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Solubility Products and Transfer Activity Coefficients of Rubidium and Cesium Tetraphenylborates and Tetraphenylarsonium Picrate in Methanol–Water Mixtures at 25 °C†

Anna Berne, Barbara Wajsbrot, Phillip D. Klahr, and Orest Popovych*

Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, New York 11210

Solubilities of rubidium tetraphenylborate ($RbBPh_4$), cesium tetraphenylborate ($CsBPh_4$), and tetraphenylarsonium picrate (Ph_4AsPi) were determined at 25 °C as a function of ionic strength, varied by means of added LiCl, in a wide range of methanol–water mixtures at intervals of about 10 wt % methanol. The solubilities were determined by spectrophotometric analysis of the saturated solutions for the tetraphenylborate and picrate ions, respectively. Constants were derived that describe the mean ionic activity coefficients of the title electrolytes and their solubility products were determined. Transfer activity coefficients for the electrolytes were calculated from their solubility products in water and the nonaqueous solvents.

Introduction

As part of our continuing study of solute–solvent interactions in nonaqueous media, we have been determining the solubility products of electrolytes containing Ph_4As^+, Ph_4P^+, and BPh_4^- ions. Solubility products are used to calculate the free energies for the transfer of electrolytes from water to nonaqueous solvents, or the corresponding transfer activity coefficients, $_m\gamma$. Our interest in these tetraphenyl ions derives from the fact that, in a popular assumption for the estimation of $_m\gamma$ values for individual ions, the $_m\gamma$'s of the Ph_4As^+ and Ph_4P^+ cations are equated to those of the BPh_4^- anion (e.g., ref 1-3). Related work reported earlier from this laboratory dealt with the solubility products of $RbBPh_4$ (4) and $KBPh_4$ (5) in anhydrous methanol as well as of $RbBPh_4$ and $CsBPh_4$ in water and anhydrous ethanol (6). Also reported from this laboratory were the solubility products of Ph_4AsPi and Ph_4PPi in ethanol–water solvents (7) and those of Ph_4PPi and $KBPh_4$ in methanol–water solvents (8).

In the present study, the solubility products of the title electrolytes were formulated as

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

where C is the solubility in mol/L, 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. The solubility was determined by analyzing saturated solutions for the picrate or the tetraphenylborate concentration spectrophotometrically. For Ph_4AsPi in solvents with methanol contents of about 50 wt % or higher, the degrees of dissociation were calculated from ion-pair association constants, K_A, derived from electrolytic-conductance data obtained in this laboratory (9). For all other electrolyte solutions, complete dissociation was assumed. The activity coefficients were evaluated, as before (7, 8, 10), 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 (11). Association between the ions of LiCl and those of the title electrolytes was found to be negligible in ethanol–water mixtures (7, 10) and was therefore disregarded here, considering that methanol–water mixtures have higher dielectric constants.

Experimental Section

The preparation and purification of $RbBPh_4$ and $CsBPh_4$ (6), Ph_4AsPi (7), LiCl (12), and the solvents (8) have been described. The solubility determinations were carried out exactly as before (8), except that solutions of $RbBPh_4$ and $CsBPh_4$ in methanol–water mixtures were stabilized by the presence of $\sim 5 \times 10^{-5}$ M NaOH.

Results and Discussion

Solubilities and Activity Coefficients. The principle of determining activity coefficients from the variation of solubility with ionic strength has been discussed by us in detail (10). It is based on the fact that the activity of a given electrolyte in a saturated solution has the same value in the pure solvent (designated by subscript 0) as in the presence of added inert salt (designated by subscript I, which denotes the total ionic strength):

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

Equation 2 is rearranged into a form convenient for extrapolation which is either

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

or, if the value of C_0 is unavailable

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

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

$$-\log f_{\pm,I} = A_1 I^{1/2} + A_2 I + A_3 I^{3/2} + ... \qquad (4)$$

Equation 4 is mathematically identical with the extended Debye–Hückel (DH) 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 (13-15) and solubility (7, 8, 10) data.

The solubilities, C, were determined spectrophotometrically from the absorption of the picrate ion in the vicinity of 355 nm and of the tetraphenylborate ion in the vicinities of 266 and 274 nm using the peak molar absorptivities reported by us earlier for the entire range of methanol–water solvents (8). As was mentioned in the Introduction, complete ionic dissociation was assumed for all the electrolytes except for Ph_4AsPi in the range of 50–100 wt % methanol. For these solutions, where ion pairing is appreciable, the degrees of dissociation α_0 and α_I required for the calculation of $f_{\pm,0}$ were evaluated at any picrate concentration C from the equation

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

where K_A is the association constant of Ph_4AsPi in a particular

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Table I. Association Constants Used in the Calculation of α for Ph_4AsPi

[MeOH], wt %	K_A	[MeOH], wt %	K_A
49.8	27.8	79.9	38.5
61.5	30.9	89.3	44.8
70.2	33.9	100.0	55.2

solvent. Association constants for Ph_4AsPi in methanol-water solvents were determined from electrolytic conductance in our laboratory (*9*). The K_A values for the specific solvent compositions employed in this study were interpolated from the above data by using the linear relationship between log K_A and $1/D$, where D is the solvent dielectric constant. In Table I, we list those K_A values actually used to calculate the degrees of dissociation for eq 3a. The activity coefficients, $f_{\pm}$, for use in eq 5 were estimated from the DH limiting law by using successive approximations with respect to α.

