(7) Luff, B. B.; Reed, R. B.; Wakefield, Z. T. *J. Chem. Eng. Data* 1972, *17*, 423-5.
(8) Linke, W. F. "Solubilities of Inorganic and Metal Organic Compounds"; American Chemical Society: Washington, DC, 1965; Vol. II, p 282.
(9) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. *NBS Tech. Note (U.S.)* 1966, *No. 270-3*.
(10) Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffe, I. *Natl. Bur. Stand. (U.S.), Circ.* 1952, *No. 500*.

Salting Effects of *p*-Aminophenol in Some Protic Solvents at 20 °C

Bharati Das*

Department of Chemistry, University of Roorkee, Roorkee, U.P., 247667, India

Ratna Ghosh

Department of Chemistry, Indian Institute of Technology, Kharagpur, W. Bengal, 721302, India

Saturation solubilities of *p*-aminophenol (PAP) in the presence of four salts, viz., NaCl, Na$_2$SO$_4$, NaClO$_4$, and KSCN, in three solvents, viz., water, ethyl acetate, and dioxane, have been determined at 20 °C. The effect of salts on the solubility of *p*-aminophenol and the salting coefficients, K_s, have been evaluated. The salting out decreases in the order Na$_2$SO$_4$ > NaCl > NaClO$_4$ > KSCN. Dioxane shows the highest salting order followed by ethyl acetate and water.

Introduction

The process of salting out is studied by shaking a solute between two immiscible solvent phases, one of them being the organic phase and the other the aqueous phase containing the salt called the salting-out agent, and then analyzing the solute concentration in one phase or both phases. However, if the information desired relates to miscible solvents, the ratio of solubilities in two separate solvents is measured and reported as the distribution coefficient. Furthermore, when protic solvents are used for salting studies, as in the present case, the ratio of the saturation solubility of the solute in pure solvent and in the presence of salt can be used to calculate the salting-out coefficient.

The solubility method has been used extensively to study the salting effect for various classes of organic compounds. Amino acids (*1, 2*), phenols and cresols (*3*), toluene (*4*), benzoyltrifluoroacetone (*5*), hydrocarbons and substituted benzenes (*6*), monoalkylbenzene (*7*), etc., in the presence of salting agents have been studied by the solubility method. The solubility technique, however, requires relatively high concentrations of organic solutes to saturate many solvents.

We have determined the saturation solubilities of *p*-aminophenol (hereafter designated PAP) in the presence of four salts (both structure makers and structure breakers), viz., sodium chloride (NaCl), sodium sulfate (Na$_2$SO$_4$), sodium perchlorate (NaClO$_4$), and potassium thiocyanate (KSCN), in three protic solvents, viz., water, dioxane, and ethyl acetate, at 20 °C. The solubility technique was utilized here, due to the reason that PAP is almost insoluble in aprotic solvents (like benzene, toluene, etc.) and the extraction technique was not suitable for the present studies.

Experimental Section

E. Merck AnalaR-grade PAP was vacuum dried over anhydrous NaOH to remove any existing traces of water. All salts, viz., NaCl, Na$_2$SO$_4$, NaClO$_4$, and KSCN, were of AnalaR grade and were used without any further purification. Dioxane and ethyl acetate of BDH AnalaR grade and water were double distilled at temperatures much below their boiling points at a recovery rate of 1.0 mL min^{-1}.

Saturation solubilities of PAP in the absence and the presence of weighed amounts of salts in different solvents were calculated. Different amounts of salt required for different molarities (from 0.2 to 2 M) for a fixed volume of solvent were shaken along with excess PAP in stoppered Corning-glass boiling tubes for about 6 h to obtain saturation with respect to PAP. After being shaken, the solutions were set aside for several hours, or until the solutions became clear. A thermostatic shaker with an arrangement for holding as many as 18 boiling tubes was used for shaking. This maintained the temperature to ±0.2 °C.

A Carl Zeiss Specord UV–vis spectrophotometer with a thermostated cell compartment and 5.0- and 1.0-cm and 1.0-mm matched quartz cells were used for absorbance measurements.

The clear solution of PAP obtained after shaking was separated (diluted where required) and its absorbance noted in the UV region at 312 nm. The concentration was found from the known values, as the Beer–Lambert law was found to be valid. The precision in all cases was better than 1.0%. The reproducible values only have been recorded in Table I.

