[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Solubilities of Benzene, Nitrobenzene and Ethylene Chloride in Aqueous Salt Solutions

BY J. H. SAYLOR, A. I. WHITTEN, IMOGEN CLAIBORNE AND P. M. GROSS

The solubilities of benzene, nitrobenzene and ethylene chloride have been determined in a number of aqueous salt solutions. It is pointed out that existing theories cannot either qualitatively or quantitatively account for the results obtained. It is probable that attractive forces of both the London type and those caused by induced dipoles are important.

The salting out of non-electrolytes already has been discussed in earlier publications.[1] Other authors have discussed the interaction of electrolytes and non-electrolytes both from the theoretical and experimental standpoints.[2]

The present work was undertaken in order to compare the salting-out of a typical non-polar substance, benzene, by a series of diverse salts with that of a polar substance, nitrobenzene. Some data on ethylene chloride of intermediate polarity were also obtained.

Experimental

Method.—Salt solutions of the approximate concentration desired were prepared by direct weighing of the salt and water and were analyzed by evaporating a known weight of salt solution and weighing the dry salt. The hydrochloric acid solutions were analyzed volumetrically.

The saturated solutions of the organic substances were prepared by shaking an excess of the substance in 500-ml. glass-stoppered cylindrical bottles in a thermostat at 30 ± 0.02°. These solutions were analyzed by means of a Zeiss combination liquid-gas interferometer as previously described.[3] The only difference in procedure was the substitution of salt solution of known concentration for water.

Materials.—Three samples of benzene were used which were purified as described by Richards and Shipley,[4] and were fractionated in all-glass stills using calibrated thermometers. The boiling point ranges were 80.12 ± 0.02°, 80.05–80.07° and 80.08–80.11°. Smith and Matheson[5] give a boiling point of 80.09_4°. Two samples of nitrobenzene were fractionated under reduced pressure in a Hickman still. The fractions used froze at 5.7 and 5.67°. International Critical Tables gives a freezing point of 5.7°. Two samples of ethylene chloride were purified by fractional distillation. The fractions used had boiling point ranges of 83.52–83.54° and 83.61–83.73°. Timmermans[6] gives a boiling point of 83.69–83.71°.

The salts were all of good grade and were used without further purification other than filtering the solution when necessary. The tetramethylammonium bromide was analyzed for bromine content. Calcd.: 51.87. Found: 51.70.

Experimental Results

Figures 1 and 2 show the logarithm of the activity coefficients of benzene and nitrobenzene as functions of salt molality while Fig. 3 gives the logarithm of the activity coefficient of ethylene chloride as function of ionic strength. The logarithms of the activity coefficients of the non-electrolytes are given as $\log_{10} S_0/S$ where S_0 is the solubility in water and S that in salt solution.[7]

Discussion of Results

Debye and McAulay,[8] Debye[9] and Butler[10] have derived equations from which it is possible to calculate the solubilities of non-electrolytes in dilute salt solutions. These equations predict that salting-out will occur in all cases if the dielectric constant of the saturated non-electrolyte solution is less than that of water and salting-in if the reverse is true. The theories predict that the logarithm of the activity coefficient of the non-electrolyte is a linear function of the ionic strength. Such a relationship is found in the present work as can be seen from Figs. 1, 2 and 3.

Quantitative tests of these theories have been made only in a few instances as the data for the dielectric constants of the saturated solutions are not known. Some measurements have been made by Albright and Williams[2] of solutions of several organic substances and the available solubility data compared with that calculated from Debye's theory. They found that the solubility data in some instances approach those calculated from Debye's theory for low salt concentrations, but in some cases salting-in occurred. The dielectric constant data for saturated solutions of benzene, nitrobenzene and ethylene chloride are not available but it is possible to obtain an idea of the agreement expected between the theory and experiment by making use of the relationships given by Debye and McAulay and by Butler. Debye and McAulay's equation is

$$\log_e \frac{S_0}{S} = \log_e f = -\frac{\lambda n_i \Sigma \nu_i z_i^2 \epsilon^2}{2D_0 rkT}$$

where

f = activity coefficient
n_i = number of salt molecules per cc.
ν_i = number of ions of one kind in molecule
z = valence of ion
T = absolute temperature
D_0 = dielectric constant of water
ϵ = charge on electron
r = mean ionic radius
k = Boltzman's constant

