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Activity Coefficients of Salts in Ethylene Dichloride from Solubility Measurements[1]

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This investigation is one of a series[2] made by the author in which the solubility method has been used to obtain information about the properties of solutions of electrolytes in various non-aqueous solvents. It has been shown that the measured solubilities are not consistent with the requirements of the approximate formulas given by Debye and Hückel in their original development of the interionic attraction theory, but are qualitatively, at least, in agreement with the extension of the theory by Gronwall, La Mer and Sandved, or the alternative treatment of Bjerrum, providing a suitable value for "a,"[3] the average ion diameter, is chosen. The measurements have been made on uni-univalent solutes at concentrations as low as less than one thousandth molal and with solvents having dielectric constants ranging from that of ethyl alcohol (25.4) to that of glacial acetic acid (6.25). Since, considering its low dielectric constant, the latter solvent seems to be abnormal both as regards the magnitude of solubilities of inorganic salts in it and their changes on the addition of a second salt, it was thought desirable to have some measurements on some other solvent of relatively low dielectric constant. Since ethylene dichloride (D. K. 10.4) is readily obtained in large quantities of reasonable purity, it was chosen. Inorganic salts are, in general, insoluble in this solvent. After trying several of the tetraalkylammonium salts, the solubility of tetramethylammonium chloride was found to be nearest that desired for the saturating salt. Since the solubilities of these salts increase with the size of the substituting alkyl groups, any number of more soluble salts, suitable for the added salt, can be made. The conductivity studies of Walden and of Kraus[4] have shown salts of this type to be strong electrolytes in ethylene chloride. Since it was expected that the effects of solvation would not be great, it was hoped that the solubility effects would vary considerably with the size of the ions of the added salt. The results, in general, show what was expected; namely, that the greatest increases in solubility (or decreases in activity coefficient) are produced by addition of salts with the smallest ions, and the least increases by salts with the largest ions.

Materials Used

Ethylene Dichloride.—Eastman "practical" grade was distilled using a Vigreux column. The fraction retained came over within 0.2° of the accepted boiling point. It was then treated with various drying agents. Probably the best criterion of purity for the purpose at hand is constancy of solubility of a given salt in it. The lowest and most consistent values of the solubility of tetramethylammonium chloride were obtained by keeping the solvent over phosphorus pentoxide for several days and then distilling from an all-glass still directly into the solubility bottles, which previously had been filled with dry air. It is essential to keep out traces of moisture since the addition of 0.02% of water nearly doubled the solubility of the salt. A cooling curve was taken on a sample of the purified solvent using a copper-constantan thermocouple and the freezing point found to be −35.3°, in agreement with the value in "International Critical Tables."

Tetramethylammonium Chloride.—Eastman tetramethylammonium bromide was treated with a suspension of silver oxide in water until a drop of the solution gave only a slight test for bromide. The resulting hydroxide solution was heated in an open dish until the odor characteristic of the tertiary amine disappeared, neutralized with hydrochloric acid, evaporated to dryness on a water-bath and the salt recrystallized several times from alcohol. Samples prepared at different times were found to have the same solubility in purified ethylene chloride.

Tetramethylammonium Picrate and Tetraethylammonium Nitrate and Picrate.—These salts were prepared from the corresponding halides by adding an equivalent amount of silver picrate or nitrate in alcoholic solution, filtering to remove the precipitated halide and recrystallizing from alcohol.

Tetraisoamylammonium Picrate.—The iodide was first made by heating equivalent amounts of triisoamylamine and isoamyl iodide to about 150° and purified by several recrystallizations from anhydrous ethyl acetate and ether. The picrate was made by treating the iodide with silver picrate and recrystallized from ether, m. p. 86°

Procedure

The method of determining solubilities has been described previously.[2a] Weighed amounts of the solvent

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[1] Presented at the Cleveland Meeting of the American Chemical Society, September, 1934.

[2] (a) Kraus and Seward, *J. Phys. Chem.*, **32**, 1294 (1928); (b) Seward and Schumb, THIS JOURNAL, **52**, 3962 (1930); (c) Seward and Hamblet, *ibid.*, **54**, 554 (1932).

[3] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928); Bjerrum, *Det. Kgl. Danske Videnskab. Selskab. Math-fys. Medd.*, [9] **7**, 1 (1926).