Results and Discussion

The salting coefficient, K_s, is most commonly determined from the solubility according to the empirical Setschenow equation (*8*)

$$\log f = \log (S^0/S) = K_s C_s \qquad (1)$$

where S^0 and S denote the solubility of PAP in pure solvent and in the presence of salt, respectively, C_s is the salt concentration, and f is the activity coefficient of PAP in the solvent when salt is added. The plot of $\log (S^0/S)$ against C_s gave straight

Table I. Saturation Solubilities of *p*-Aminophenol in Water, Ethyl Acetate, and Dioxane in the Presence of Salts at 20 °C

[salt], M	Na_2SO_4 [PAP], M	$\log S^\circ/S$	NaCl [PAP], M	$\log S^\circ/S$	$NaClO_4$ [PAP], M	$\log S^\circ/S$	KSCN [PAP], M	$\log S^\circ/S$
				Water				
0.0	0.005 35		0.005 35		0.005 35		0.005 35	
0.2	0.005 19	0.0123	0.005 28	0.0057	0.005 39	-0.0032	0.005 47	-0.0096
0.4	0.005 07	0.0225	0.005 16	0.0157	0.005 43	-0.0064	0.005 59	-0.0190
0.6	0.004 96	0.0328	0.005 04	0.0259	0.005 51	-0.0127	0.005 75	-0.0313
0.8	0.004 88	0.0399	0.004 96	0.0328	0.005 55	-0.0159	0.005 83	-0.0373
1.0	0.004 72	0.0544	0.004 88	0.0399	0.005 59	-0.0191	0.005 98	-0.0483
1.2	0.004 57	0.0694	0.004 72	0.0544	0.005 63	-0.0221	0.006 10	-0.0569
1.4	0.004 41	0.0839	0.004 65	0.0609	0.005 71	-0.0282	0.006 22	-0.0654
1.6	0.004 25	0.0999	0.004 57	0.0684	0.005 72	-0.0283	0.006 34	-0.0737
1.8	0.004 17	0.1082	0.004 49	0.0761	0.005 75	-0.0313	0.006 46	-0.0818
2.0	0.003 94	0.1328	0.004 41	0.0839	0.005 79	-0.0343	0.006 57	-0.0892
				Dioxane				
0.0	0.012 09		0.012 09		0.012 09		0.012 09	
0.2	0.011 62	0.0172	0.011 70	0.0142	0.012 32	-0.0081	0.012 32	-0.0081
0.4	0.011 16	0.0347	0.011 50	0.0217	0.012 55	-0.0162	0.012 79	-0.0244
0.6	0.010 69	0.0534	0.011 40	0.0305	0.012 90	-0.0281	0.013 25	-0.0397
0.8	0.010 23	0.0725	0.011 20	0.0346	0.013 02	-0.0322	0.013 48	-0.0472
1.0	0.009 65	0.0978	0.010 81	0.0486	0.013 48	-0.0472	0.013 95	-0.0621
1.2	0.009 30	0.1139	0.010 58	0.0579	0.013 83	-0.0584	0.014 41	-0.0762
1.4	0.008 83	0.1364	0.010 46	0.0628	0.013 95	-0.0621	0.014 88	-0.0901
1.6	0.008 37	0.1597	0.010 23	0.0725	0.014 18	-0.0692	0.015 11	-0.0968
1.8	0.007 90	0.1847	0.010 00	0.0824	0.014 41	-0.0762	0.015 58	-0.1101
2.0	0.007 55	0.2044	0.009 76	0.0929	0.014 65	-0.0834	0.016 04	-0.1227
				Ethyl Acetate				
0.0	0.011 81		0.011 81		0.011 81		0.011 81	
0.2	0.011 36	0.0168	0.011 59	0.0081	0.012 04	-0.0083	0.012 04	-0.0083
0.4	0.010 90	0.0348	0.011 59	0.0081	0.012 04	-0.0083	0.012 27	-0.0165
0.6	0.010 45	0.0531	0.011 36	0.0168	0.012 27	-0.0165	0.012 72	-0.0322
0.8	0.010 00	0.0722	0.011 13	0.0257	0.012 50	-0.0246	0.012 95	-0.0400
1.0	0.009 77	0.0823	0.011 13	0.0257	0.012 50	-0.0246	0.013 18	-0.0476
1.2	0.009 54	0.0927	0.010 90	0.0348	0.012 72	-0.0322	0.013 40	-0.0546
1.4	0.009 09	0.1136	0.010 68	0.0436	0.012 72	-0.0322	0.013 63	-0.0622
1.6	0.008 63	0.1362	0.010 45	0.0531	0.012 95	-0.0400	0.014 09	-0.0766
1.8	0.008 40	0.1479	0.010 22	0.0627	0.013 18	-0.0476	0.014 54	-0.0903
2.0	0.008 18	0.1594	0.010 00	0.0723	0.013 40	-0.0548	0.014 77	-0.0971