λ is defined by $D = D_0(1 - \lambda n)$ where D is the dielectric constant of the saturated aqueous solution of non-electrolyte and n the number of molecules

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(1) P. M. Gross, *Z. physik. Chem.*, **6B**, 215 (1929); P. M. Gross, *Chem. Revs.*, **13**, 91 (1933).

(2) P. S. Albright, THIS JOURNAL, **59**, 2098 (1937); P. S. Albright and J. W. Williams, *Trans. Faraday Soc.*, **33**, 247 (1937); J. W. Belton, *ibid.*, **33**, 653 (1937); G. M. Goeller and A. Osol, THIS JOURNAL, **59**, 2132 (1937); J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); G. Scatchard and M. A. Benedict, THIS JOURNAL, **58**, 837 (1936); R. W. Wright, L. S. Stuber and P. S. Albright, *ibid.*, **61**, 228 (1939).

(3) P. M. Gross and J. H. Saylor, *ibid.*, **53**, 1744 (1931).

(4) T. W. Richards and J. W. Shipley, *ibid.*, **36**, 1828 (1914).

(5) E. R. Smith and H. Matheson, *Bur. Standards J. Research*, **20**, 641 (1938).

(6) J. Timmermans, *Bull. soc. chim. Belg.*, **24**, 244 (1910).

(7) Tables summarizing the experimental data are available as Document 3424 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(8) P. Debye and J. McAulay, *Physik. Z.*, **26**, 22 (1925).

(9) P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

(10) J. A. V. Butler, *J. Phys. Chem.*, **33**, 1015 (1929).

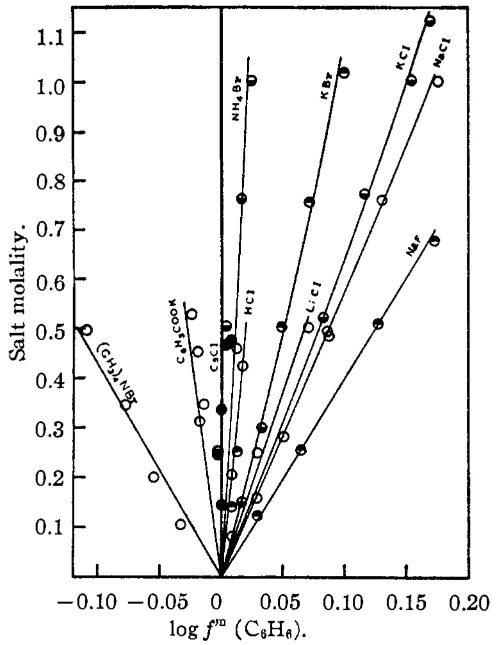

Fig. 1.—The logarithm of the activity coefficient of benzene as a function of salt molality.

