Solubility Products and Transfer Activity Coefficients of Potassium Picrate, Potassium Tetraphenylborate, and Tetraphenylphosphonium Picrate in Methanol–Water Mixtures at 25 °C†

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Solubility (ion-activity) products of potassium picrate, potassium tetraphenylborate, and tetraphenylphosphonium picrate were determined at 25 °C over the entire range of methanol–water mixtures at intervals of about 10 wt% methanol. Molar absorptivities of picrate and tetraphenylborate ions in the near-ultraviolet region of the spectrum were obtained for the entire range of methanol–water solvents. Solubilities of the title electrolytes were determined by spectrophotometric analysis of their saturated solutions. Mean ionic activity coefficients of the electrolytes in saturated solutions were evaluated from the variation of solubility as a function of ionic strength varied by means of added lithium chloride. Transfer activity coefficients for the electrolytes were calculated from their solubility products in water and the nonaqueous solvents.

The manner in which the solvation of an electrolyte varies as a function of the solvent medium is often expressed quantitatively in terms of the free energies for the transfer of that electrolyte from one solvent to another or the corresponding transfer activity coefficients (*11*). Because the latter are usually calculated from solubility products, it is important to have available accurate values for the thermodynamic solubility products of electrolytes both in water and in the nonaqueous solvents of interest. As part of a broad program of study in this laboratory of solute–solvent interactions in nonaqueous media, we have been determining the solubility products of a number of electrolytes, particularly those containing tetraaryl and tetraalkyl ions. Earlier communications from this laboratory reported on the solubility products of potassium and triisoamyl-*n*-butylammonium picrates and tetraphenylborates (*7*) as well as tetraphenylphosphonium and tetraphenylarsonium picrates (*3*), all in ethanol–water solvents. Also for anhydrous methanol, the solubility products of KPi (Pi = picrate) and $KBPh_4$ (*12*) as well as Ph_4PPi (*13*) have already been reported by us. In the present study, some of this work has been extended to methanol–water mixtures. The particular emphasis on salts containing Ph_4P^+, Ph_4As^+, and BPh_4^- ions stems from the fact that in a popular assumption for the estimation of transfer activity coefficients for individual ions, the transfer activity coefficients of the Ph_4P^+ and Ph_4As^+ cations are equated to those of the BPh_4^- anion (e.g., *1*, *10*, *13*).

Table I. Peak Molar Absorptivities of Picrate and Tetraphenylborate Ions in Methanol-Water Solvents at 25 °C

wt % MeOH	picrate $10^{-4}\epsilon_{max}$ at 355 nm	BPh_4^- $10^{-3}\epsilon_{max}$ 266 nm	BPh_4^- $10^{-3}\epsilon_{max}$ 274 nm
0^a	1.44	3.23^b	1.99^b
	1.43^b	3.225^d	2.100^d
	1.44^c	3.25^c	2.06^c
10	1.45	3.28	2.03
20	1.47	3.26	2.02
30	1.49	3.24	2.05
40	1.50	3.24	2.07
50	1.51	3.15	2.06
60	1.52	3.10	2.07
70	1.53	3.10	2.08
80	1.54	3.03	2.08
90	1.55	3.09	2.13
100^a	1.56	3.02	2.12
	1.56^c	3.00^c	2.12^c

[a] Water. [b] Reference 7. [c] Reference 12. [d] Reference 9.

