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SOLUBILITY OF THALLOUS IODATE IN ETHYL ALCOHOL-WATER MIXTURES

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In two important papers Scatchard^{1,2} has shown that the simple electrostatic formula first given by Born for the electrical work of transferring charged spheres of average radius r from a medium of dielectric D_1 to one of dielectric D_2 , namely,

$$\log_{10} \frac{S_1}{S_2} = \frac{0.4343}{2r} \frac{\epsilon^2}{kT} \left(\frac{1}{D_2} - \frac{1}{D_1} \right)$$

accounts for the solubility data on sodium chloride and potassium chloride in ethyl alcohol-water mixtures over the entire composition range by using such plausible values as $r = 1.31$ and 1.35 \AA . He was careful to remark, however, that this simplified theory works better than one has any right to expect.

In connection with our solubility studies³ on thallos iodate in aqueous salt solutions, we have tested whether this formula would also apply to thallos iodate-alcohol-water mixtures. This salt has the obvious advantage that its solubility is so small that the correction for interionic attraction is negligible in the absence of added salts. The Debye-Hückel limiting law is adequate⁴ to correct for this effect if desired. The ease with which iodates may be determined enables determinations of the solubility to be made with sufficient precision when considerable alcohol is present.

Experimental

The preparation of the salt and method of analysis have been described in detail previously.³ The ethyl alcohol was redistilled from caustic potash and silver nitrate and the solvents made up by weight. Density measurements were made in each case as a check on the accuracy of this procedure.

Discussion

The data are tabulated in Table I, the solubility being expressed in micro (10^{-6}) moles per liter. Column 6 shows that $\log S_{\text{H}_2\text{O}}/S_{\text{alcohol}}$, when divided by the mole fraction, drifts steadily downward by 22%. On the other hand, Column 7 shows that $\log S_{\text{H}_2\text{O}}/S_{\text{alc.}}$ is an almost linear function (to within 7%) of the weight percentage of alcohol over the same concentration range. In Column 8 we give $(-\log f_0)$, the correction for interionic attraction in each solvent employed in calculating Column 9. The linear relation in respect to weight percentage is unaltered.

¹ Scatchard, *THIS JOURNAL*, **47**, 2098 (1925).² Scatchard, *Chem. Rev.*, **3**, 383 (1927).³ La Mer and Goldman, *THIS JOURNAL*, **51**, 2632 (1929).⁴ Ref. 3, p. 2640, Fig. 2.

TABLE I
SOLUBILITIES OF THALLOUS IODATE IN ETHYL ALCOHOL-WATER MIXTURES AT 25°

Wt. % alcohol	Soly. · 10 ⁶ mole/liter	Density measured	N Mole fraction alcohol	Log $\frac{S_{H_2O}}{S_{alc.}}$	Log $\frac{S_{H_2O}}{S_{alc.}} \cdot \frac{N}{N}$	Log $\frac{S_{H_2O}}{S_{alc.}}$ Wt. %	-log f_0	$\frac{-\log f}{\text{Wt. \%}}$
0.00	1841	0.99708	0.0000	0.0000	0.0217
4.25	1416	.9894	.01706	.1140	6.68	0.0268	.0204	0.0264
11.56	914.7	.9780	.0488	.3037	6.21	.0263	.018	.0260
21.37	503.8	.9644	.0960	.5627	5.86	.0263	.016	.0262
31.61	297.1	.9478	.1530	.7921	5.17	.0251	.014	.0249
40.51	134.5	.9304	.2105	1.1363	5.39	.0280	.011	.0277
46.91	83.2	.9167	.2569	1.3449	5.24	.0287	.013	.0285
94.71	Solubility too small to be detected.							

It is unfortunate that Nernst's⁵ measurements on the dielectric constants of alcohol-water mixtures do not extend below about 46 weight per cent., so that we might compare the solubility changes with the concentration dependence of $1/D$ without resorting to interpolation over the interval 0 to 46% alcohol. If Equation 1 is to hold, $1/D$ must be more nearly proportional to the weight concentration than to the mole fraction in this range of concentration. This question should be investigated with more modern experimental methods.

If we substitute in Equation 1 for D_1 and D_2 , the values 78.8 (H₂O) and 49.6 (46.91% alcohol) and for S_1 and S_2 the solubility of thallos iodate in moles per liter, we compute $r = 0.78 \text{ \AA}$. The volume molar scale has been used in this connection by most investigators but it implies that if there were no electrical effects, the molar solubility would be constant in all solvents. There is no adequate justification for such an ideal law. If we assume Raoult's law to be the ideal, which law demands that the components in the liquid state mix in all proportions without change of volume or of heat content, then the solubility in terms of mole fraction should be identical in the absence of electrical or other effects.

Although volume no longer appears explicitly in this ideal law, the choice of molecular weights for the components used in calculating the mole fraction implies it through the Avogadro hypothesis. Assuming the molecular weights of alcohol and water to be 46 and 18.02, respectively, we get $N_1 = 33.26 \cdot 10^{-6}$ and $N_2 = 2.29 \cdot 10^{-6}$. Substituting these values for S_1 and S_2 we find $r = 0.90 \text{ \AA}$. as the average radii of the Tl⁺ and IO₃⁻ ions, on the assumption that the non-ideality arises solely from the net charges on the ions and that our assumptions of the molecular weights of water and alcohol are correct for their mixtures.