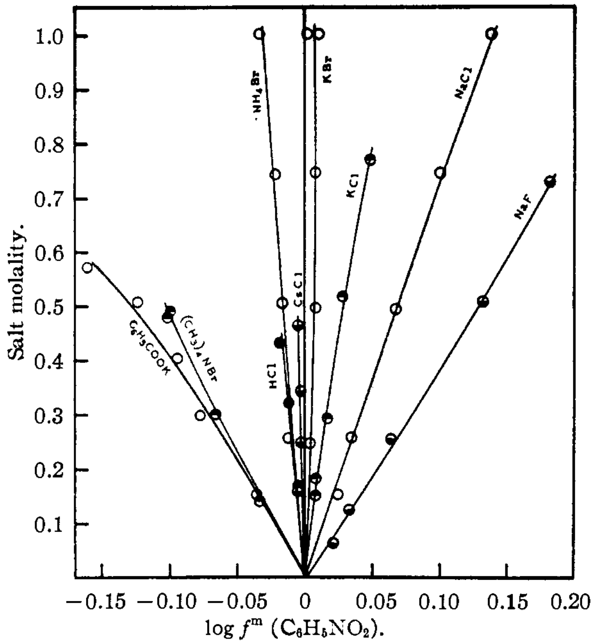

Fig. 2.—The logarithm of the activity coefficient of nitrobenzene as a function of salt molality.

of non-electrolyte per cc. According to Butler

$$\lambda = \frac{4\pi(\alpha_A - \alpha_B)\partial V_B}{D_0}$$

where $4\pi(\alpha_A - \alpha_B)$ is the difference between the dielectric constants of the water and non-electrolyte molecules and ∂V_B is the volume of a non-electrolyte molecule. If it is assumed that the dielectric constants of these molecules are the same as the macroscopic dielectric constants and that ∂V_B can be calculated from the molar volume of the non-electrolyte, then

$$\lambda = \frac{(D_0 - D_B)\partial V_B}{D_0}$$

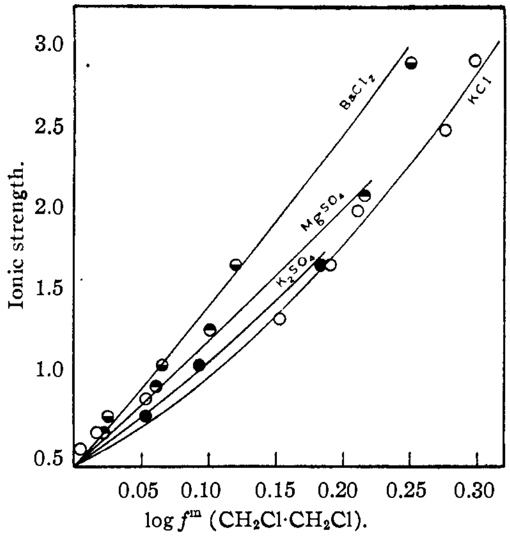

Fig. 3.—The logarithm of the activity coefficient of ethylene chloride as a function of salt molality.

When this value for λ is substituted in the Debye–McAulay equation, the present data can be used to calculate the parameter r, the mean radius of the salt. In these calculations salt molality is used instead of salt molarity but this introduces a negligible error in view of the other assumptions.

The values of $\log_{10}f^m$ at a salt concentration of 0.500 m are obtained from a large scale plot of the data. Values for the radii calculated from these values of $\log_{10}f^m$ are given in columns 4 and 5 of Table I. For benzene these are of reasonable order of magnitude for the salts with smaller ions and with the exception of LiCl are in the same order as that expected from crystal data. Lithium ions have been found to exhibit this anomaly previously.[11]

TABLE I

THE LOGARITHMS OF THE ACTIVITY COEFFICIENTS OF BENZENE IN 0.500 m SALT SOLUTIONS AT 30°

Salt	$\log_{10} f^m$ C_6H_6	$\log_{10} f^m$ $C_6H_5NO_2$	$r \times 10^8$ Butler–Debye C_6H_6	$r \times 10^8$ Butler–Debye $C_6H_5NO_2$	$r \times 10^8$ Belton C_6H_6
NaF	0.125	0.130	1.08	0.68	13.55
NaCl	.088	.069	1.55	1.28	9.57
KCl	.080	.029	1.71	3.05	8.71
LiCl	.067		2.04		7.31
KBr	.051	.008	2.68	11.0	6.13
HCl	.020	− .012 (0.3 M)	6.81		2.37
NH_4Br	.012	− .016	11.36		2.82
CsCl	.000	− .005			0.706
C_6H_5COOK	−.028	− .07 (0.3 M)			.157
$(CH_3)_4NBr$	−.118	−0.64 (0.3 M)			.033

