Solubility Products of Potassium and Triisoamyl–*n*-butylammonium Picrates and Tetraphenylborates in Ethanol-Water Mixtures at 25° C.

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Solubility (ion-activity) products of potassium picrate (KPi), potassium tetraphenylborate ($KBPh_4$), and triisoamyl–*n*-butylammonium picrate (TABPi) were determined at 25° C. over the entire range of ethanol-water solvents, and those of triisoamyl–*n*-butylammonium tetraphenylborate (TAB BPh_4), in 40 to 100 weight % ethanol in water. Molar absorptivities of picrate and tetraphenylborate ions were obtained as a function of ethanol-water composition in the visible and ultraviolet regions of the spectrum, respectively. Saturated solutions of the title electrolytes were analyzed quantitatively by spectrophotometry. Mean ionic activity coefficients of the electrolytes in saturated solutions were evaluated from studies of their solubility as a function of ionic strength varied by means of added lithium chloride. At solubilities $< 10^{-3}$ M, activity coefficients obeyed the limiting Debye-Hückel law.

IN SOLVENTS where association into ion pairs cannot be neglected, the solubility product of a uni-univalent electrolyte, K_s, can be expressed in terms of the mean ionic activity, $a_{\pm}$, of its saturated solution in the form:

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

where C is the analytical solubility in moles per liter, α is the degree of dissociation, and $f_{\pm}$ is the mean ionic activity coefficient on the molar scale. In the present study, the solubility, C, was determined directly by preparing saturated solutions of the electrolytes in pure solvents and determining picrate or tetraphenylborate concentrations spectrophotometrically. [Tetraphenylborate is the IUPAC name for the $B(C_6H_5)_4^-$ ion (*6*). Most of the literature uses the term "tetraphenylboride."] The activity coefficients, $f_{\pm}$, were evaluated by the solubility method of Brønsted and La Mer (*1*). This method is based on the variation exhibited by the activity coefficient and hence by the solubility when the ionic strength of a saturated solution is increased by addition of an inert "solvent salt." In this study, lithium chloride was used to vary the ionic strength of the saturated solutions and the resulting changes in solubility were determined by spectrophotometry, as in the case of pure solvents. The degree of dissociation, α, for the title electrolytes and for LiCl was calculated from the ion-pair association constants determined in a study of electrolytic conductance reported earlier (*3*). Because it was impractical to determine C, α, and $f_{\pm}$ for a given electrolyte at a series of identical solvent compositions, values of C and α were interpolated, wherever necessary, for ethanol-water compositions at which $f_{\pm}$ was determined.

EXPERIMENTAL

Sodium tetraphenylborate (Fisher certified 100.0%) was used as received. Preparation and purification of KPi, $KBPh_4$ (*10*), TAB BPh_4 (*2*), and TABPi (*3*) have been described. The purification of LiCl and of the solvents, as well as the method of preparing ethanol-water mixtures of known composition, has been reported (*3*).

The solubilities were determined at intervals of about 10 weight % ethanol with or without added lithium chloride. The solvent salt was added at six to 10 different concentrations ranging from about 2 to 200 times the molar solubility of the electrolyte. The solutions were saturated by shaking with a large excess of solid electrolyte in water-jacketed flasks on a Burrell wrist-action shaker. Water circulated through the flasks from a bath maintained at 25.00° ± 0.01° C. by a proportional temperature controller (Yellow Springs Instrument Co. Model 72). The actual temperature of the bath was determined, to ±0.01° C., by an NBS certified thermometer. A solution was considered saturated when successive weekly analyses agreed to about 1%. This agreement was achieved after 2 weeks of equilibration for solutions with no added LiCl and after one month for solutions with added LiCl. After the suspensions settled they were filtered, if necessary, through Gelman Metricel filters of 0.20-micron pore size in a filtration syringe and diluted to proper concentration range, and their spectra were recorded on a Cary Model 14 spectrophotometer.

RESULTS AND DISCUSSION

Absorptivities. Molar absorptivities for the broad picrate maximum at 355 mμ were determined over the entire range of ethanol-water mixtures at about 10 weight % intervals on solutions of KPi and TABPi. Both electrolytes were used in order to test the possibility that ion pairing might influence molar absorptivity. Studies of electrolytic conductance (*3*) disclosed KPi to be partially associated only in ethanol-water mixtures containing more than 75 weight % ethanol, while TABPi exhibited partial association throughout the ethanol-water range. However, both KPi and TABPi turned out to have the same absorptivity in each ethanol-water solvent. Molar absorptivities for the characteristic tetraphenylborate peaks at about 266 and 274 mμ were obtained' over the range of ethanol-water mixtures using sodium tetraphenylborate. These absorptivities are independent of the associated cation (*8*, *9*) and are fairly insensitive to solvent composition, as has been observed for acetonitrile-water mixtures (*8*). All absorptivities are compiled in Table I at 10 weight % intervals from water to ethanol and compared with literature values for the pure solvents.

