

Solubility Products of Tetraphenylarsonium and Tetraphenylphosphonium Picrates in Ethanol–Water Solvents at 25°C

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Solubility (ion-activity) products of tetraphenylarsonium picrate (Ph₄As Pi) and tetraphenylphosphonium picrate (Ph₄P Pi) were determined at 25°C over the entire range of ethanol–water solvents at intervals of about 10 wt % ethanol. Solubilities of the title electrolytes were determined by spectrophotometric analysis of their saturated solutions for the picrate ion. Mean ionic activity coefficients of the electrolytes in saturated solutions were evaluated from the variation of solubility as a function of ionic strength adjusted by means of added lithium chloride. In solvents containing more than 70 wt % ethanol, ion-pair association constants and limiting equivalent conductances of the title electrolytes were derived from measurements of electrolytic conductance at 25°C.

The changes in the free energies (1, 10) and enthalpies (2, 9) accompanying the transfer of individual ions from one solvent to another are sometimes estimated by assuming that the corresponding changes for the tetraphenylarsonium (Ph₄As⁺), tetraphenylphosphonium (Ph₄P⁺) or triisooamyl-*n*-butylammonium (TAB⁺) cation can be equated to those for the tetraphenylborate (BPh₄⁻) anion. Because the free energies for the transfer of electrolytes are usually calculated from solubility products, accurate thermodynamic values of the latter are indispensable for a meaningful split of the free energy into individual ionic components. Earlier communications from this laboratory reported on the ion-pair association (5) and the solubility products (6) of some TAB⁺ and BPh₄⁻ salts in ethanol–water solvents. Now analogous studies were extended to Ph₄As⁺ and Ph₄P⁺ picrates.

In ethanol–water solvents containing 70 or more wt % ethanol, incomplete dissociation of the title electrolytes must be taken into account, and their solubility products, K_s , can be expressed in the form:

$$K_s = (C\alpha f_{\pm})^2 = a_{\pm}^2 \quad (1)$$

where C is the solubility in moles per liter, α is the degree of dissociation, f_{\pm} is the mean ionic activity coefficient on the molar scale, and a_{\pm} is the mean ionic activity in the saturated solution. In the present study, values of α in solutions below 70 wt % ethanol were taken to be unity. For solutions of higher ethanol content, α was calculated from the ion-pair association constants K_A , obtained from measurements of electrolytic conductance as a function of concentration. The solubility, C , was determined by preparing saturated solutions of the electrolytes in pure solvents and analyzing for the picrate concentration spectrophotometrically. The activity coefficients, f_{\pm} , were evaluated from the variation of solubility as a function of ionic strength (3) which was varied, as in our previous study (6), by means of added LiCl. Corrections for the partial ion pairing of LiCl were computed from its association constants reported earlier (5).

EXPERIMENTAL

The title electrolytes were prepared by combining hot equimolar ethanolic solutions of picric acid (Baker analyzed reagent) and Ph₄As Cl or Ph₄P Cl (or Ph₄P Br) (Alfa Inor-

ganics), respectively. Water was added to incipient cloudiness, followed by dissolution with a minimum amount of hot ethanol. The crystals which separated upon cooling were washed with water, purified by double recrystallization from ethanol–water mixtures, and dried at 80–90°C in vacuo for 24 hr. The electrolytes were recrystallized once more prior to the determination of their conductances. The purification of LiCl, KCl, and of the solvents, the method of preparing ethanol–water mixtures of accurately known composition, as well as the apparatus and the procedure for electrolytic conductance measurements, have been described (5). The conductance cell contained slightly platinized platinum electrodes with a cell constant of 0.0099332 based on the 0.01 demal aqueous KCl standard (8).