In solvents where ion pairing cannot be neglected, the solubility product of a uni-univalent electrolyte, K_s, can be expressed in the form

$$K_s = (C\alpha f_\pm)^2 = a_\pm^2 \qquad (1)$$

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, the solubility, C, was determined by preparing saturated solutions of the electrolytes and analyzing spectrophotometrically for the picrate or the tetraphenylborate concentration. Values of the degree of dissociation, α, were calculated from ion-pair association constants, K_A, evaluated from electrolytic-conductance data obtained in this laboratory (*14*). Measurable association was observed for Ph_4PPi in solvents containing above 50 wt% methanol and for KPi in solvents containing above 60 wt% methanol. At lower methanol contents, α was assumed to be unity. Similarly, complete dissociation was assumed for $KBPh_4$ in all methanol–water mixtures, since even in anhydrous methanol its association is known to be almost negligible ($\alpha = 0.96$ is saturated solution (*12*)). The activity coefficients $f_\pm$ were evaluated, as in our previous studies (*3*, *7*), by the method of Brønsted and La Mer (*4*), from the variation of the solubility as a function of ionic strength varied by means of added LiCl. Lithium chloride is known to be completely dissociated in methanol–water solvents (*8*). The potential association between the ions of LiCl and those of the title electrolytes was generally found to be negligible in ethanol–water mixtures (*3*, *7*) and was therefore disregarded in the present study, considering that methanol–water mixtures have higher dielectric constants.

Experimental Section

Sodium tetraphenylborate (Fisher certified 100.0%) was used as received. Preparation and purification of KPi, $KBPh_4$ (*12*), Ph_4PPi (*3*), and LiCl (*6*) have been described. Certified ACS spectranalyzed methanol (Fisher Scientific Co.) was used without further purification. At 25 °C, it had a density of 0.7865 g/mL, which agreed well with the literature value of 0.7866 g/mL (*2*). Distillation of this methanol brought about no changes in the observed solubilities, within experimental error, and was therefore deemed unnecessary.

Methanol–water mixtures were prepared by combining appropriate volumes of the methanol and deionized water. The densities of the mixtures were then determined gravimetrically in quadruplicate by using class A 100-mL volumetric flasks. The

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Table II. Association Constants Used in the Calculation of α

KPi		Ph_4PPi	
wt % MeOH	K_A	wt % MeOH	K_A
100.0	31.8	100.0	53.5
90.1	28.0	89.7	42.7
80.4	18.1	80.4	36.6
70.4	12.8	70.2	32.1
60.5	6.81	60.3	28.9
		50.1	26.4

precise weight percent composition of a particular mixture was read from a large-scale plot of density vs. weight percent methanol prepared from literature data (*2*).

The solubilities were determined at intervals of about 10 wt % methanol with and without added lithium chloride, employing essentially the same procedure and apparatus as before (*3*), except for the following modifications. In the case of $KBPh_4$ the solvent contained 2×10^{-5} M NaOH and was deaerated with argon presaturated with the solvent vapor. Both measures served to retard decomposition of the BPh_4^-, presumably by removing carbon dioxide and other acidic contaminants. The concentrations of added LiCl ranged from about 2 to 1000 times the molar solubility of the electrolyte in the pure solvent. The absorbancies of the saturated solutions were recorded on a Cary Model 17 spectrophotometer at the 355-nm maximum for the picrate ion and at the 266- and the 274-nm maxima for the tetraphenylborate ion. A solution was considered saturated when successive analyses several days apart differed by no more than 0.6% for the picrate and about 1% for the tetraphenylborate, which are the respective precisions of the spectrophotometric determinations of these ions. The solutions were monitored for possible decomposition by measuring the peak-height ratios of the UV bands characteristic of the tetraphenyl ions.

Results and Discussion

Absorptivities. Molar absorptivities, ϵ_{max}, for the broad picrate maximum in the vicinity of 355 nm were determined over the entire range of methanol-water solvents at about 10 wt% intervals by using solutions of KPi. In order to test the possible effect on the absorptivities of partial association into ion pairs, we determined values of ϵ_{max} for the picrate ion in solutions of Ph_4PPi in the range of 70–100 wt % methanol. The picrate absorptivities derived from KPi and Ph_4PPi solutions agreed to