[4] Walden, "Salts, Acids and Bases," McGraw-Hill Book Co., Inc., New York, 1929, p. 260; Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

salt were added to a known amount of solvent and brought to equilibrium with an excess of the saturating salt by stirring in a thermostat at 25° for twenty-four hours. This time appeared to be ample since successive saturations gave the same values. Determination of the solubility of the chloride at different temperatures showed only slight changes, so accurate temperature control is not needed. After removing a sample of solution (about 1000 g.) through a filter, the sample was weighed, the solvent recovered by distillation for re-use, and the chloride in the residue determined gravimetrically as silver chloride. The density of the pure solvent was used in calculating concentrations from the weights.

Results

Some preliminary experiments made before the solvent had been dried completely are given in Table I to show that, although the solubilities are markedly increased by the presence of small amounts of impurities (probably water), the relative increase produced by addition of a second salt is about the same as in the pure solvent. Table II shows the measurements in the purified solvent. Where check values appear they were made by independent saturations, in nearly every case made at different times. All concentrations are given in moles of salt per liter of solvent. The calculated values of the logarithm of square root of the ion product ratio and the square root of total salt concentration are included for the purpose of comparing with the theory.

TABLE I

SOLUBILITY OF TETRAMETHYLAMMONIUM CHLORIDE AT 25° IN THE PRESENCE OF TETRAETHYLAMMONIUM NITRATE IN UNPURIFIED ETHYLENE DICHLORIDE

Concn. $(C_2H_5)_4NNO_3$ $\times 10^4$	Solubility $(CH_3)_4NCl$ $\times 10^4$		$-1/2 \log$ Pi_0/Pi	$\sqrt{C} \times 10^2$
0.00	1.86	1.87	0.000	1.36
.39	2.09		.050	1.57
1.44	2.54		.135	1.99
3.80	3.47		.271	2.70
6.67	4.35		.368	3.32
16.45	7.30		.592	4.87

Discussion

Inspection of Table II shows that the solubility effects vary markedly with the added salt. The increase in solubility of tetramethylammonium chloride produced by the presence of one millimole of tetraethylammonium nitrate per liter of solution was 289%. The same concentration of tetraethylammonium picrate caused a 98% increase, while tetraisoamylammonium picrate increased the solubility by only 69%. While the solubility of the saturating salt is too small for very accurate measurement and the average deviation of individual determinations from the mean is 1.9%, the experimental uncertainties are small relative to the differences observed with the different added salts. The addition of a salt with a common ion, as might be expected in a solvent of low dielectric constant, produces only a slight decrease in solubility.

TABLE II

SOLUBILITY OF TETRAMETHYLAMMONIUM CHLORIDE IN THE PRESENCE OF ADDED SALTS IN ETHYLENE DICHLORIDE AT 25°

(a) Added Salt Tetramethylammonium Picrate

Concn. $(CH_3)_4NO$-$C_6H_2(NO_2)_3$ $\times 10^4$	Sol. $(CH_3)_4NCl$ $\times 10^4$ (anal.)			Sol. $(CH_3)_4NCl$ $\times 10^4$ (mean)	$-\frac{1}{2} \log \frac{Pi_0}{Pi}$	$\sqrt{C}$ $\times 10^2$
0.00	1.15	1.11	1.17	1.143	0.000	1.07
3.75	0.820		0.854	0.837	.233	2.15
7.51	.866		.866	.866	.371	2.89
11.25	.980		.994	.987	.482	3.50

(b) Added Salt Tetraethylammonium Nitrate

Concn. $(C_2H_2)_4NNO_3$						
0.00	1.15	1.11	1.17	1.143	0.000	1.07
2.67	2.11		2.31	2.21	.286	2.21
5.00	3.04		3.16	3.11	.433	2.85
10.00	4.40		4.49	4.44	.589	3.80

(c) Added Salt Tetraethylammonium Picrate

Concn. $(C_2H_5)_4NO$-$C_6H_2(NO_2)_3$ $\times 10^4$						
0.00	1.15	1.11	1.17	1.143	0.000	1.07
5.00	1.67		1.77	1.72	.178	2.59
10.00	2.32		2.20	2.26	.297	3.50

(d) Added Salt Tetraisoamylammonium Picrate

Concn. $(C_5H_{11})_4NO$-$C_6H_2(NO_2)_3$ $\times 10^4$						
0.00	1.15	1.11	1.17	1.143	0.000	1.07
5.00	1.59		1.66	1.62	.152	2.57
10.00	1.80		1.91	1.85	.210	3.45

The relation of the activity coefficient of the salt and the measured solubilities is given by the equation

$$-\log f = -\frac{1}{2} \log \frac{Pi_0}{Pi} - \log f_0$$

where f and f_0 are the activity coefficients of the salt in the given solution and in the pure solvent, respectively, and Pi and Pi_0 the product of the concentrations of the ions of the saturating salt in the solution and pure solvent. Since f_0 is a constant, plotting the values of $-1/2 \log (Pi_0)/Pi$ against some function of the concentration gives a curve which shows how $-\log f$ varies with the salt concentration.