The data points expressed as log $(\alpha_f C_f/\alpha_0 C_0)$ (eq 3a) or log $(\alpha_f C_f)$ (eq 3b) 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, 7-13 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 DH 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. 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 II. 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 DH limiting law.

In addition to the A coefficients, the program computes the value of the intercept from eq 3a or 3b as well as the precision of that intercept. When eq 3a is used, the intercept is log $f_{\pm,0}$, which is the logarithm of the mean ionic activity coefficient in the saturated solution in the absence of added LiCl. When eq 3b is used, the intercept is log $a_{\pm}$, which is the logarithm of the mean ionic activity of the electrolyte in the saturated solution. Equation 3b was used for those systems where a reliable value of C_0 could not be obtained because of decomposition. This was true for all $CsBPh_4$ solutions and for $RbBPh_4$ in some of the solvents.

The tables listing the solubilities of $RbBPh_4$, $CsBPh_4$, and Ph_4AsPi as a function of LiCl concentration are available as supplementary material (see paragraph at end of text regarding supplementary material). Table II summarizes the solubilities, degrees of dissociation, and activity coefficients in the pure solvents (when available) or the mean ionic activities of the saturated solutions. Also listed are the A coefficients from eq 4.

Table III lists the solubility products, K_s, calculated from the data in Table II and their precisions estimated by the method of propagation of errors. All the solubility products of Ph_4AsPi are of excellent precision, the average error being only 3%. On the other hand, the solubility products of the tetraphenylborates are inherently less precise and accurate due to the well-known tendency of the BPh_4^- ion to decompose. Thus, the average precision of the $RbBPh_4$ data is only 8% and that of the "good" $CsBPh_4$ data is 6%. In the last average, the datum for $CsBPh_4$ in 49.9% MeOH was excluded because of its poor precision of 29%. However, this point was retained in Table

Table II. Solubilities, Activities and Activity Coefficients in Saturated Solutions, and Degrees of Dissociation at 25 °C

[MeOH], wt %	10^4C_0, mol/L	$f_{\pm,0}$	$10^4a_{\pm}$	A_{DH}	A_1	A_2	A_3	A_4
			$RbBPh_4$ ($\alpha = 1$ assumed)					
88.9	5.18	0.873 ± 0.047		1.49	1.48	−2.53	1.72	
79.3	4.79	0.912 ± 0.089		1.26	1.38	−3.03	2.86	
69.0	3.99	0.959 ± 0.037		1.08	1.07	−3.73	10.25	−10.73
61.2			2.60 ± 0.20	0.970	1.00	−0.837		
50.3	2.13	0.978 ± 0.048		0.844	0.829	−0.604		
40.2			1.15 ± 0.04	0.747	0.750	−0.656		
29.5			0.767 ± 0.36	0.665	0.644	−0.698	0.370	
21.5			0.629 ± 0.71	0.614	0.650	−2.12	4.35	−3.33
			$CsBPh_4$ ($\alpha = 1$ assumed)					
100.0			5.04	1.90	1.81	−3.59	4.22	−2.17
89.1			4.49	1.49	1.26	−1.97	1.77	−0.724
79.8			4.07	1.27	1.03	−1.18	0.487	
70.7			3.34	1.11	1.16	−1.89	1.34	
61.1			3.09	0.969	0.567	−0.440	0.0864	
49.9			1.83	0.839	0.747	−0.177	−3.91	4.45
39.9			1.22	0.745	0.661	−0.878	0.432	
29.5			0.749	0.663	0.630	−0.698	0.167	
20.1			0.474	0.607	0.559	−0.934	0.660	

Ph_4AsPi

[MeOH], wt %	10^3C_0, mol/L	α_0	$f_{\pm,0}$	A_{DH}	A_1	A_2	A_3	A_4
100.0	13.2	0.808	0.688 ± 0.012	1.90	1.83	−2.47	1.12	
89.3	9.73	0.837	0.758 ± 0.008	1.50	1.58	−2.40	1.31	
79.9	6.58	0.875	0.821 ± 0.010	1.27	1.29	−1.91	0.985	
70.2	4.11	0.915	0.873 ± 0.015	1.10	1.08	−1.47	0.457	
61.5	2.44	0.946	0.907 ± 0.010	0.974	0.966	−1.75	1.53	−0.557
49.8	1.16	0.973	0.943 ± 0.007	0.838	0.821	−1.83	2.39	−1.38
38.3	0.468	1.000	0.990 ± 0.019	0.741	0.674	−1.08	0.544	
29.3	0.224	1.000	0.981 ± 0.006	0.662	0.626	−1.43	1.94	−1.21
19.5	0.105	1.000	0.965 ± 0.012	0.603	0.633	−1.31	0.962	
11.0	0.0571	1.000	1.011 ± 0.011	0.559	0.562	−1.84	4.20	−4.26
water	0.0349[a]	1.000						

[a] Reference 7.