Table II. Salting Coefficients of *p*-Aminophenol at 20 °C

solvent	salts Na_2SO_3	NaCl	$NaClO_4$	KSCN
water	0.057 ± 0.001^a	0.042 ± 0.001	-0.017 ± 0.002	-0.045 ± 0.001
ethyl acetate	0.083 ± 0.002	0.034 ± 0.002	-0.026 ± 0.001	-0.047 ± 0.002
dioxane	0.097 ± 0.002	0.046 ± 0.001	-0.041 ± 0.002	-0.059 ± 0.003

^{a} Standard error.

lines for all the salts studied in the case of each solvent (Figure 1). The values of K_s were calculated from the slopes. The saturation solubilities of PAP in different solvents in the presence of different salts are listed in Table I. The K_s values are listed in Table II.

Table I shows that, in the presence of salts, the saturation solubility of PAP is almost the same in dioxane and ethyl acetate followed by water.

Considering the salting effect of different salts, one finds that positive values of K_s are obtained in the presence of Na_2SO_4 and NaCl and negative values in the presence of $NaClO_4$ and KSCN. The salting out decreases markedly in the order Na_2SO_4 > NaCl > $NaClO_4$ > KSCN. The order agrees with our previous studies carried out with naphthols (*9*). The low salting effect of $NaClO_4$ and KSCN is due to the "structure-making" property of these salts. Among the structure makers, KSCN has a greater structure-making tendency than $NaClO_4$ and hence shows more salting in than the latter. The ionic charge also plays an important role in salting out: the greater the ionic charge, the greater the salting out. Among the structure breakers Na_2SO_4 has a greater charge than NaCl and hence

the greatest salting out is obtained in studies with Na_2SO_4.

A positive K_s signifies an increase in the activity coefficient of PAP and the occurrence of salting out. The reverse phenomenon is solute stabilization or salting in corresponding to negative K_s and decreased activity coefficient. Salt increases the activity coefficient of an organic solute in water and decreases that of water. This accompanies a salting-out process. In the reverse phenomenon of salting in, electrostatic theories predict a higher dielectric constant in the aqueous solutions of organic solute than in pure water. In ternary aqueous ionic solutions, it is not easy to interpret the activity coefficient data in terms of dielectric saturation. A more illuminating and integrated approach is then through the so-called chemical theory where one considers all possible interactions that may arise in such solutions. The observed thermodynamic parameters of transfer of nonelectrolyte from water to salt solution or from water to an immiscible hydrocarbon phase can then be regarded as a balance between several competitive equilibrium processes. The salting out may in part be explained by the fact that the salts are preferentially solvated with solvent molecules. Thus, the availability of solvent for the nonelectrolyte is de-
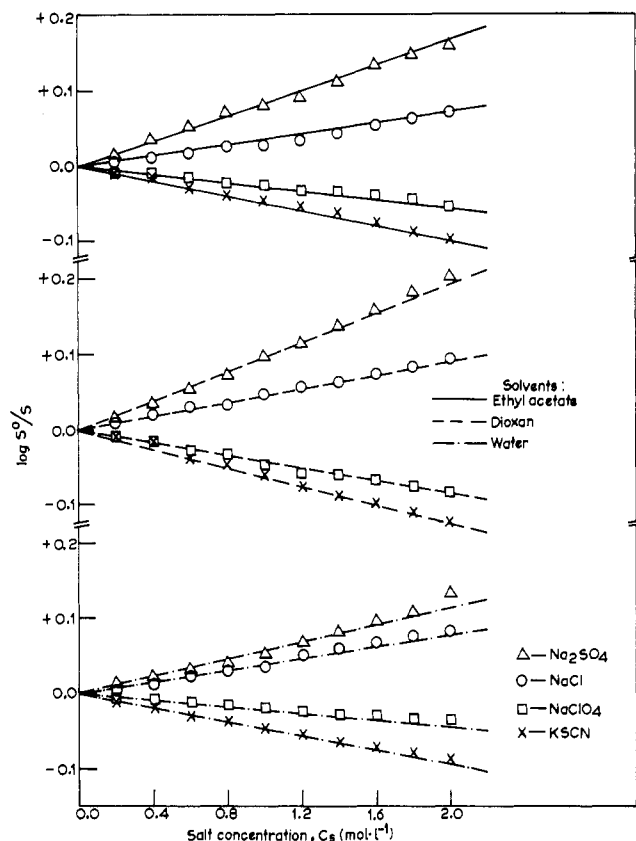
Figure 1. Solubility changes for *p*-aminophenol as a function of salt concentration.