Table III. Solubilities, Degrees of Dissociation, and Activity Coefficients at 25 °C

					coefficients from eq 4			
wt % MeOH	10^3C_0, mol/L	α_0	$f_{\pm,0}$	A_{DH}	A_1	A_2	A_3	A_4
				KPi				
100.0	8.30 8.58[b]	0.891	0.721 ± 0.007	1.90	1.88	−3.02	2.48	−0.832
90.1	8.62	0.888	0.766 ± 0.008	1.52	1.51	−2.19	1.56	−0.482
80.4	10.3	0.904	0.792 ± 0.004	1.28	1.17	−1.39	0.605	
70.4	12.1	0.919	0.787 ± 0.014	1.11	1.14	−1.73	1.50	−0.619
60.5	13.7	0.911	0.811 ± 0.011	0.962	0.926	−1.22	0.777	−0.210
49.7	14.6	1.000	0.824 ± 0.020	0.835	0.823	−1.23	0.993	−0.380
40.1	15.0	1.000	0.839 ± 0.013	0.746	0.722	−0.919	0.427	
29.8	15.2	1.000	0.854 ± 0.009	0.663	0.657	−0.851	0.401	
19.9	16.1	1.000	0.854 ± 0.011	0.605	0.642	−0.836	0.410	
10.1	18.7	1.000	0.862 ± 0.004	0.556	0.559	−0.696	0.326	
water	23.1 24.2[b]	1.000	0.871 ± 0.017	0.509	0.464	−0.476	0.160	
				Ph_4PPi				
100.0	14.2	0.785	0.677 ± 0.007	1.90	1.84	−2.58	1.28	
89.7	11.0	0.822	0.748 ± 0.013	1.51	1.56	−2.73	2.47	−0.988
80.4	7.77	0.857	0.829 ± 0.008	1.28	1.11	−1.39	0.562	
70.2	4.92	0.902	0.871 ± 0.009	1.10	0.995	−1.60	1.37	−0.575
60.3	2.83	0.940	0.912 ± 0.008	0.960	0.796	−1.03	0.440	
50.1	1.44	0.968	0.942 ± 0.003	0.840	0.731	−1.12	0.609	
40.1	0.680	1.000	0.960 ± 0.002	0.746	0.725	−1.58	1.71	−0.625
29.8	0.292	1.000	0.976 ± 0.004	0.663	0.688	−1.69	1.94	
19.9	0.136	1.000	0.987 ± 0.007	0.605	0.643	−1.91	2.58	
9.8	0.0682	1.000	0.997 ± 0.008	0.555	0.553	−0.813		
water	0.0420 0.0451[c]	1.000	0.993[a]	0.509				
				$KBPh_4$				
100.0	3.11[b]	0.958[b]						
89.4	2.22	1.000	0.882 ± 0.032	1.50	1.38	−2.04	1.28	−0.343
79.7	1.92	1.000	0.854 ± 0.020	1.27	1.21	−1.74	0.819	
69.6	1.64	1.000	0.913 ± 0.004	1.06	1.06	−2.28	2.70	−1.40
58.8	1.20	1.000	0.935 ± 0.029	0.941	0.905	−1.70	1.52	−0.574
50.8	1.04	1.000	0.918 ± 0.038	0.839	0.847	−0.849		
40.0	0.586	1.000	0.964 ± 0.003	0.745	0.697	−1.72	2.50	−1.70
29.8	0.372	1.000	0.969 ± 0.009	0.663	0.753	−3.12	8.41	−9.04
20.0	0.261	1.000	0.988 ± 0.014	0.605	0.558	−1.11	0.750	
9.8	0.220	1.000	0.981 ± 0.017	0.555	0.585	−2.60	7.95	−9.16
water	0.174[b]							

[a] Calculated from the D-H limiting law. [b] Reference 12. [c] Reference 3.

three significant figures, indicating that they were independent of the nature of the cation and of the extent of association. We reported earlier that picrate absorptivities were cation independent in ethanol–water solvents as well (*7*).

