

Electrolytic Conductance & Ionic Association of Potassium, Tetraphenylarsonium & Tetraphenylphosphonium Picrates in Methanol-Water Mixtures

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Electrolytic conductances of potassium picrate (KPi), tetraphenylarsonium picrate (Ph_4AsPi) and tetraphenylphosphonium picrate (Ph_4PPi) have been determined at 25°C in methanol-water mixtures containing approximately 60, 70, 80, 90 and 100 wt % methanol. In all the cases, limiting equivalent conductances, Δ_0 , and ion-pair association constants have been derived using the Shedlovsky function. For three of the solute-solvent systems, it is also possible to obtain results by Fuoss' parametric analysis. Using the present and the literature data, a comparison has been made between the conductance parameters derived from the Fuoss—1974 parametric analysis and those from earlier conductance functions. Also reported are the values of λ_0 , Walden products and Stokes radii for the single ions in 100% and 64.0% methanol. Variation of the Stokes radii with solvent composition is discussed in terms of structural and solvation effects.

MUCH work in our laboratory has been done on the determination of transfer free energies of electrolytes containing tetraphenylarsonium (Ph_4As^+), tetraphenylphosphonium (Ph_4P^+) triisooamyl-*n*-butylammonium (TAB^+) and tetraphenylborate (BPh_4^-) as reference ions. The free energies for the transfer of an electrolyte from a reference medium (usually water) to other media are usually expressed in the form of transfer activity coefficients (medium effects)¹ and calculated from thermodynamic solubility products in water and in the nonaqueous solvent of interest. In solvents where ion pairing is appreciable it is necessary to determine the degree of ionic association before a solubility product can be evaluated from solubility data. Therefore, the primary objective of the present study is to determine the degree of ionic association for the title electrolytes in those methanol-water solvents where it is expected to be appreciable. Earlier communications from this laboratory reported analogous conductance studies for these and other electrolytes in ethanol-water solvents^{2,3}. Another objective of the present study is to gain additional insight into the magnitude of ion size parameters and limiting transference numbers of the ions and the manner in which they vary with the solvent medium in the methanol-water system.

Potassium picrate has been included in this study as a convenient bridge for the correlation of the properties of the reference ions and the picrate ion with those of the more common ions and also because its conductance parameters in methanol could be compared with literature values.

Materials and Methods

The preparation and purification of potassium picrate⁴ (KPi) and of tetraphenylarsonium picrate

(Ph_4AsPi) and tetraphenylphosphonium picrate (Ph_4PPi)³ as well as the purification of methanol⁴ have been described earlier. The method of preparing methanol-water mixtures of accurately known composition was analogous to that of preparing ethanol-water mixtures². Deionized water with a specific conductance of the order of 3×10^{-7} mho cm^{-1} was used.

The apparatus and procedure for conductance measurements were essentially the same as previously described², except that a Wayne-Kerr model B-224 bridge was used. Temperature stability in the 25.00°C bath was improved by circulating water at 25.00°C through the coils. The conductance cell, filled with slightly platinized platinum electrodes, has a cell constant of 0.0095422 ± 0.000018 as determined from measurements with 0.03-0.07 M aqueous KCl solutions using the equation of Chiu and Fuoss. Preparation and transfer of solutions involving anhydrous methanol were carried out in a dry box.

Results

Table 1 summarizes the relevant physical properties of the methanol-water solvents actually employed. The wt % methanol (designated as *w*), was obtained from the measured solvent density, d_0 , by extrapolation.