creased. Hence, the free energy of the latter will rise; the largest change to be expected is that with the cation having the highest charge density. Apparently, the larger and more poorly hydrated ions have the opposite effect on the nonelectrolyte so

that the free energy of the nonelectrolyte decreases and its solubility increases.

The salting out of PAP decreases in the order dioxane > ethyl acetate > water. This can be explained by considering that the ion-pair solvate in dioxane is more stabilized due to its low dielectric constant which precludes the solvation of the nonelectrolyte; hence, greater salting out is obtained. In ethyl acetate, due to the presence of two alkyl groups, the interaction with the aromatic part of PAP is greater and hence the salting out is less than in dioxane. In water, the salting out is even less and this can be explained by the stronger H bonding between water and PAP with acceptor sites. This effect predominates in spite of the greater solvation of the ions in water.

Literature Cited

(1) McMeekin, T. L.; Cohn, E. J.; Weare, J. H. *J. Am. Chem. Soc.* **1936**, *58*, 2173–81.
(2) Cohn, E. J.; Edsal, J. "Proteins, Amino Acids and Peptides"; Reinhold: New York, 1943; p 200.
(3) Korenman, Ya. I.; Bortnikova, R. N. *Tr. Khim. Khim. Tekhnol.* **1974**, 127–8.
(4) Sado, E.; Kito, S.; Ito, Y. *J. Chem. Eng. Data* **1975**, *20*, 373–5.
(5) Yoshimura, Y.; Suzuki, N. *Talanta* **1978**, *25*, 489–91.
(6) Aquan-Yuen, M.; Mackay, D.; Shiu, W. Y. *J. Chem. Eng. Data* **1979**, *24*, 30–4.
(7) Ben-Naim, A.; Wilf, J. *J. Phys. Chem.* **1980**, *84*, 583–5.
(8) Setschenow, J. *Z. Phys. Chem.* **1889**, *4*, 117.
(9) Ghosh, R.; Das, B. *J. Indian Chem. Soc.* **1981**, *58*, 1108–10.

Properties of SOCl$_2$-Based Electrolytes. 1. Conductivity, Viscosity, and Density

Hanumanthiya V. Venkatasetty*

Honeywell, Inc., Corporate Technology Center, Bloomington, Minnesota 55420

Stanislaw Szpak

Naval Ocean Systems Center, San Diego, California 92152

Specific conductivities, kinematic viscosities, and densities of SOCl$_2$-AlCl$_3$-LiCl electrolytes covering a wide range of compositions and temperatures were measured. A need for this information became evident when attempts were made to extend operational capabilities of highly energetic Li/SOCl$_2$ batteries to higher discharge rates. As we attempt to increase the rate of discharge, a new set of requirements must be met and new design concepts must be advanced to overcome ensuing difficulties. Most of these difficulties are traced to non-steady-state operation. Technical evaluations of any particular design can be made only if pertinent data are available.

In the past decade, new and highly energetic Li batteries have been developed (*1*). Among them, the Li/SOCl$_2$ system represents a new class of electrochemical energy conversion device—where the oxidant is at the same time solvent and depolarizer. The SOCl$_2$ molecules oxidize the metallic surface of the Li negative with the formation of a protective LiCl film and act as a solvent for Lewis acids, e.g., AlCl$_3$, thus providing ionic conductivity. They also function as a depolarizer yielding sulfur, sulfur dioxide, and chloride ions in the course of the cathodic process. Energy density of 600 W h kg^{-1}, in reserve, low rate configuration design, is routinely realized (*2, 3*).

Recent efforts are directed toward the development and construction of cells capable of operation at high rates.