The solubilities were determined at intervals of about 10 wt % ethanol with or without added lithium chloride employing essentially the same procedure and apparatus as before (6), except for a significant improvement in the method of preparing saturated solutions. This consisted of subjecting the suspensions to the dispersing action of an ultrasonic generator (the Maxomatic from the L & R Manufacturing Co.) for a period of about 2 hr prior to their equilibration on the shakers at 25.00°C. The use of the ultrasonic generator reduced the time needed for equilibration from 2–4 weeks (6) to an average of 3 days. A solution was considered saturated when successive analyses several days apart differed by no more than 0.6%, which is the precision of the spectrophotometric analysis for the picrate ion. The absorbancies were measured on a Cary Model 14 spectrophotometer at the 355-nm picrate maximum, which is independent of the cation. The concentrations were calculated using the molar absorptivities for the above maximum determined previously over the entire ethanol–water range (6). Throughout the procedure, the solutions were monitored by inspection of their uv bands characteristic of tetraphenyl cations (not used for analysis), whose peak-height ratios are sensitive to decomposition. As a rule, exposure to ultrasonic waves caused no decomposition.

RESULTS AND DISCUSSION

Electrolytic Conductance. In the solvents containing from 70–100 wt % ethanol, the conductance of the title electrolytes was measured over the approximate concentration range of 10⁻⁴–10⁻³M with the sole purpose of evaluating their ion-pair association constants. Values of K_A

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were derived along with the limiting equivalent conductances, Λ_0 , from the Shedlovsky equation (7, 12):

$$\frac{1}{\Lambda S_{(x)}} = \frac{K_A C A f_{\pm}^2 S_{(x)}}{\Lambda_0^2} + \frac{1}{\Lambda_0} \quad (2)$$

where Λ is the equivalent conductance and $S_{(x)}$ is the Shedlovsky function defined in the section on nomenclature. All calculations in this study were carried out on an IBM 360 computer using FORTRAN programs. Table I lists the values of K_A , Λ_0 , their standard deviations, the measure density d_0 and the specific conductance, k_0 of the solvents.

With the aid of the association constants, K_A , values for the ion-pair dissociation, α , at a given concentration, C , were calculated from Equation 3:

$$\alpha = \frac{-1 + (1 + 4 K_A C f_{\pm}^2)^{1/2}}{2 K_A C f_{\pm}^2} \quad (3)$$

where the activity coefficient f_{\pm} was estimated from the limiting Debye-Hückel (D-H) law by a process of successive approximations (6). Where the solvent compositions in the solubility and activity coefficient determinations differed somewhat from those at which the K_A 's were determined, values of

K_A for the specific solvent composition of interest were interpolated from linear plots of $\log K_A$ vs. $1/D$, where D is the dielectric constant of the solvent.

Solubilities and Activity Coefficients. The determination of activity coefficients from the variation of solubility as a function of ionic strength, I , has been discussed in detail (6). To summarize, one equates the mean ionic activity of a saturated solution in the pure solvent and in the presence of added inert salt (LiCl in this case), designated by subscripts 0 and I , respectively:

$$(\alpha_0 C_0 f_{\pm,0}) = (\alpha_I C_I f_{\pm,I}) \quad (4)$$

Equation 4 is then rearranged into a form convenient for extrapolation:

$$\log \frac{\alpha_I C_I}{\alpha_0 C_0} = \log f_{\pm,0} - \log f_{\pm,I} \quad (5)$$

in which $\log f_{\pm,I}$ is replaced by a power series in $I^{1/2}$:

$$-\log f_{\pm,I} = A_1 I^{1/2} + A_2 I + A_3 I^{3/2} + \dots \quad (6)$$

Equation 6 is mathematically identical with the extended D-H equations, but has the advantage of being a polynomial, for which curve-fitting computer programs are generally available. Equation 6 has been used for the formulation of activity coefficients in the analysis of emf (4, 11) and solubility (6) data. A computer program selects the best least-squares fit to the experimental data points expressed as $\log (\alpha_I C_I / \alpha_0 C_0)$ as a function of $I^{1/2}$ to a predetermined order in $I^{1/2}$. The intercept of the above function is the logarithm of the mean ionic activity coefficient in the saturated solution of the electrolyte without added LiCl, $\log f_{\pm,0}$. Table II shows the results of the activity-coefficient calculations, including the A coefficients of the power terms in Equation 6 and the solubility products, K_s . The degree of the polynomial employed in a given curve fitting, which is identical with the number of the A coefficients listed, was chosen on the basis of agreement between the coefficient A_1 computed from experimental data and the theoretical D-H limiting slope, A_{DH} . In the absence of experimental error, the two would be identical. The range of precision in the above computation of $f_{\pm,0}$, was 0.3–4%, a