TABLE 1 — PROPERTIES OF METHANOL-WATER MIXTURES AT 25°C

Methanol (wt %)	$10^7 k_0$	d_0	<i>D</i>	100 η_0 , Poise
100	0.5-5.7	0.7869	32.64	0.544
90.0	1.5	0.8148	37.92	0.770
80.2	4.1	0.8418	42.48	1.002
80.1	3.9	0.8422	42.53	1.004
70.1	4.0	0.8676	47.05	1.223
70.0	4.0	0.8680	47.10	1.225
60.1	3.5	0.8901	51.55	1.399

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TABLE 2 — CONDUCTANCE OF KPi IN METHANOL-WATER MIXTURES AT 25°C

100% Methanol				90.0% Methanol		80.2% Methanol	
Run 1		Run 2		10°C	Δ	10°C	Δ
10°C	Δ	10°C	Δ	10°C	Δ	10°C	Δ
3.8475	93.97	6.3636	92.47	1.0410	80.28	8.8173	66.45
6.2033	92.43	8.2060	91.42	2.1439	79.31	8.9172	66.38
7.0465	91.99	9.4506	90.46	4.3633	78.01	13.262	65.40
8.2204	91.41	10.687	90.24	5.5795	77.35	13.485	65.37
9.3282	90.72	14.336	88.54	6.3975	76.99	14.337	65.16
				8.1029	76.46		
				8.3250	76.37		
				8.4295	76.33		
70.1% Methanol		60.1% Methanol					
10°C	Δ	10°C	Δ				
7.8756	61.44	3.6356	58.02				
8.6456	61.31	6.2673	57.51				
10.379	60.96	9.2239	57.08				
11.726	60.73	9.8099	56.99				
13.190	60.50	11.366	56.79				
		13.227	56.55				
		15.062	56.35				

 TABLE 3 — CONDUCTANCE OF Ph₄AsPi IN METHANOL-WATER MIXTURES AT 25°C

100% Methanol				90.0% Methanol			
Run 1		Run 2		Run 3		10°C	Δ
10°C	Δ	10°C	Δ	10°C	Δ	10°C	Δ
1.2182	82.40	1.4530	82.22	1.4308	82.23	3.1094	61.40
1.6338	81.94	2.1878	81.47	1.7634	81.76	4.1946	60.79
2.7535	80.71	2.9060	80.68	2.0931	81.28	6.2434	59.75
3.2972	80.34	4.3642	79.57	2.8020	80.64	6.0744	59.97
3.6073	80.12	4.4325	79.50	3.7387	79.78	9.1500	58.67
3.6797	80.00	4.8542	79.34	4.2245	79.44	10.129	58.30
3.8656	79.86	5.5867	78.77	4.9910	78.94		
4.6669	79.31	5.8299	78.60	5.3429	78.65		
80.1% Methanol		70.0% Methanol		60.1% Methanol			
10°C	Δ	10°C	Δ	10°C	Δ		
7.4780	47.39	2.3641	41.82	1.2131	36.98		
7.9510	47.08	3.4715	41.40	2.8446	36.38		
9.0030	47.02	3.7090	41.32	3.4635	36.30		
9.9650	46.65	4.4128	41.13	4.1519	36.07		
11.990	46.32	6.4145	40.64	4.5844	36.05		
13.980	45.54			5.6187	35.83		

 TABLE 4 — CONDUCTANCE OF Ph₄Pi IN METHANOL-WATER MIXTURES AT 25°C

100% Methanol				90.0% Methanol	
Run 1		Run 2		10°C	Δ
10°C	Δ	10°C	Δ	10°C	Δ
1.7983	82.67	1.2301	83.39	1.9897	63.12
2.8839	81.46	2.0150	82.44	2.4488	62.80
4.0739	80.46	4.1412	80.58	2.9150	62.44
6.2779	78.84	4.6975	80.18	4.2529	61.67
7.1025	78.35	5.0564	79.84	7.5417	60.23
7.2977	78.27			7.7025	60.21
80.2% Methanol		70.0% Methanol		60.1% Methanol	
10°C	Δ	10°C	Δ	10°C	Δ
2.3642	50.87	2.3681	42.43	2.8550	39.02
3.2507	50.51	2.8857	42.29	3.6346	38.84
4.4500	50.04	4.1581	41.88	3.9198	38.81
5.5009	49.70	4.9959	41.66	4.3531	38.65
6.3441	49.39	5.6451	41.53	5.1526	38.48
		5.9499	41.47		

tion from a large-scale graph of the literature values⁵ of d_0 versus wt % methanol. Similarly interpolated from literature data⁵ were the viscosity η_0 and the dielectric constant, D , for each of the mixtures. Tables 2–4 list the molar concentrations, C , and the equivalent conductances, Λ of the various electrolytes in different compositions of methanol-water mixture.