Similarly, ϵ_{max} values for the tetraphenylborate peaks in the vicinity of 266 and 274 nm were determined on solutions of sodium tetraphenylborate also over the full range of methanol–water solvents at approximately 10 wt % intervals of methanol. The results for both anions are summarized in Table I and compared with the literature values for water and methanol. Tetraphenylborate absorption has long been known as independent of the associated cation (*9*, *12*).

Values of absorptivities required for analytical calculations at specific uneven solvent compositions were interpolated from large-scale graphs. Considering the relative insensitivity of ϵ_{max} to solvent composition, such interpolations result in no significant error. Beer's law was found to hold for both the picrate and the tetraphenylborate ion over the range of concentrations corresponding to absorbancies below 2.0.

Solubilities and Activity Coefficients. In the determination of activity coefficients from the variation of solubility as a function of ionic strength, which was discussed by us in detail (*7*), one takes advantage of the fact that the mean ionic activities of saturated solutions of a given electrolyte in the pure solvent and in the presence of added inert salt (LiCl in this case) are equal:

$$(\alpha_0 C_0 f_{\pm,0}) = (\alpha_I C_I f_{\pm,I}) \tag{2}$$

where subscripts I and 0 refer to saturated solutions with and without added LiCl, respectively, and I denotes ionic strength. Equation 2 is rearranged into a form convenient for extrapolation:

$$\log (\alpha_I C_I/\alpha_0 C_0) = \log f_{\pm,0} - \log f_{\pm,I} \tag{3}$$

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

$$-\log f_{\pm,I} = A_1 I^{1/2} + A_2 I + A_3 I^{3/2} + \ldots \tag{4}$$

Equation 4 is mathematically identical with the extended Debye–Hückel (D-H) equations but has the form of a polynomial, for which curve-fitting computer programs are available. It has been applied successfully in the past to the formulation of activity coefficients in the interpretation of emf (*5*, *15*) and solubility (*3*, *7*) data.

At any picrate concentration C, the degrees of dissociation α_0 and α_I required for the calculation of $f_{\pm,0}$ were evaluated from the equation

$$\alpha = \frac{-1 + (1 + 4K_A C f_\pm{}^2)^{1/2}}{2K_A C f_\pm{}^2} \tag{5}$$

where K_A is the association constant of KPi or Ph_4PPi in a particular solvent. Association constants for the above picrates in methanol–water solvents were determined from electrolytic conductance in our laboratory (*14*). The K_A values for the specific solvent compositions employed in this study were interpolated from the above data by using the linear relationships between $\log K_A$ and $1/D$, where D is the solvent dielectric constant. In Table II we list those K_A values actually used to calculate the degrees of dissociation for eq 3. The activity coefficients, $f_\pm$, for use in eq 5 were estimated from the D-H limiting law by using successive approximations with respect to α.

The data points expressed as $\log (\alpha_I C_I/\alpha_0 C_0)$ were fitted as a function of $I^{1/2}$ by the method of least squares, using an IBM 370-145 computer. For each electrolyte–solvent combination, 8–12 data points were used. Fits were obtained for first- through fourth-order polynomials and the best function to describe the activity coefficients was chosen on the basis of agreement between the coefficients A_1 and the theoretical D-H limiting slope, A_{DH}. In the absence of experimental error, the two should be equal. Once the A coefficients characteristic of a given electrolyte and solvent are known, the activity coefficient can be calculated at any ionic strength by using eq 4.