Table I. Conductance Results at 25°C

Wt % ethanol	K_A	Λ_0	d_0	$10^8 k_0$
Ph ₄ As Pi				
100.0	100.4 ± 1.2	44.38 ± 0.02	0.7851	10.9
93.0	70.7 ± 1.9	39.46 ± 0.03	0.8047	21.9
80.9	41.7 ± 0.5	32.33 ± 0.01	0.8367	8.9
68.8	11.6 ± 1.4	27.93 ± 0.03	0.8658	6.4
Ph ₄ P Pi				
100.0	114.5 ± 1.0	46.95 ± 0.03	0.7851	8.4
93.4	76.4 ± 0.2	40.03 ± 0.01	0.8044	4.0
82.5	44.9 ± 0.7	33.32 ± 0.01	0.8324	44.6
72.3	27.6 ± 1.7	28.93 ± 0.03	0.8578	27.5

Table II. Solubilities, Degrees of Dissociation, Activity Coefficients, and Solubility Products at 25°C

Wt % ethanol	C_0 , (mol/l.) × 10 ³	α_0	$f_{\pm,0}$	A_{DH}	A_1	A_2	A_3	A_4	K_s , ($C_0 \alpha_0 f_{\pm,0}$) ²
Ph ₄ As Pi									
100.0	3.15	0.880	0.716	2.96	3.10	-6.30	5.25	...	3.94 × 10 ⁻⁶
93.3	4.10	0.887	0.738	2.57	2.50	-4.80	3.65	...	7.20 × 10 ⁻⁶
80.7	4.84	0.908	0.774	1.92	1.90	-3.80	3.17	...	1.16 × 10 ⁻⁵
70.7	4.22	0.959	0.818	1.53	1.55	-3.31	3.07	...	1.10 × 10 ⁻⁵
60.9	3.21	0.994	0.849	1.26	1.49	-2.43	7.33 × 10 ⁻⁶
50.9	2.08	1.000	0.899	1.05	1.09	-2.67	2.92	...	3.49 × 10 ⁻⁶
39.7	0.985	1.000	0.949	0.864	0.782	-1.54	1.40	...	8.74 × 10 ⁻⁷
30.3	0.398	1.000	0.964	0.746	0.759	-1.03	-4.88	17.2	1.47 × 10 ⁻⁷
20.4	0.138	1.000	0.981	0.650	0.615	-1.35	1.58	...	1.82 × 10 ⁻⁸
10.2	0.0590	1.000	0.989	0.584	0.570	-1.26	1.22	...	3.41 × 10 ⁻⁹
Water	0.0349	1.000	0.993 ^a	0.509	1.20 × 10 ⁻⁹ pK = 8.8 (1)
Ph ₄ P Pi									
100.0	3.44	0.861	0.714	2.96	2.96	-4.90	0.540	5.54	4.47 × 10 ⁻⁶
93.2	4.70	0.875	0.722	2.56	2.52	-5.09	5.02	-1.73	8.79 × 10 ⁻⁶
80.8	5.72	0.899	0.762	1.93	1.91	-3.70	3.45	-1.22	1.53 × 10 ⁻⁵
70.6	5.11	0.931	0.832	1.53	1.32	-1.98	1.18	...	1.56 × 10 ⁻⁵
61.0	3.99	0.965	0.858	1.26	1.16	-1.97	1.34	...	1.09 × 10 ⁻⁵
50.7	2.42	1.000	0.922	1.04	1.02	-1.91	1.48	...	4.96 × 10 ⁻⁶
39.3	1.18	1.000	0.945	0.859	0.764	-1.21	0.863	...	1.25 × 10 ⁻⁶
31.2	0.545	1.000	0.963	0.756	0.748	-1.57	1.96	-0.977	2.76 × 10 ⁻⁷
19.9	0.160	1.000	0.978	0.646	0.553	-0.705	2.45 × 10 ⁻⁸
10.0	0.0762	1.000	0.986	0.571	0.566	-1.14	0.937	...	5.65 × 10 ⁻⁹
Water	0.0451	1.000	0.992 ^a	0.509	2.00 × 10 ⁻⁹

