μ	γ_u	$(\log \gamma_u)/\mu$	SALT	μ	γ_u	$(\log \gamma_u)/\mu$
KAc[4]	0.126	1.033	0.1110	CsNO$_3$[3]	0.126	0.953	−0.1658
	0.254	1.061	0.1010		0.253	0.924	−0.1355
	0.515	1.115	0.0918		0.514	0.888	−0.1003
	1.060	1.224	0.0828				
				NH$_4$NO$_3$[4]	0.126	0.976	−0.0833
RbNO$_3$[3]	0.126	0.975	−0.0873		0.254	0.952	−0.0842
	0.253	0.955	−0.0790		0.516	0.930	−0.0610
	0.512	0.946	−0.0470		1.064	0.879	−0.0526
	1.047	0.936	−0.0274				

the salt solution, and the fourth the quotient of logarithm of activity coefficient by ionic strength.

The results are also shown in figure 1, in which the quotients in column 4 are plotted against the square roots of the ionic strengths.

The measurements with iodine are the most accurate. With sodium sulfate and nitrate the quotient $(\log \gamma_u)/\mu$ is nearly constant, as was the case with gases. The ionic strength of the sodium dihydrogen phosphate (taken equal to its molality) is not simply determined and the variation from constancy is probably due to this cause. The results with the phenylthiourea and *o*-nitrobenzaldehyde are not very accurate, but they show the same

TABLE 3

Activity coefficient of o-nitrobenzaldehyde[5] *in aqueous salt solutions at 25°*

Solubility in water = 0.01534 M at 25°

SALT	μ	γ_u	$(\log \gamma_u)/\mu$	SALT	μ	γ_u	$(\log \gamma_u)/\mu$
HCl	0.505	0.959	−0.0362	NaNO$_3$	1.032	0.718	−0.139
	1.019	0.920	−0.0355		2.130	0.680	−0.079
	2.080	0.838	−0.0369				
				KCl	1.031	1.108	0.0400
HNO$_3$	0.508	0.711	−0.292		2.120	1.144	0.0276
	1.030	0.599	−0.216				
				KNO$_3$	0.511	0.725	−0.274
NaCl	1.018	1.205	0.0795		1.043	0.694	−0.152
	2.076	1.604	0.0990		2.170	0.625	−0.094
NaNO$_3$	0.508	0.756	−0.239				

qualitative agreement with the demands of equation 1 of the previous paper as was shown by the gases.

The measurements with iodine at 25° and 35° also show that the quotient is somewhat larger (salting out effect is larger) at the lower temperature.

THE SALTING-OUT ORDER OF THE IONS

The use of the quotient of the logarithm of the activity coefficient by the ionic strength rather than the molality or the equivalent molality, as a measure of the salting-out effect, gives us a new basis for arranging the salting-out series of the ions. The valence of the ion in our new series is of little importance. For example, barium chloride and potassium chloride have about the same effect.

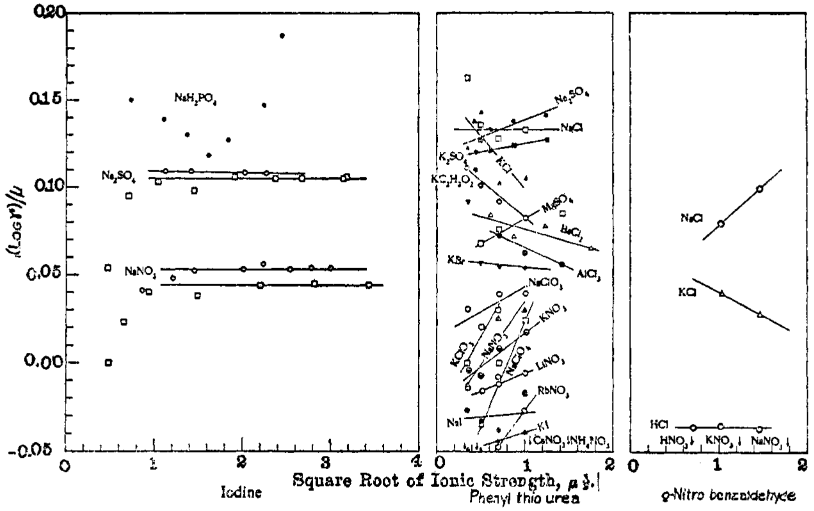

FIG. 1. SALTING-OUT EFFECT OF SALTS ON NON-ELECTROLYTES

It is impossible to fix an absolute order on the basis of the rather approximate data considered, but we may place the negative ions in the order of their decreasing salting-out effect about as follows: hydroxide; sulfate and carbonate; chlorate, bromate, chloride, acetate, iodate and perhalide; bromide and iodide;

nitrate. For the positive ions the order is approximately as follows: sodium; potassium; lithium, barium, rubidium, calcium, nickel, cobalt, magnesium, ferrous, zinc, cesium, manganous, aluminium, ferric, and chromic; ammonium; hydrogen.

Referring to figure 1, and to figures 1 and 2 of the preceding article, it is interesting to note that the spread of the values is different for the different non-electrolytes. That is, the difference between the effect of sodium hydroxide and nitric acid is large in some cases (cf. oxygen), and in some cases small (cf. nitrous oxide). Also the relative position with reference to a negligible effect, zero value of $(\log \gamma_u)/\mu$, is variable. Thus, all the values in the case of oxygen are positive, while many of those for phenylthiourea are negative. We have not discovered any relation between these observations and properties of the non-electrolytes.

In the case of *o*-nitrobenzaldehyde the effect of nitric acid and the nitrates was very large negatively. This may be due to the nitro group in the non-electrolyte.

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