An attempt has been made to interpret all of our conductance data by means of the parametric analysis published by Fuoss⁶ using his computer programme for the calculation⁷ of three parameters viz. the limiting equivalent conductance (Λ_0), the ion-pair association constant, (K_A) and the distance parameter (R) the latter is the distance from the center of the cation of an ion pair within which a unique partner can be found for a paired ion. Unfortunately, the Fuoss parametric analysis gave results for only three of the solvent-electrolyte systems from the present study and for only three additional sets of conductance data reported earlier from this labo-

ratory^{2,3}. It is significant that Fuoss' parametric analyses of our data was successful mostly for solutions in anhydrous alcohols, where the solvent correction to total conductance was of the order of 1 ppt or less. In aqueous alcohol mixtures, where the solvent correction was of the order of 10-50 times greater, the precision of conductance data was undoubtedly reduced.

Consequently, values of Δ_0 and K_A for all the systems were derived using the Shedlovsky equation⁸ :

$$\frac{1}{\Delta_0(z)} = \frac{K_A C \Delta f^2 \pm S(z)}{\Delta_0^2} + \frac{1}{\Delta_0} \quad \dots(1)$$

TABLE 5 — CONDUCTANCE PARAMETERS OBTAINED BY THE SHEDLOVSKY EQUATION

Methanol (wt %)	Δ_0	K_A	Walden Product
<i>KPi</i>			
60.1	59.50 ± 0.01	6.67 ± 0.21	0.8324
70.1	64.35 ± 0.01	12.67 ± 0.25	0.7870
80.2	70.48 ± 0.02	17.97 ± 0.37	0.7062
90.0	81.97 ± 0.08	28.0 ± 4.7	0.6312
100 (Run 1)	99.28 ± 0.06	29.0 ± 1.0	0.5401
100 (Run 2)	99.67 ± 0.05	34.48 ± 0.63	0.5427
100 (Avg.)	99.48	31.76	0.5412
<i>Ph₄AsPi</i>			
60.1	37.75 ± 0.04	28.4 ± 5.1	0.5281
70.0	43.25 ± 0.03	33.9 ± 2.4	0.5298
80.1	51.23 ± 0.14	43.0 ± 3.6	0.5143
90.0	64.59 ± 0.05	45.7 ± 1.7	0.4973
100 (Run 1)	85.23 ± 0.04	46.3 ± 2.4	0.4636
100 (Run 2)	85.33 ± 0.06	46.4 ± 2.5	0.4642
100 (Run 3)	85.32 ± 0.07	55.2 ± 4.6	0.4641
100 (Avg.)	85.29	49.3	0.4640
<i>Ph₄PPi</i>			
60.1	40.40 ± 0.02	28.7 ± 1.9	0.5652
70.0	43.86 ± 0.02	27.7 ± 1.5 ^a	0.5373
80.2	52.81 ± 0.02	35.8 ± 1.1	0.5292
90.0	65.56 ± 0.04	44.7 ± 2.4	0.5048
100 (Run 1)	86.27 ± 0.04	55.9 ± 2.2	0.4693
100 (Run 2)	86.28 ± 0.03	51.2 ± 1.2	0.4694
100 (Avg.)	86.28	53.5	0.4694

^aExcluded from log K_A versus 1/D plots.

where f_{\pm} is the mean ionic activity coefficient estimated from the Debye-Hückel limiting law using successive approximations with respect to the degree of dissociation. The Shedlovsky function is defined as

$$S(z) = \{z/2 + [1 + (z/2)^2]^{1/2}\}^2,$$

$$\text{where } z = S\Delta_0^{-3/2}(C\Delta)^{1/2} \text{ and } S = \alpha\Delta_0 + \beta$$

In the above expressions,

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

All calculations were carried out on an IBM 370/145 computer using FORTRAN programmes. The conductance parameters and constants obtained by the Shedlovsky equation are summarized in Table 5. A comparison of the Δ_0 and K_A values obtained by the Shedlovsky equation and by Fuoss' parametric analysis for the conductance data from this laboratory is shown in Table 6. In Table 7, a further comparison is made of Δ_0 and K_A values for KPi in 100% methanol calculated by three different equations from the high precision data of Coplan and Fuoss⁹.