^a Calculated from the D-H limiting law.

typical relative error being about 1%. By the method of propagation of errors, the largest uncertainty in α_0 was estimated to be about 0.8%, and the overall precision in the determination of the K_i 's ranged from 0.9–4.5%. No complications were encountered from a potential association between the ions of the title electrolytes and those of LiCl. That there is no appreciable association between Li^+ and Pi^- ions in ethanol–water solvents was reported from this laboratory earlier (6). In the present study, conductance measurements have shown that also $\text{Ph}_4\text{As Cl}$ and $\text{Ph}_4\text{P Cl}$ are completely dissociated in ethanol–water solvents.

NOMENCLATURE

A_{DH} = Debye-Hückel limiting slope
 A_1, A_2, A_3 = empirical coefficients of power terms of $I^{1/2}$ in Equation 6
 a_{\pm} = mean ionic activity, mol/l.
 C = concentration of electrolyte, mol/l.
 C_0 = solubility in pure solvent, mol/l.
 C_I = solubility in presence of added salt at ionic strength I , mol/l.
 d_0 = density of solvent, g/ml
 D = dielectric constant of solvent
 f_{\pm} = mean ionic activity coefficient of electrolyte referred to infinite dilution in given solvent as standard state
 $f_{\pm,0}$ = mean ionic activity coefficient in absence of added salt
 $f_{\pm,I}$ = mean ionic activity coefficient in presence of added salt at ionic strength I
 I = ionic strength, mol/l.
 k_0 = specific conductance of solvent, mho/cm
 K_A = ion-pair association constant, l./mol
 K_s = solubility product of an electrolyte, $\text{mol}^2/\text{l.}^{-2}$
 M = mol/l. of solution
 S = Onsager coefficient, $\alpha\Lambda_0 + \beta$ where

$$\alpha = \frac{0.8204 \times 10^6}{(DT)^{3/2}} \text{ and } \beta = \frac{82.501}{\eta(DT)^{1/2}} \text{ where } \eta$$

is viscosity in poises
 $S_{(z)}$ = Shedlovsky function $\{z/2 + [1 + (z/2)^2]^{1/2}\}^2$,
 where $z = S\Lambda_0^{-3/2}(CA)^{1/2}$
 w = wt % ethanol in mixture with water

GREEK LETTERS

α = degree of dissociation into ions
 α_0 = degree of dissociation into ions in pure solvent
 α_I = degree of dissociation in presence of added salt at an ionic strength I
 Λ = equivalent conductance at finite concentration, mho l./cm mol
 Λ_0 = limiting equivalent conductance, mho l./mol $^{-1}$ cm $^{-1}$

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Isopiestic Studies of Some Aqueous Electrolyte Solutions at 80°C

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Isopiestic ratios to NaCl of KCl, LiCl, BaCl₂, and Na₂SO₄ in water at 80.22°C are reported. Empirical equations for R and ϕ as functions of molality are given which reproduce the results within the experimental uncertainty of better than 0.001 for the range of molality covered by the measurements.

A previous paper (2) described an apparatus and procedure that yielded isopiestic data at 60°C of quality comparable to the best at 25°C and showed promise of extension to higher temperatures. This paper describes modifications of the former system that have proved equally successful at 80°C. Earlier work had raised questions about the consistency of data at temperatures below and above this point. Data at 80°C are reported for KCl, LiCl, BaCl₂, and Na₂SO₄ over a range of concentrations. These results are evaluated briefly with

respect to their relationship to our previous measurements at lower temperatures and the literature data at higher temperatures.

EXPERIMENTAL

The apparatus and procedure used were essentially the same as those developed previously (2). Minor modifications were made in apparatus and procedure to overcome difficulties attending the increase in temperature. Triethylene glycol was substituted for ethylene glycol as bath liquid because of its

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