Beer's law was found to hold for both ions throughout the range of concentrations corresponding to absorbances

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Table I. Molar Absorptivities of Picrate and Tetraphenylborate Ions in Ethanol-Water Mixtures at 25° C.

Wt. % Ethanol	Picrate $a \times 10^{-4}$ at 355 Mμ	Tetraphenylborate $a \times 10^{-3}$	
		266 mμ	274 mμ
0.00 (water)	1.43	3.23	1.99
	1.44 (*9*)	3.25 (*9*)	2.06 (*9*)
		3.225 (*8*)	2.100 (*8*)
10.0	1.43	3.21	2.02
20.0	1.45	3.19	2.05
30.0	1.48	3.18	2.06
40.0	1.51	3.16	2.08
50.0	1.54	3.15	2.08
60.0	1.55	3.13	2.09
70.0	1.56	3.11	2.09
80.0	1.57	3.08	2.09
90.0	1.58	3.03	2.10
100.0	1.60	2.97	2.10

Table II. Solubilities of Electrolytes in Ethanol-Water Mixtures at 25° C.

Wt. % Ethanol	(Moles per Liter of Solution) × 10^3			
	KPi	TABPi	$KBPh_4$	TAB BPh_4
0.00 (water)	24.2 (*9*)	0.226 (*9*)	0.174 (*9*)	
	24.1 (*11*)		0.178 (*8*)	
	23.3		0.182 (*10*)	
10.0	18.0	0.282	0.220^a	
20.0	16.0	0.406	0.340	
30.0	17.9	0.903	0.670	
40.0	20.5	2.30	1.33	0.0210
46.0	21.9	4.12	2.08	0.0512
50.0^a	22.1	5.25	2.37	0.060
60.0	19.1	10.3	2.80	0.121
70.0	14.2	18.4	2.89	0.297
80.0	7.64	29.4	2.11	0.594
90.0	3.23	43.3	1.09	0.730
100.0	1.04	62.7	0.504	1.18
	6.89 (*4*)			

^{a} Interpolated.

<2.0. The absorptivities used for calculations at specific uneven solvent compositions were obtained by interpolation from large-scale plots.

Solubility. All solubilities except those of KPi (*9, 11*), $KBPh_4$ (*8, 9*), and TABPi (*9*) in water, and of KPi in ethanol (*4*) are reported here for the first time. Although Fischer (*4*) determined the solubilities of KPi also in ethanol-water mixtures, the composition of his solvents was stated as volume per cent ethanol, without specifying unambiguously the method of preparing the mixtures. Because volumes of ethanol and water are not additive, one cannot convert with certainty Fischer's solvent compositions to weight per cent, in order to compare his results with those of the authors.

All solutions of the tetraphenylborates were deaerated to prevent decomposition. Nevertheless, some tended to decompose on prolonged equilibration with solvent. This, coupled with very low solubility, prevented the authors from obtaining reliable values for the solubility of TAB BPh_4 below approximately 40 weight % ethanol. For more soluble systems, the decomposition did not seriously affect the accuracy of the solubility determinations, as its presence was readily detectable from the resulting significant changes in the ultraviolet spectrum of the tetraphenylborate ion. When a sample was found to be decomposed, the determination was repeated. The solubilities are listed at 10 weight % intervals of solvent composition in Table II.

The precision of our spectrophotometric analytical method is estimated to be 0.6%, based on the standard deviation in the analysis of saturated solutions of KPi in 92.3 weight % ethanol. The accuracy of the over-all solubility determination was estimated to be 1.5% for the picrates and 3.0% for the tetraphenylborates, based on measurements of KPi and $KBPh_4$ solubilities in 92.3 and 100% ethanol, respectively.