The theory however does not give probable values for the radii of even the smaller ions when they are calculated from the nitrobenzene data. On the basis of the dielectric constants of the non-electrolyte, the theory predicts the order of salting out to be benzene > ethylene chloride > nitrobenzene. Belton[2] pointed out that the theory should apply only to a non-polar solute and a non-polar solvent and he extended the theory in an effort to take into account the case of polar molecules. His equation is

[11] W. Biltz, *Z. physik. Chem.*, **43**, 41 (1903).

$$\log_e f = \frac{n_1 4\pi \Sigma z_i^2 \epsilon^2}{2D_0^2 rkT}\left[\frac{D_0 - 1}{D_0 + 2}\frac{M_0}{d_0}\frac{3}{4N} - \frac{\mu^2}{3kT} - \frac{D_1 - 1}{D_1 + 2}\frac{M_1}{d_1}\frac{3}{4\pi N} + \frac{\mu_1}{3kT}\right] + \frac{n'4\ r\ z_i\epsilon(\mu_0 - \mu_1)}{D_0kT}$$

where the subscripts 0 and 1 refer to solvent and solute, respectively: M = molecular weight, d = density, N = Avogadro's number, μ = dipole moment and the other symbols have the same significance as previously. Values for radii calculated from this equation from the data for $\log_{10} f'''$ are given in column 6 of Table I. The radius as defined by Belton is a mean distance of approach of the ions and the non-electrolyte. It is seen that the radii decrease as the crystal radii increase. It might be argued as does Belton that the larger values in the case of NaF, NaCl and LiCl are caused by the hydration of the ions but such an argument is of doubtful validity. However, it is interesting that positive values of the parameter r are obtained from the data for benzene.

If the radius calculated for KCl is used to calculate the solubility of nitrobenzene in 0.5 M KCl, salting-in is predicted where actually salting-out is found. As Belton points out, the use of the Clausius–Mosotti equation is a very doubtful approximation. The dipole moments are also likely to be different when the substances are dissolved in water. Furthermore it is doubtful if any of these theories can be legitimately applied where salt concentrations are as high as those used in the present work.

It has been previously suggested[1,12] that anions salt-in while cations salt-out and that the final result depends upon which effect predominates. It is seen from the present work, however, that this generalization may be dubious as tetramethylammonium bromide markedly increases the solubility of both benzene and nitrobenzene. The tendency to salt-in is seen to increase with the size of the ions involved whether they are cations or anions. This clearly indicates that additional interaction terms of the London–van der Waals type must be considered more fully than in present quantitative theories. Such interaction forces involve the polarizability of salt ions, solvent molecules and non-electrolyte solute molecules as well as the special force fields originating from any component dipoles that may be present. Such component dipoles for example, would be present in the system water, nitrobenzene and benzoate ion.

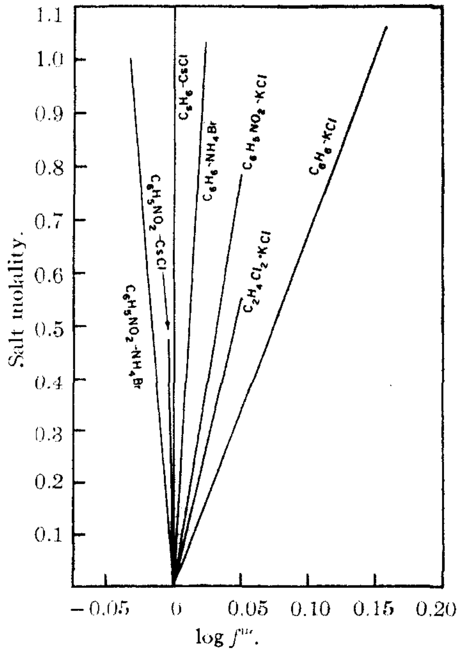

Fig. 4.—A comparison of the logarithms of the activity coefficient of benzene, ethylene chloride and nitrobenzene.