Discussion

Walden products and Stokes radii — It is evident from the comparative results in Tables 6 and 7 that the values of Δ_0 remain essentially the same regardless of the conductance function from which they are derived. Therefore, it is convenient to consider first any information obtainable from the Δ_0 's, as it should be virtually free of ambiguity. Table 5 lists the limiting conductance, viscosity, and Walden products for the electrolytes. More informative, however, from the point of view of ion-solvent interactions are the Walden products of single ions, which can be calculated when limiting equivalent conductances for the single ions are known. Stokes radii for the ions, R_s , can then be calculated from the relationship,

TABLE 6 — COMPARISON OF Δ_0 AND K_A VALUES OBTAINED FROM THE SHEDLOVSKY EQUATION AND VIA FUOSS PARAMETRIC ANALYSIS⁶

[Data from this Laboratory]

System	Δ_0		K_A		$R_s \text{ \AA}$
	Shedlovsky	Fuoss 1974	Shedlovsky	Fuoss 1974	Fuoss 1974
KPi 60.1% Methanol-Water	59.50 ± 0.01	59.51 ± 0.03	6.67 ± 0.21	11.8 ± 4.4	17.2
KPi 100% Methanol	99.67 ± 0.01	99.67 ± 0.01 ^a	34.48 ± 0.12	48.37 ± 0.15 ^{a,b}	21.5
Ph ₄ PPi 100% Methanol	86.28 ± 0.03	86.30 ± 0.04 ^b	51.2 ± 1.2	66.7 ± 1.6 ^b	21.5
Ph ₄ PPi ⁽¹⁶⁾	46.95 ± 0.03	46.78 ± 0.02 ^b	114.5 ± 1.0	125.6 ± 0.7 ^b	25.6
100% Ethanol					
Ph ₄ AsPi ⁽¹⁶⁾	44.38 ± 0.02	44.39 ± 0.01 ^b	100.4 ± 1.2	113.9 ± 0.4 ^b	21.0
100% Ethanol					
LiCl ⁽¹⁵⁾	39.98 ± 0.01 ^c	39.99 ± 0.02	15.7 ± 0.4 ^c	57.2 ± 2.8	21.1
92.3% Ethanol-Water					

(a) Calculated from only four best points, omitting point 4.

(b) Obtained by the SCAN method^{7,10}.

(c) Calculated from the Fuoss-Onsager equation¹¹ by the x-y method.

($a_j = 3.73$)^e

TABLE 7 — COMPARISON OF CONDUCTANCE PARAMETERS FOR KPi IN 100% METHANOL OBTAINED BY DIFFERENT EQUATIONS

[Data of Coplan and Fuoss ⁹]				
	Run	Δ_0	K_A	$R_s, \text{\AA}$
Shedlovsky	I	99.11 ± 0.02	26.67 ± 0.30	—
	II	99.21 ± 0.01	26.71 ± 0.11	—
Fuoss-Onsager ¹¹	I	99.22 ± 0.01	15.4 ± 0.3	—
	II	99.27 ± 0.03	12.3 ± 1.7	—
	III	99.28 ± 0.06	12.8 ± 3.9	—
Fuoss ⁶	I	99.27 ± 0.01	34.6 ± 1.5	14.09
	II	Calculation failed		—
	III	99.32 ± 0.05	36.0 ± 4.9	15.96