Activity Coefficients. The experimental determination of activity coefficients from solubility is based on the dependence of the activity coefficient of a saturated solution on its ionic strength. This dependence is most simply illustrated by the limiting form of the Debye-Hückel (D-H) law, $\log f_\pm = -AI$, where A is the D-H limiting slope and I is the ionic strength. As I is increased, $f_\pm$ will decrease, and since the activity of a saturated solution is a constant at a given temperature, independent of ionic strength, a decrease in the activity coefficient will result in an increase in the solubility, C, so that the constancy of $a_\pm$ in Equation 1 is maintained. Expressions similar to Equation 1 can be written for saturated solutions of an electrolyte in a pure solvent, designated by subscript o:

$$(a_{\pm,o})^2 = (\alpha_o C_o f_{\pm o})^2 \tag{2}$$

and in the presence of a solvent salt at ionic strength I:

$$(a_{\pm,I})^2 = (\alpha_I C_I f_{\pm,I})^2 \tag{3}$$

Since $a_\pm^2$ is independent of ionic strength, it is possible to equate the two expressions in a given solvent, rearranging them into a form convenient for extrapolation:

$$\log \frac{\alpha_I C_I}{\alpha_o C_o} = \log f_{\pm,o} - \log f_{\pm,I} \tag{4}$$

for purposes of extrapolation, $-\log f_{\pm,I}$ is replaced by a function of $I^{1/2}$:

$$\log \frac{\alpha_I C_I}{\alpha_o C_o} = \log f_{\pm,o} + F(I^{1/2}) \tag{5}$$

A plot of $\log \alpha_I C_I / \alpha_o C_o$ *vs.* $I^{1/2}$ will yield as the intercept the logarithm of the mean ionic activity coefficient of a saturated solution of the electrolyte. If the D-H limiting law is valid for the solutions studied, the plot will be linear with a slope equal to A of the D-H limiting law. More frequently, however, measurements must be carried out over ranges of higher ionic strength, where the activity coefficient does not vary linearly with $I^{1/2}$, so that a curvature is observed in plots of $\log (\alpha_I C_I / \alpha_o C_o)$ *vs.* I. Both linear and nonlinear extrapolations are illustrated in Figure 1. For systems where the curvature is observed, it may still be possible to extrapolate the linear portion of the curves at low I, or the whole set of data can be expressed by a higher-order polynomial in $I^{1/2}$. The latter is equivalent to expressing the activity coefficient as a power series in $I^{1/2}$:

$$-\log f_\pm = A_1 I^{1/2} + A_2 I + A_3 I^{3/2} + \ldots \tag{6}$$

where the first term on the right-hand side of Equation 6 represents the D-H limiting law. Equation 6 is derived directly from the more familiar D-H equation with extended terms, but can be evaluated more conveniently than the latter with the aid of standard polynomial curve-fitting programs (*12*). Data presented here were analyzed on an IBM 1620 computer with such a program, using the method of least squares. For systems in which the activity coefficients are adequately described by the D-H limiting law throughout the range of ionic strengths studied, the

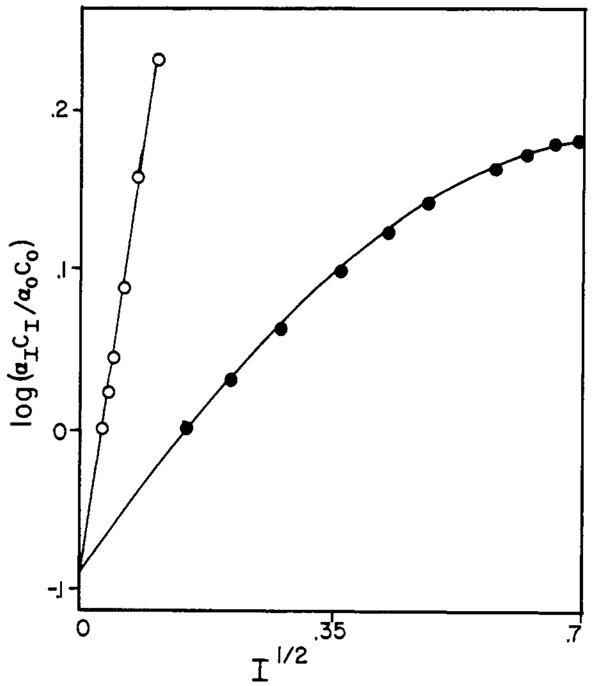

Figure 1. Extrapolations according to Equation 5

● KPi in 51.0% ethanol ○ KPi in anhydrous ethanol

Second-order polynomial in $I^{1/2}$ gives a slightly better fit (Table III)

program stops the calculation at the first-order polynomial in $I^{1/2}$—i.e., a straight line is fitted to data points according to Equation 5. For systems where $f_{\pm}$ curves as a function of $I^{1/2}$, the program selects that order of the polynomial which best describes the activity coefficient (Equation 6). In either case, the intercept is $\log f_{\pm,o}$—the logarithm of the activity coefficient of the electrolyte in its saturated solution with no added LiCl.