Table IV. Solubility Products and Transfer Activity Coefficients at 25 °C

wt % MeOH	K_s $(C_0\alpha_0 f_{\pm,0})^2$	$\log {}_m\gamma_\pm{}^2$ (molar scale)
	KPi	
100.0	$(2.85 \pm 0.07) \times 10^{-5}$	1.15
90.1	$(3.44 \pm 0.22) \times 10^{-5}$	1.07
80.4	$(5.41 \pm 0.11) \times 10^{-5}$	0.87
70.4	$(7.68 \pm 0.30) \times 10^{-5}$	0.72
60.5	$(1.02 \pm 0.02) \times 10^{-4}$	0.60
49.7	$(1.45 \pm 0.05) \times 10^{-4}$	0.45
40.1	$(1.58 \pm 0.04) \times 10^{-4}$	0.41
29.8	$(1.69 \pm 0.03) \times 10^{-4}$	0.38
19.9	$(1.89 \pm 0.04) \times 10^{-4}$	0.33
10.1	$(2.60 \pm 0.02) \times 10^{-4}$	0.19
water	$(4.05 \pm 0.12) \times 10^{-4}$	0.00
	3.93×10^{-4} [a]	
	Ph_4PPi	
100.0	$(5.69 \pm 0.45) \times 10^{-5}$	−4.51
89.7	$(4.57 \pm 0.22) \times 10^{-5}$	−4.42
80.4	$(3.04 \pm 0.22) \times 10^{-5}$	−4.24
70.2	$(1.50 \pm 0.04) \times 10^{-5}$	−3.93
60.3	$(5.88 \pm 0.14) \times 10^{-6}$	−3.53
50.1	$(1.73 \pm 0.04) \times 10^{-6}$	−3.00
40.1	$(4.26 \pm 0.04) \times 10^{-7}$	−2.39
29.8	$(8.12 \pm 0.08) \times 10^{-8}$	−1.67
19.9	$(1.80 \pm 0.02) \times 10^{-8}$	−1.02
9.8	$(4.62 \pm 0.06) \times 10^{-9}$	−0.42
water	$(1.74 \pm 0.03) \times 10^{-9}$	0.00
	2.00×10^{-9} [b]	
	$KBPh_4$	
100.0	5.86×10^{-6} [c]	−2.30[c]
89.4	$(3.84 \pm 0.20) \times 10^{-6}$	−2.12
79.7	$(2.69 \pm 0.10) \times 10^{-6}$	−1.96
69.6	$(2.24 \pm 0.03) \times 10^{-6}$	−1.88
58.8	$(1.26 \pm 0.06) \times 10^{-6}$	−1.63
50.8	$(9.12 \pm 0.55) \times 10^{-7}$	−1.49
40.0	$(3.19 \pm 0.05) \times 10^{-7}$	−1.04
29.8	$(1.30 \pm 0.03) \times 10^{-7}$	−0.65
20.0	$(6.65 \pm 0.17) \times 10^{-8}$	−0.36
9.8	$(4.66 \pm 0.13) \times 10^{-8}$	−0.20
water	2.94×10^{-8} [c]	0.00

[a] Reference 7. [b] Reference 3. [c] Reference 12.

In addition to the A coefficients, the program computes the value of the intercept from eq 4, $\log f_{\pm,0}$, which is the logarithm of the mean ionic activity coefficient in the saturated solution without added LiCl, as well as the precision of that intercept. The experimentally determined activity coefficients, $f_{\pm,0}$, were then introduced into eq 5 to calculate the α_0's which are listed in Table III. It is interesting that the values of α_0 calculated by using the experimentally determined activity coefficients differed by only a few parts per thousand from those calculated by using activity coefficients estimated from the D-H limiting law.

The tables listing solubilities of KPi, Ph_4PPi, and $KBPh_4$ as a function of LiCl concentration are available as supplementary material. Table III summarizes the solubilities, degrees of dissociation, activity coefficients in the pure solvents, and the A coefficients from eq 4. In Table IV we list the solubility products, K_s, calculated from the data in Table III via eq 1 and the transfer activity coefficients (medium effects). The relative precision of the K_s values was estimated by the method of propagation of errors to be in the range of 1–4% for KPi and 1–8% for Ph_4PPi and $KBPh_4$. The absolute precision for each constant is included in Table IV. Transfer activity coefficients are calculated from solubility products, almost invariably in logarithmic form, by using the relationship