TABLE 8 — LIMITING EQUIVALENT CONDUCTANCES, WALDEN PRODUCTS AND STOKES RADII OF SINGLE IONS

Ion/parameter	Wt % Methanol	
	100	64.0 (50.0 mol %) ^a
K^+		
λ_0	52.38	38.06
	(ref. 12)	(refs. 13, 14)
t_+	0.5274	0.6209
$\lambda_0 + \eta_0$	0.2850	0.5092
R_s	2.88	1.61
PI^-		
λ_0^c	46.94	23.2 ₄
t (in KPi)	0.4726	0.379 ₁
$\lambda_0^- \eta_0$	0.2553	0.311 ₀
R_s	3.21	2.63
Ph_4As^+		
λ_0^d	38.35	16.4 ₆
t_+	0.4496	0.415
$\lambda_0^+ \eta_0$	0.2086	0.220 ₂
R_s	3.93	3.72
Ph_4P^+		
λ_0^e	39.34	18.2 ₆
t_+	0.4560	0.440
$\lambda_0^+ \eta_0$	0.2140	0.244 ₃
R_s	3.83	3.35

- (a) $\eta_{0.0} = 1.338$ cp
 (b) The limiting transference numbers of the cations refer to the picrates.
 (c) $\Delta_0(KPi) - \lambda_0(K^+)$
 (d) $\Delta_0(Ph_4AsPi) - \lambda_0(Pi^-)$
 (e) $\Delta_0(Ph_4PPi) - \lambda_0(Pi^-)$

$$R_s \text{ (in } \text{\AA}) = \frac{0.8194 Z |}{\Delta_0 \eta_0} \dots(2)$$

where Z is the ionic charge.

Accurate values of λ_0 (+ are available for 100% methanol (= 52.38)¹² and 64.0% methanol (50.0 mol %). Combining it with $\Delta_0(KPi) = 99.32$, which is an average of our own and literature data, yields $\lambda_0(Pi^-) = 46.94$. Values of λ_0 for Ph_4As^+ and Ph_4P^+ ions are then obtained from the λ_0 's of the corresponding picrates determined in this study. In 64.0% methanol, $\lambda_0(K^+) = 38.06$ is obtained by combining $\Delta_0(KCl) = 75.10$ (ref. 13) and t_+ (in KCl) = 0.5068 (ref. 14). The λ_0 's for other ions in 64.0% methanol are calculated by difference from those of the picrates interpolated from the results of the present study. The interpolated Δ_0 's are : $KPi = 61.3$; $Ph_4AsPi = 39.7$ and $Ph_4PPi = 41.5$. All the parameters calculated for single ions, including transference numbers, Walden

products and Stokes radii (from Eq. 2) are compiled on Table 8.

Appreciable variation in the Walden product and therefore the Stokes radius of an ion as a function of the solvent is generally regarded as an index of specific ion-solvent interactions, including structural effects. A reasonable constancy of the above parameters in different solvents as well as an approximate agreement between crystallographic and Stokes radii is interpreted as indicative of absence of specific solvation effects. The data in Table 8 shows that the Stokes radii of the Ph_4As^+ and Ph_4P^+ ions differ little between 100% and 64.0% methanol ($R_s = 3.93$ and 3.72, respectively, for Ph_4As^+ and 3.83 and 3.35 for Ph_4P^+). The van der Waals' radii are estimated to be 4.30 (ref. 15) and 4.28 (ref. 16) for Ph_4As^+ and 4.28 for Ph_4P^+ (ref. 16). No conductance data are available for the Ph_4P^+ and Ph_4As^+ ions in water, but a comparison between methanol and water can be made for their structural analog, the tetraphenylborate anion. Thus, in methanol, $\lambda_0(BPh_4^-) = 36.50$ (ref. 12) and in water, 19.69 (ref. 17), corresponding Stokes radii are 4.13 and 4.67 respectively. Similar values for the Stokes radii of the BPh_4^- ion were reported¹⁸ in acetonitrile (4.11), nitrobenzene (4.12) and nitromethane (4.14). The van der Waals' radius of the BPh_4^- ion has been estimated^{15,16} to be 4.21. The small increase in the Stokes radius in water, relative to the van der Waals' radius, undoubtedly reflects the well-known hydrophobic structure-making characteristic of bulky organic ions.