The variety of both salts and non-electrolytes in the present data is sufficient to show clearly the inadequacy of existing quantitative treatments. The difference in the behavior of the non-electrolytes used can be seen in Fig. 4. Benzene is a symmetrical non-polar molecule which is so large with respect to the smaller water molecules surrounding it in solution that the latter may perhaps still be treated as a continuum. Nitrobenzene differs but little from it in volume but has a very large unshielded localized dipole. The molecule ethylene chloride is smaller, lacking in symmetry, with two component dipoles.

While no attempt will be made here to evaluate quantitatively the forces which it appears necessary to consider in the salting-out (or -in) phenomenon, a qualitative description of these in the light of the present results will indicate the direction which modifications and extensions of existing theories might take. For the most general case of the system polar solvent, ions and polar solute, three interactions should be considered, probably in the following order of importance: (1) London forces between water molecules and solute, (2) competition for water molecules between the solute and the surrounding ions, (3) special dipole field interactions between the polar solute, the solvent and the ions. The last effect appears to be particularly important in the case of large unsymmetrical ions such as the benzoate. In the mobile situation involved, (1) and (3) appear to cause increased solubility while (2) causes decreased solubility. The net effect determines whether salting-out or salting-in occurs. The effect (1) has either been overlooked or inadequately taken into account in existing theories. As pointed out previously,[1] (2) is an effect which essentially immobilizes some water molecules as a solvent medium for the solute. In general, the effect of (3) has been ignored. Its importance is indicated by a comparison of the present data for nitrobenzene and benzene and by the particular case of the salting-in of both solutes by potassium benzoate.

Before the completion of this paper, the results of an investigation of the solubility of benzene in aqueous salt solutions by McDevit and Long[13] were made available to us. Their data are in essential agreement with ours except for the case of CsCl. Their quantitative treatment approaches the problem from a new direction and considers other properties of the salt solutions for the de-

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(12) H. R. Kruyt and C. Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926).

(13) W. F. McDevit and F. A. Long, THIS JOURNAL, **74**, 1773 (1952).

velopment of a theory of the salting-out or salting-in phenomenon. Such an approach appears adequate for the non-polar solute benzene which is considered. Their method is of such generality that it promises to provide the necessary foundation from which a more complete theory including the effects (1) and (3) discussed above may be formulated.

The treatment of McDevit and Long is somewhat reminiscent of the much earlier concept of Tammann[14] of an "internal pressure" (Binnendruck). He defined the increase in internal pressure of a salt solution in terms of the external pressure that would have to be applied to pure water in order to make properties such as the temperature of maximum density the same as for the salt solutions. Attempts were made by Euler[15] and Geffcken[16] to correlate the solubility of various substances in salt solutions with increases in internal pressure as calculated by Tammann.

However the values of the lowering of the maximum density of water as given by Geffcken[16] show poor correlation with our data for the salting-out of benzene by NaCl, KCl, LiCl, KBr and NH_4Br. Somewhat better correlation is found with the data for the relative compressibility of the salt solutions. Of perhaps more importance is the difficulty that this earlier concept of "internal pressure" does not appear to be capable of predicting the existence of the "salting-in" such as found in the case of nitrobenzene.[17]

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(14) G. Tammann, *Z. physik. Chem.*, **11**, 676 (1893).

(15) H. Euler, *ibid.*, **31**, 369 (1899).

(16) G. Geffcken, *ibid.*, **49**, 289 (1904).

(17) We are grateful to the reviewer, Dr. J. H. Hildebrand, for recalling to our attention this earlier "internal pressure" concept of Tammann, *et al.*

DURHAM, N. C.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

Heat of Vaporization and Other Properties of Dioxane, Water and Their Mixtures

BY ROBERT D. STALLARD AND EDWARD S. AMIS

The water–dioxane system has been studied with respect to refractive indices, specific heats, absorption of dioxane by sulfuric acid, and both total and partial specific and molal heats of vaporization. Various plots of different types of heats against compositions and dielectric constants have been discussed. An attempt has been made to explain the forms of the curves relative to the various types of intermolecular forces involved in the liquid mixture. Empirical equations relating the composition of the solutions to some of the variables have been evolved by methods of least squares and of averages.