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

[MeOH], wt %	K_s	log $_m\gamma_\pm^2$, molar scale
	$RbBPh_4$	
100.0	$(8.62 \times 10^{-7\,a})^b$	$(-2.48)^b$
88.9	$(2.04 \pm 0.16) \times 10^{-7}$	−1.85
79.3	$(1.92 \pm 0.27) \times 10^{-7}$	−1.82
69.0	$(1.47 \pm 0.08) \times 10^{-7}$	−1.71
61.2	$[(6.76 \pm 0.74) \times 10^{-8}]^b$	$(-1.37)^b$
50.3	$(4.34 \pm 0.31) \times 10^{-8}$	−1.18
40.2	$(1.32 \pm 0.06) \times 10^{-8}$	−0.66
29.5	$(5.88 \pm 0.39) \times 10^{-9}$	−0.31
21.5	$(3.96 \pm 0.63) \times 10^{-9}$	−0.14
water	$(2.89 \pm 0.09) \times 10^{-9}$	0.00
	$CsBPh_4$	
100.0	$(2.54 \pm 0.13) \times 10^{-7}$	−2.21
89.1	$(2.01 \pm 0.05) \times 10^{-7}$	−2.10
79.8	$(1.66 \pm 0.06) \times 10^{-7}$	−2.02
70.7	$(1.12 \pm 0.08) \times 10^{-7}$	−1.85
61.1	$[(9.51 \pm 0.94) \times 10^{-8}]^b$	$(-1.78)^b$
49.9	$[(3.34 \pm 0.98) \times 10^{-8}]^c$	$(-1.33)^c$
39.9	$(1.48 \pm 0.13) \times 10^{-8}$	−0.97
29.5	$(5.61 \pm 0.46) \times 10^{-9}$	−0.55
20.1	$(2.24 \pm 0.13) \times 10^{-9}$	−0.15
water	$(1.58 \pm 0.09) \times 10^{-9\,d}$	−0.00
	Ph_4AsPi	
100.0	$(5.37 \pm 0.37) \times 10^{-5}$	−4.65
89.3	$(3.80 \pm 0.12) \times 10^{-5}$	−4.50
79.9	$(2.24 \pm 0.10) \times 10^{-5}$	−4.27
70.2	$(1.07 \pm 0.04) \times 10^{-5}$	−3.95
61.5	$(4.37 \pm 0.15) \times 10^{-6}$	−3.56
49.8	$(1.14 \pm 0.02) \times 10^{-6}$	−2.98
38.3	$(2.14 \pm 0.06) \times 10^{-7}$	−2.25
29.3	$(4.83 \pm 0.06) \times 10^{-8}$	−1.61
19.5	$(1.02 \pm 0.02) \times 10^{-8}$	−0.93
11.0	$(3.33 \pm 0.06) \times 10^{-9}$	−0.44
water	$1.20 \times 10^{-9\,e}$	0.00

[a] Reference *4*. [b] This value appears to be of poor accuracy. [c] This value appears to be of good accuracy, despite its poor precision. [d] Reference *6*. [e] Reference *7*.

III (in brackets) because it appears to be of good accuracy. The accuracy of our solubility products can only be inferred from the manner in which they vary as a function of solvent composition. On this basis, it appears that the K_s values for the $RbBPh_4$ and $CsBPh_4$ in 61% MeOH are of lower accuracy than the rest of the data and are, therefore, tabulated in brackets. Their accuracy may be even lower than the precision, which is of the order of 10%.

Transfer activity coefficients were calculated from solubility products by using the relationship

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

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 standard free energy of the electrolyte in the given nonaqueous medium and in water. Significantly, in the methanol-water system, the transfer activity coefficients of Ph_4AsPi generally agree within experimental error with those of Ph_4PPi reported earlier from this laboratory (*8*).

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 in a saturated solution, 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
D	dielectric constant of the solvent
$f_\pm$	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, mol²/L²
$_sK_s$	solubility product in a nonaqueous solvent, mol²/L²
$_wK_s$	solubility product in water, mol²/L²
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 coefficients (medium effect)
$_m\gamma_\pm$	mean ionic transfer activity coefficient of an electrolyte

Registry No. $RbBPh_4$, 5971-93-7; $CsBPh_4$, 3087-82-9; Ph_4AsPi, 19599-99-6; MeOH, 67-56-1.

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Supplementary Material Available: Three tables showing the solubilities of the title electrolytes as a function of LiCl concentration (10 pages). Ordering information is given on any current masthead page.