Evidently, the tetraphenyl ions, which form the basis for a number of extra thermodynamic assumptions requiring a relative 'ideality' with respect to solvation effects are indeed free of any major ion-solvent interactions that would be reflected in the variation of their Stokes radii.

In contrast to tetraphenyl ions, the K^+ ion exhibits a considerable variation in its Walden products and Stokes radii with the solvent, $\lambda_0 + \eta_0$ in 64.0% methanol being 44% greater than in 100% methanol. As a result, the Stokes radius of the K^+ ion drops from a value of 2.88 in methanol to 1.61 in 64.0% methanol. In water, $\lambda_0(K^+) = 73.55$ so that using $\eta_{R,0} = 0.8903$ cp, the Walden product becomes 0.6548 and the Stokes radius 1.25, which is below the crystallographic radius of 1.33. The above variations can be interpreted in terms of the effect of the K^+ ion on the structure of solutions. In aqueous solutions, the K^+ ion acts as a structure-breaker and the reason why its mobility is high relative to that of other solutes of comparable radii lies in the fact that a structure-breaking ion decreases the local viscosity by breaking some of the hydrogen bonds in the three-dimensional network of liquid water. No such effects are observed in nonaqueous solvents, which are generally less structured than water, and in those solvents the mobility of structure-breaking ions is not excessive.

Kay and Evans¹⁹ found that Walden products of structure-breaking ions in water decreased with increasing temperature and pressure. Since the effect of increased temperature and pressure is to

cause a partial breakdown of the three-dimensional water structure, it means that as the temperature or the pressure is increased the ions become less effective structure breakers and their mobility decreases¹⁹. There is evidence that addition of a nonaqueous solvent to water causes a breakdown in the water structure as well. This structure-breaking has been invoked to interpret the sharp increase in basicity, resulting in a basicity maximum, upon addition of ethanol, acetone or dioxane to water, as measured by the Hammett acidity function²⁰, H_0 . A similar pattern of basicity is reflected in the variation of the transfer activity coefficients for the proton, estimated in this laboratory for the entire range of ethanol-water^{21,22} and methanol-water²² solvents. The basicity maxima, which for the above alcohols occur in the region of 60-80 wt %, are believed to correspond to regions of minimum solvent structure and this is where one would expect the K^+ ion to behave most 'ideally' on reference to Stokes law. Indeed, it might not be fortuitous that at 64.0% methanol $R_s = 1.61$, though there undoubtedly exists a methanol-water mixture where the correspondence to the crystallographic radius of 1.33 is even closer. As the solution becomes richer in methanol, solvation by methanol molecules gradually becomes a factor and the effectiveness of K^+ as a structure-maker (in alcoholic media) is reflected in the gradual increase of the R_s . A contributing cause to this is the dielectric relaxation effect, which may be partly responsible for increase in the Stokes radius of the picrate ion with increase in methanol content, although specific solvation of the picrate ion by methanol molecules via strong dispersion interactions is well known²³ and is likely to be a factor here.

It was shown by Fuoss²⁴ and later by Zwanzig²⁵ that even in the absence of specific solvation, Walden products vary with the solvent dielectric constant due to the dielectric relaxation effect, which opposes the motion of ions. Fuoss derived a relationship between the Stokes radius in a real solvent of dielectric constant D and R_∞ , the hydrodynamic radius of an ion in a hypothetical solvent of infinite dielectric constant, where electrostatic forces would be reduced to zero²⁴:

$$R_s D = DR_\infty + B \quad \dots(3)$$

Equation (3) was applied to our data by interpolating the values of ionic transference numbers, t_+ and t_- , for each solvent composition at which the Λ_{0s} of the title electrolytes were determined and the Walden products and the Stokes radii of single ions were then calculated on their basis. Plots of $R_s D$ versus D are roughly linear for all the ions. R_∞ values calculated by the method of least squares are: 3.53 (Ph_4As^+), 2.49 (Ph_4P^+) and for Pi^- , 1.55 (from Ph_4PPi), 1.59 (from Ph_4AsPi) and 1.69 (from KPi). It is significant that Eq. (3) is inapplicable to the K^+ ion, yielding a negative value of R_∞ , which has no physical meaning. Evidently, structural and other solvation effects overwhelm the dielectric relaxation effect in this case. With the exception of the Ph_4As^+ ion, the remaining ions have R_∞ values much smaller than the ion sizes

normally associated with them. This suggests that in methanol-water media, Eq. (3) cannot account fully even for the behaviour of the less solvated ions.