If the solubility in pure solvent, C_o, is unavailable, a rearranged form of Equation 4 can be used:

$$\log \alpha_I C_I = \log (\alpha_o C_o f_{\pm,o}) - \log f_{\pm,I} \qquad (7)$$

In this case, the intercept from a plot of ($\log \alpha_I C_I$) *vs.* $I^{1/2}$ evaluates directly the mean activity of the saturated solution of the electrolyte in the pure solvent, $a_{\pm,o}$.

Table III shows the results of the above calculations, including the A-coefficients of the different power terms of $I^{1/2}$ in Equation 6. Coefficient A_1 ideally should be equal to the D-H limiting slope, A_{DH}, and the latter is included in Table III for comparison. Any solvent-electrolyte combination studied here can be described by Equation 5, in which $F(I)$ is replaced by the power series in $I^{1/2}$ with A-coefficients specific to that system. The degree of polynomial to which the calculation was carried is indicated by the number of the A-coefficients listed. No significant improvement in the curve-fitting was observed when the calculation was extended to the next higher order.

A side problem of significant proportion in this work was the estimation of the degree of ion-pair dissociation

Table III. Activity Coefficients, Degrees of Dissociation and Solubility Products of Electrolytes in Ethanol-Water Mixtures at 25° C.

Wt. % Ethanol	C_o (Moles/L.) × 10^2	α_o	$f_{\pm,o}$	A_{DH}	Coefficients from Equation 6			K_{sp} $(C_o\alpha_o f_{\pm,o})^2$
					A_1	A_2	A_3	
				KPi				
100.0	0.104	0.857	0.807	2.96	3.05	0.982	...	5.19×10^{-7}
92.3	0.251	0.888	0.766	2.51	2.54	−2.49	...	2.91×10^{-6}
84.8[a]	...	0.970	...	2.11	1.11	−0.168	...	1.24×10^{-5}
68.3	1.52	0.985	0.654	1.46	1.98	−4.17	3.56	9.58×10^{-5}
58.8	1.95	1.000	0.723	1.21	1.25	−1.69	...	1.99×10^{-4}
51.0	2.20	1.000	0.807	1.05	0.681	−0.410	...	3.15×10^{-4}
37.3	1.98	1.000	0.813	0.832	0.754	−0.872	0.405	2.59×10^{-4}
20.6	1.59	1.000	0.887	0.652	0.437	−0.165	...	1.99×10^{-4}
Water	2.33	1.000	0.851	0.509	0.617	−1.14	0.813	3.93×10^{-4}
				TABPi				
100.0	6.27	0.810	0.328	2.96	2.80	−3.18	1.31	2.78×10^{-4}
86.4[a]	...	0.848	...	2.20	2.15	−2.53	1.06	2.62×10^{-4}
67.3	1.60	0.854	0.742	1.43	1.24	−1.34	0.528	1.03×10^{-4}
53.6	0.710	0.922	0.876	1.10	0.702	−0.478	...	3.29×10^{-5}
38.4	0.202	0.976	0.945	0.848	0.540	−0.351	...	3.48×10^{-6}
30.0[b]	0.0903	0.989	0.950	0.743	...	...	...	7.19×10^{-7}
20.0[b]	0.0406	0.996	0.970	0.652	...	...	...	1.54×10^{-7}
10.0[b]	0.0282	0.997	0.978	0.573	...	...	...	7.56×10^{-8}
Water[b]	0.0226	1.000	0.983	0.509	...	...	...	4.94×10^{-8}
				$KBPh_4$				
100.0	0.0504	0.949	0.849	2.96	3.90	−7.55		1.65×10^{-7}
78.1	0.235	0.986	0.819	1.81	2.25	−3.47		3.61×10^{-6}
60.6	...	0.998	...	1.25	1.30	−3.11		7.71×10^{-6}
38.4	...	1.000	...	0.846	0.749	−0.820		1.58×10^{-6}
30.0[b]	0.0670	1.000	0.958	0.743	...	...		4.12×10^{-7}
20.0[b]	0.0340	1.000	0.972	0.652	...	...		1.09×10^{-7}
10.0[b]	0.0220	1.000	0.981	0.573	...	...		4.66×10^{-8}
Water[b]	0.0174	1.000	0.985	0.509	...	...		2.94×10^{-8} (*9*)
				TAB BPh_4				
100.0	0.118	0.886	0.842	2.96	2.44	−5.86	8.38	7.74×10^{-7}
78.1[c]	0.0450	0.986	0.946	1.81	0.703	...		1.76×10^{-7}
60.6	0.0148	0.998	0.957	1.25	1.17	−0.985		2.00×10^{-8}