The development of the interionic attraction theory by Gronwall, La Mer and Sandved[5] leads

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(5) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 388 (1928).

to the following expression for uni-univalent salts in ethylene chloride at 25°

$$-\log f = \frac{10.5\sqrt{C}}{1 + .895\,a\sqrt{C}} - \frac{63.2(X_3)}{a^3} - \frac{1730(X_5)}{a^5}$$

where C is the total salt concentration in moles per liter, a is the average ion diameter in Ångströms, and X_3 and X_5 are functions of a and C whose values have been calculated and tabulated by these authors. The first term at the right will be recognized as the original Debye–Hückel approximation and indicates a value of 10.4 for the limiting slope. To compare the measured changes in $-\log f$ with those called for by the theory, the calculated values of $-1/2 \log (Pi_0/Pi)$ have been plotted against the square root of total salt concentration in the accompanying figure.

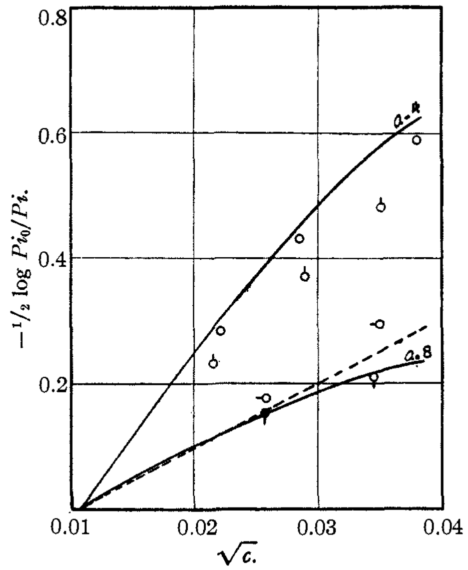

Fig. 1.—Added salt: ○, $(C_2H_5)_4NNO_3$; ȯ, $(CH_3)_4NPi$; -○, $(C_2H_5)_4NPi$; ♀, $(C_5H_{11})_4NPi$; – – –, limiting slope.

Inspection of the figure shows that except for the case of the isoamyl salt these are marked positive deviations from the limiting slope. It appears, therefore, that without assigning negative values to a, the experiments do not fit the theory, if only the first term of the equation is considered. If the whole expression is used, however, it is found that the results are, qualitatively at least, in agreement when reasonable values of a are assumed. The upper and lower curves show how $-\log f$ would change with the square root of the salt concentration, according to the extended equation, when a is assumed to be four and eight Ångströms, respectively. A rough estimate based on the limiting conductances of some of these salts, assuming that the limiting conductance values are inversely proportional to the ion diameters, indicates ion diameters within this range for these mixtures. If we compare the effects produced by the three picrates we find, as predicted by the theory, the greatest decrease in activity coefficient produced by the tetramethylammonium ion and least by the tetraisoamylammonium ion. Comparing the effect of tetraethylammonium nitrate with the picrate, we also find the nitrate ion to be much more effective in changing the activity coefficient than the larger picrate ion.

If conductance data on the salts employed were available it would be possible to obtain a quantitative comparison with the solubility measurements by employing the dissociation constants of the salts as determined by the method of Fuoss and Kraus.[6] Since it is found by their method that salts with smaller ions have smaller dissociation constants, it would follow that the increase in solubility produced by adding a salt without a common ion would be greater the smaller its ions. It is evident then that the solubility measurements are qualitatively in agreement with this alternative treatment as well as with the extension of the Debye–Hückel theory by Gronwall, La Mer and Sandved.

Summary

Measurements of the solubility of tetramethylammonium chloride in ethylene dichloride in the presence of added quaternary ammonium salts have been made.

It is shown that the decrease in activity coefficient of the saturating salt varies considerably with the added salt and that the decreases are greater the smaller the ions of the added salt.

Employing plausible values for the ion diameter, curves showing the variation of activity coefficients with the square root of the salt concentration are obtained from the Gronwall, La Mer and Sandved development of the Debye–Hückel theory which agree reasonably well with the experimental curves.

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[6] Fuoss and Kraus, THIS JOURNAL, 55, 476 (1933).