Association constants and ion-size parameters — In Table 6 a comparison is made between the values of association constants K_A obtained by the Shedlovsky equation and by Fuoss' parametric analysis using the data from this laboratory. In order to ascertain that the above comparison is not distorted due to the relatively lower precision of our data, a similar comparison was made in Table 7 for the K_A values derived by the two functions from the high-precision data of Coplan and Fuoss⁹. Excellent agreement is observed between the K_A values for KPi in methanol obtained by us and in the former study⁹. It may be seen that K_A values calculated by Fuoss' parametric approach are always larger than those derived by the older Shedlovsky or Fuoss-Onsager functions. This is a consequence of a broader definition of ion pairing in the Fuoss parametric analysis⁶, where all ions that find a unique partner between the contact distance a and the distance parameter R are considered to be associated. R is the radius of a sphere centered at the cation of the ion-pair within which not only electrostatic attraction, but also other specific short-range interactions, both ion-ion and ion-solvent, take place. Beyond the distance R , the solvent can be treated as a continuum. The above definition of R suggests that it should correspond closely to the distance of dielectric saturation, within which the solvent properties are modified by the ionic field. It is estimated that in methanol dielectric saturation extends to distances of up to 15Å from the center of an ion²⁶. The agreement between this estimate and the R values of 14 and 16 for KPi in methanol (Table 7) is remarkable. The R values for methanol solutions obtained in this study are somewhat higher (21.5) and might reflect experimental errors. It is noteworthy that the increase in K_A 's calculated by the Fuoss analysis⁶ relative to the Shedlovsky function appears to vary with the dielectric constant of the solvent. Thus, for 60.1% methanol ($D=51.55$) the increase is 76%, for methanol ($D=32.64$) the increase is ~30% and for ethanol ($D=24.3$) it is only ~10% (Table 6). This may be illustrative of a phenomenon pointed out by Fuoss⁶ that K_A in solvents of lower dielectric constant is determined primarily by the contact distance a and is insensitive to the distance R . Thus, in solvents of lower dielectric constant, K_A can be adequately formulated by the classical Bjerrum theory⁶, where ions are considered paired within the distance from a to $e^2/2DkT$; in the latter e is electronic charge, k is the Boltzmann constant and T is absolute temperature.

The association constants obtained by the Shedlovsky function in this study have been analyzed by the classical relationship²⁷:

$$\log K_A = \log K_A^0 + \frac{e^2}{2.303 a D k T} \quad \dots(4)$$

Plots of $\log K_A$ versus $1/D$ are approximately linear for Ph_4AsPi and Ph_4PPi , but exhibited a pronounced concave-down curvature for KPi at high

methanol contents, so that here a linear plot could be fitted only in the range of 60-90% methanol. The values of the contact distance a (in Å) obtained via Eq. (4) are 9.87 for Ph₄AsPi, 9.85 for Ph₄PPi and 2.84 for KPi. On the basis of our understanding of ion sizes, the first two values are much too high, unless we invoke the possibility of solvent-separated ion-pairs. The latter, however, must be weighed against the possibility that we may be dealing here with an artifact resulting from the shortcomings of the Shedlovsky function. On the other hand, the ion-size parameter for KPi is very reasonable. However, the relative magnitudes of the association constants of KPi and the picrates of the tetraphenyl ions are determined primarily by the pre-exponential term K_A° , which is 0.165 for KPi, 10.2 for Ph₄AsPi and 9.56 for Ph₄PPi. K_A° is determined to a large extent by the difference in the solvation energy of the free ions and the corresponding ion pairs²⁷. The low value of K_A° for KPi relative to those for Ph₄PPi and Ph₄AsPi reflects the much greater solvation of the K⁺ ion as opposed to the Ph₄As⁺ and Ph₄P⁺ ions. Additionally, strong dispersion forces between the tetraphenyl cations and the picrate anion would tend to increase the K_A s beyond their values predicted from coulombic considerations.