$$\log {}_m\gamma_{\text{electrolyte}} \equiv \log {}_m\gamma_\pm{}^2 = \log {}_wK_s - \log {}_sK_s \tag{6}$$

where ${}_{m}\gamma$ is the transfer activity coefficient (medium effect) and subscripts w and s denote aqueous and nonaqueous solvent, respectively. A transfer activity coefficient is a measure of the difference between the free energy of the electrolyte in the given nonaqueous medium and in water; a positive value of log ${}_{m}\gamma$ indicates that the electrolyte is more favorably solvated in water than in the nonaqueous solvent. This is in fact observed for KPi throughout the methanol–water range. However, both $KBPh_4$ and Ph_4PPi have negative values of log ${}_{m}\gamma$, indicating more favorable solvation (lower free energy) in the nonaqueous media than in water. This is to be expected since the large polarizable tetraphenyl ions are strongly solvated via dispersion interactions by the more polarizable methanol molecules. In general, the trends in solubilities and transfer activity coefficients observed here for methanol–water solvents parallel those reported by us earlier for ethanol–water solvents (*3*, *7*, *13*).

Glossary

A_{DH}	Debye–Hückel limiting slope
A_1, A_2, A_3	empirical coefficients of power terms of $I^{1/2}$ in eq 4
$a_{\pm}$	mean ionic activity, mol/L
C	solubility 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
$f_{\pm}$	mean ionic activity coefficient of electrolyte, molar scale
$f_{\pm,0}$	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_A	ion-pair association constant, L/mol
K_s	solubility product of an electrolyte, mol^2/L^2
${}_{s}K_s$	solubility product in a nonaqueous solvent, mol^2/L^2
${}_{w}K_s$	solubility product in water, mol^2/L^2
M	mol/L of solution

Greek Letters

α	degree of dissociation into ions
α_0	degree of dissociation into ions in pure solvent
α_I	degree of dissociation in the presence of added salt at ionic strength I
${}_{m}\gamma$	transfer activity coefficient (medium effect)
${}_{m}\gamma_{\pm}$	mean ionic transfer activity coefficient of an electrolyte
ϵ_{max}	maximum molar absorptivity

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Supplementary Material Available: Solubilities of the title electrolytes as a function of LiCl concentration, Tables I, II, and III (11 pages). Ordering information is given on any current masthead page.

Studies of Self-Association in Nonaqueous Solvents by Titration Calorimetry. Halogen-Substituted Acetic and Propionic Acids in Benzene

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A calorimetric enthalpy of dilution technique was used to obtain apparent relative molar enthalpy (ϕ_L) data for the following carboxylic acids in benzene at 25.00 ± 0.07 °C: acetic, chloroacetic, bromoacetic, iodoacetic, propionic, 2-chloropropionic, and 3-chloropropionic. The data are interpreted in terms of a monomer–dimer equilibrium and values of the thermodynamic parameters K, $\Delta H°$, and $\Delta S°$ for dimerization are reported. The effect of small amounts of water in the benzene was studied and it was found to be most pronounced for the acids of greatest aqueous acid strength.

The self-association of carboxylic acids through hydrogen bond formation is known to occur in nonpolar solvents. Equilibrium constants for these associations have been determined by a variety of techniques, among which are infrared spectroscopy, distribution measurements, dielectric constant measurements, and others. Values of $\Delta H°$ and $\Delta S°$ have been reported much less frequently.

A calorimetric enthalpy of dilution technique has been developed (*13*, *15*) by which K as well as $\Delta H°$ for these associations can be determined from measurements carried out at a single temperature. The apparent relative molar enthalpy, ϕ_L, is determined and related to the thermodynamic parameters of association. This technique has been applied to the study of carboxylic acid self-association in nonpolar solvents (*17–20*). This paper reports the results of calorimetric investigations of acetic, chloroacetic, bromoacetic, iodoacetic, propionic, 2-chloropropionic, and 3-chloropropionic acids in benzene and of the effects of trace amounts of water on the association reactions.

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