[a] Mean ionic activity evaluated directly via Equation 7. [b] Activity coefficients calculated from Debye-Hückel limiting law. [c] Calculation stopped at first-order polynomial in $I^{1/2}$ because of scatter of points.

for the electrolytes of interest and of the total ionic strength at each concentration of added LiCl. From the association constants K_A determined previously (*3*) it is possible to calculate

$$\alpha = \frac{-1 + (1 + 4\,K_ACf_\pm^{\,2})^{1/2}}{2K_ACf_\pm^{\,2}} \tag{8}$$

at each concentration, C, of a given electrolyte. The activity coefficient, $f_\pm$, required in this calculation was estimated from the limiting D-H law. Because such estimation presumes prior knowledge of total ionic strength, which in turn depends on the degree of dissociation of each electrolyte in the solution, a process of successive approximations was employed to calculate the value of $f_\pm$ for a given solution, as well as the individual values of α for each electrolyte. D-H limiting values of $f_\pm$ can be used throughout the concentration range to extract α from K_A by means of Equation 8, because in most cases $f_\pm$ was introduced into K_A in its limiting form originally. Even in the case of association constants for which the activity coefficients were originally computed from a D-H expression with an ion-size parameter, the use of the limiting D-H activity coefficients in Equation 8 introduces no significant error, as α is a rather insensitive function of $f_\pm$.

Calculation of ionic strength in solvents of low dielectric constant was complicated by the possibility of association between the ions of the electrolyte studied and those of LiCl. For example, in the study of KPi, we have to consider not only the formation of K^+Pi^- and Li^+Cl^- ion pairs, but the pairing into K^+Cl^- and Li^+Pi^- as well. The two other possible ion pairs which could result from a combination of LiCl with the title electrolytes are TAB^+Cl^- and $Li^+BPh_4^-$. The last two electrolytes are known to be completely dissociated in methanol (*7, 13*) and were assumed to be dissociated throughout the ethanol-water range. Conductance measurements by the authors on LiPi in 92.3 weight % ethanol revealed only slight association in this solvent ($K_A = 18.9 \pm 0.5$, $\Lambda_o = 52.78 \pm 0.02$), so that no correction was applied for Li^+Pi^- ion-pairing in any of the solvents. Only for K^+Cl^- did the association constants available in the literature (*5*) indicate appreciable ion-pairing in ethanol-rich solvents, so that a correction for it was incorporated in the calculations between about 65 and 100 weight % ethanol.

A graphical comparison of experimental activity coefficients with their counterparts from the D-H limiting law as a function of solvent composition indicates that they coincide below solubilities of 10^{-3} M.

NOMENCLATURE

A_{DH} = Debye-Hückel limiting slope
$A_1, A_2, A_3, \ldots$ = empirical coefficients of power terms of $I^{1/2}$ in Equation 6
a = molar absorptivity, liter·mole^{-1}·cm.$^{-1}$
$a_\pm$ = mean ionic activity, moles per liter
$a_{\pm,o}$ = mean ionic activity in pure solvent, moles per liter
$a_{\pm,I}$ = mean ionic activity in the presence of added solvent salt at ionic strength I, moles per liter
C = solubility, moles per liter
C_o = solubility in pure solvent, moles per liter
C_I = solubility in presence of added solvent salt at ionic strength I, moles per liter
$F(I)$ = function of ionic strength
$f_\pm$ = mean ionic activity coefficient of electrolyte referred to infinite dilution in given solvent as standard state
$f_{\pm,o}$ = mean ionic activity coefficient in absence of added solvent salt
$f_{\pm,I}$ = mean ionic activity coefficient in presence of added solvent salt at ionic strength I
I = ionic strength, moles per liter
K_A = ion-pair association constant, liter·mole^{-1}
K_s = solubility product of an electrolyte, mole^2·liter^{-2}
M = moles per liter of solution

Greek Letters

α = degree of dissociation into ions
α_o = degree of dissociation into ions in pure solvent
α_I = degree of dissociation into ions in presence of added solvent salt at an ionic strength I
Λ_o = limiting equivalent conductance, mho·liter·mole^{-1}·cm.$^{-1}$
μ = micron = 10^{-4} cm.

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