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References

1. POPOVYCH, O., *Transfer activity coefficients : Medium effects in Treatise on analytical chemistry, Part I. Vol. 1*, edited by I. M. Kolthoff and P. J. Elving (Wiley-Interscience, New York), 1978, Chap. 12.
2. DILL, A. J. & POPOVYCH, O., *J. chem. Eng. Data*, **14** (1969), 156.
3. BERNE, D. H. & POPOVYCH, O., *J. chem. Eng. Data*, **17** (1972), 178.
4. CHIU, Y. C. & FUOSS, R. M., *J. phys. Chem.*, **72** (1968), 4123.
5. BATES, R. G. & ROBINSON, R. A., *Acid-base behaviour in methanol-water solvents in Chemical physics of ionic solutions*, edited by B. E. Conway and R. G. Barradas (Wiley-Interscience, New York), 1966, Chap. 12.
6. FUOSS, R. M., *Proc. natl. Acad. Sci. USA*, **71** (1974), 4491.
7. FUOSS, R. M., Private communication.
8. SHEDLOVSKY, T., *J. Franklin Inst.*, **225** (1938), 739; FUOSS, R. M. & SHEDLOVSKY, T., *J. Am. chem. Soc.*, **71** (1949), 1496.
9. COPLAN, M. A. & FUOSS, R. M., *J. phys. Chem.*, **68** (1964), 481.
10. FUOSS, R. M., *J. phys. Chem.*, **79** (1975), 525.
11. FUOSS, R. M. & ONSAGER, L., *J. phys. Chem.*, **61** (1957), 688.
12. KUNZE, R. W. & FUOSS, R. M., *J. phys. Chem.*, **67** (1963), 385.
13. SCHIFF, H. I. & GORDON, A. R., *J. chem. Phys.*, **16** (1948), 336.
14. SHELTON, L. W., DAVIES, J. A. & GORDON, A. R., *J. chem. Phys.*, **16** (1948), 340.
15. BAX, D., DELIGNY, C. L. & ALFENNAAR, M., *Rec. Trav. Chim.*, **91** (1972), 453.
16. KIM, J. I., *J. phys. Chem.*, **82** (1978), 191.
17. SKINNER, J. F. & FUOSS, R. M., *J. phys. Chem.*, **68** (1964), 1882.
18. COETZEE, J. F. & CUNNINGHAM, G. P., *J. Am. chem. Soc.*, **87** (1965), 2529.
19. KAY, R. L. & EVANS, D. F., *J. phys. Chem.*, **70** (1966), 2325; KAY, R. L., *Ionic transport in water and mixed aqueous solvents in Water—A comprehensive treatise*, edited by F. Franks, Vol. 3 (Plenum Press, New York), 1973, Chap. 4.
20. BRAUDE, F. A. & STERN, E. S., *J. chem. Soc.*, (1948), 1976.
21. POPOVYCH, O. & DILL, A. J., *Anal. Chem.*, **41** (1969), 456.
22. POPOVYCH, O., *Anal. Chem.*, **46** (1974), 2009.
23. GRUNWALD, E. & PRICE, E., *J. Am. chem. Soc.*, **86** (1964), 4517.
24. FUOSS, R. M. *Proc. natl. Acad. Sci. USA*, **45** (1959), 807.
25. ZWANZIG, R., *J. chem. Phys.*, **38** (1963), 1603, 1605.
26. ALFENNAAR, M. & DELIGNY, C. L., *Rec. Trav. Chim.*, **86** (1967), 929.
27. HOWES, J. L. & KAY, R. L., *J. phys. Chem.*, **69** (1965), 2420.