Introduction

It was thought to be of interest to study the dioxane–water system with respect to certain thermodynamic and other properties. This system was selected because of the prominence it has received in mixed solvent studies of chemical kinetics, conductivity of electrolytes, and physical properties of liquids. Data are available in the literature on dielectric constants, densities and other physical properties of the liquids and their mixtures. Furthermore, dioxane is a good solvent for a wide variety of substances and is miscible with water in all proportions.

Apparatus.—The apparatus consisted of five main subdivisions; the pressure regulating devices, the air-drying and purification trains, the air-tempering or preconditioning system, the calorimeter proper with the appended electrical systems, and the freezing trap for the collection of the sample.

The pressure mechanism consisted of three 20-liter carboys in series (see Fig. 1), each provided with an escape valve consisting of a 10-mm. tube, the end of which is immersed under a layer of mercury, the pressure in the system being regulated by the depth of the mercury. Fine adjustment is achieved by adding a layer of water above the mercury. The large volume of the system makes any sudden fluctuation in pressure almost impossible, although small fluctuations (about 0.5 mm. on a sulfuric acid filled manometer, M) do occur due to bubbling through the mercury. Further regulation is achieved by a screw-clamp, S_1, and the needle valve, v. The air, now at constant pressure, is passed to the drying train, which consists of three towers filled with soda lime, calcium chloride and phosphorus pentoxide, in that order. These are of glass, sealed with paraffined cork stoppers. After passing the phosphorus pentoxide tube, all connecting tubing is of glass or metal with the minimum of rubber tubing for joints. Leaving the purifying train, the air enters the tempering system through the Y-tube, Y, the pinch clamp S_2 being closed in normal operation, and the three way stopcock, W_1, being thrown so as to by-pass the presaturator, P, which is needed only in the determination of heat capacity at the end of the determination. The pressure inside the system may be read at any instant on the manometer, M.

Within the tempering system, the air is passed down the internal $^3/_{16}''$ copper tube, and out through the space between the inner and the 1.5″ thin-walled copper outer tube. The space between the two concentric pipes is filled with a roll of copper screen, to stir the ascending air and assist in the attainment of a thermal equilibrium with the bath. To ensure that the air is at the temperature of the thermostat, it is then passed through the coil, C, consisting of twenty feet of $^3/_{16}''$ copper tubing.

Thence it enters the calorimeter proper, through the water-jacketed inlet tube, I, and passes through the liquid, and out of the water-jacketed outlet tube, O, through the electrically heated conveyor tube, F, to the sample trap, J, immersed in an acetone–carbon dioxide refrigerating mixture contained in the dewar flask, D_2. On the air outlet side of the calorimeter and beyond, all connections are made with lightly greased standard taper glass joints.

It was found in the calibration with water that this apparatus gave results that were consistently about 1.5 to 2.5% too high, as referred to the Bureau of Standards figures for water. The high results were due to heat leakage out of the top of the system. It was not found practicable to correct heat leakage out the top of the system except by extensive remodeling of the apparatus, but a correction factor was worked out which, when applied to subsequent results, gave a satisfactory calibration.

The calorimeter is seated on a cork block inside the dewar flask, D_1, being held concentric with it by the insulating rings of cork, X. The dewar flask itself is contained in the copper submarine, G, being held in place by the masonite spacer discs, E, and rests on cork blocks to insulate it further from the submarine. To prevent convection within the submarine, the space between the dewar flask and the walls of the submarine is packed with glass wool. A cardboard collar, not shown in the drawing, serves to keep the glass wool from overflowing into the mouth of the dewar