Either value of r , namely, 0.78 or 0.90 \AA ., is a trifle smaller than one might expect for the average radii from other methods of measurement. On the other hand, it actually proves to be as large as the parameter " a ,"

⁵ Nernst, *Z. physik. Chem.*, 14, 622 (1894).

representing the distance of closest approach of the ions computed with the aid of the general solution of the Debye-Hückel interaction theory.⁶ If the ions are spherical and no forces of deformation intrude, " a " should equal $2r$.

Table II gives the results of computations based upon the solubility data in dilute salt solutions. In the case of uni-univalent solvent salts the calculations can be made with fewer mathematical complications than is the case with higher valence solvent salts.

TABLE II
CALCULATION OF " a " FOR THALLOUS IODATE FROM ACTIVITY COEFFICIENTS OBTAINED BY SOLUBILITY METHOD. " a " IN Å. UNITS (DATA BY LA MER AND GOLDMAN, REF. 3, PAGE 2639)

Solvent	κ	$-\log f$	" a_{1st} "	" a_g "
0.05 M KNO ₃	0.07505	0.1120	+0.39	+1.57
.10 M KNO ₃	.10512	.1525	+ .56	+1.50
.30 M KNO ₃	.18073	.2509	+ .59	+1.34
.10 M NaNO ₃	.10512	.1514	+ .64	+1.55
.05 M KCl	.07512	.1242	- .94	+1.15
.10 M KCl	.10515	.1751	- .74	+1.05
.10 M NaCl	.10515	.1742	- .69	+1.10

Column 4 gives the value of " a " computed from the first or Debye approximation on the customary assumption that all individual " a " values in the ternary mixture: water, TlIO₃, and 1,-1 solvent salt, are equal. By the use of a graphical plot representing the fictitious values of " a_{1st} " which correspond to the same $-\log f$ value computed for a given " $a_{general}$ " and a definite value of the Debye κ or $\sqrt{\mu}$, we can readily translate any value of " a_{1st} " into its " $a_{general}$ " value. These values are given in Column 5. No sensible error is introduced in the case of symmetrical valence types in water by considering the fifth approximation equal to the general solution if $a/Z^2 < 0.8 \text{ Å}$.⁷ The " a_g " values in the nitrate solvents are almost equal to $2r$, but the " a_g " values in the chloride solvents, although no longer absurdly negative as is the case for the " a_{1st} ," are still somewhat small. In other words, the neglected higher terms in the Debye theory account for the nitrate data on a purely theoretical basis involving only one parameter but are not quite sufficient to account for the chloride data. Undoubtedly other forces leading to deformation of the ions or complex chloride ion formation occur and must be taken into account for a precise representation of the data. Similar behavior has been noted for lead iodate in 0.1 N chloride solvents.⁸ We should point out, however, that a com-

⁶ Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

⁷ The data for this conversion valid for infinite dilution have been given by La Mer, *Trans. Am. Electrochem. Soc.*, 51, 507 (1927), page 547. The conversion values for finite concentrations will be published later.

⁸ La Mer and Goldman, *THIS JOURNAL*, 52, 2791 (1930).

putation for " a " values constitutes a very critical test of the Debye-Hückel theory. The fact that the highly simplified picture employed by Debye and Hückel represents the facts for Pb^+ and Tl^+ , which are known to form complexes with chloride ions at higher concentrations, as closely as it does is more remarkable than are the comparatively insignificant deviations just mentioned.

Summary

The solubility of thallos iodate has been measured in ethyl alcohol-water mixtures ranging from zero to 47% ethyl alcohol. The values of the average radii calculated using Born's formula for the electrostatic work of transfer are compared with the values of the parameter " a " computed from the interaction theory for the solubility in salt solutions as extended by Gronwall, La Mer and Sandved.

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THE HEAT CAPACITIES AT LOW TEMPERATURES OF MANGANESE SULFIDE, FERROUS SULFIDE AND CALCIUM SULFIDE¹

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Pursuing its general program of study of the thermodynamic properties of metals, oxides and sulfides which are important in metallurgical processes, the Pacific Experiment Station of the U. S. Bureau of Mines has determined the heat capacities of the sulfides of manganese, iron and calcium. The thermodynamic properties of these sulfides have both theoretical interest and practical importance. The heat capacities of the oxides corresponding to these sulfides have been determined, which enables an interesting comparison to be made.³ Knowledge of the entropies of these sulfides was especially desired for use in connection with studies of the desulfurization of iron.

The method, apparatus and accuracy have been described in previous publications,⁴ but it may be noted that between the sets of experiments

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³ Millar, *THIS JOURNAL*, 50, 1875 (1928); 51, 215 (1929); Parks and Kelley, *J. Phys. Chem.*, 30, 47 (1926).

⁴ Anderson, *THIS JOURNAL*, 52, 2296, 2712 (1930).