at higher pH (*12*) and the substantial disagreement of calculated cell transference numbers with the moving boundary ones of Fritz and Fuget (*6*) provided further evidence of this systematic error.

All measurements with both Cu and Hg_2SO_4 electrodes were done in the absence of air using recrystallized $CuSO_4$. It is possible that equilibrating all solutions with Cu metal, with the associated lowering of the pH, might improve both electrode types. However, there will also be an additional liquid junction potential arising from the extra species created by the equilibration.

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Apparent Molal Volumes of Aqueous Tetraphenyl Arsonium Chloride Solutions at 0°, 25°, and 50° C

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The apparent molal volumes, Φ_V's, of dilute (0.002–0.1*m*) aqueous solutions of tetraphenyl arsonium chloride (Ph_4AsCl) have been determined at 0°, 25°, and 50° C from precision density measurements. The Φ_V's, as a function of $(c)^{1/2}$, approach limiting law behavior at all the temperatures studied. The deviations of the Φ_V's from the limiting law are positive at 0°, and negative at 25° and 50° C. The Φ_V's at infinite dilution have been extrapolated with the aid of the limiting law. The effect of temperature on the Φ_V^0's of the Ph_4AsCl solutions is similar to other common electrolytes, in that $\partial^2\Phi_V^0/\partial T^2 = \partial\Phi_E^0/\partial T$ is negative. The ion-ion and ion-water interactions responsible for the observed behavior of the Φ_V's for Ph_4AsCl solutions are briefly discussed.

The thermodynamic properties of electrolytes with a hydrocarbon portion—e.g., the symmetrical tetraalkylammonium halides, R_4NX's—have been the subject of considerable interest in recent years. The concentration and temperature behavior of the apparent molal volumes, Φ_V's, of organic electrolytes appear to be abnormal compared to common electrolytes like NaCl (*7, 11, 12*). The Φ_V's of organic electrolytes have large negative deviations from the Debye-Hückel limiting law (*1, 3, 7, 11, 12*) and the infinite dilution Φ_V^0's do not appear to go through a maximum as a function temperature (*7, 11, 12*) like the more common electrolytes—e.g., NaCl—(*3, 9*).

This study on the Φ_V's of dilute tetraphenyl arsonium chloride (Ph_4AsCl) solutions was made to provide precise data that may prove useful in interpreting the ion-ion and ion-water interactions of electrolytes with a hydrocarbon portion. The Φ_V^0 of the Ph_4As^+ ion can be used to examine the effect of the aromatic ring on ion-water interactions and compared to the Φ_V^0 results for the R_4N^+ ion (*1, 3, 7, 11, 12*) and the BPh_4^- ion (*8*).

Table I. Density of Aqueous Tetraphenyl Arsonium Chloride Solutions as Function of Concentration and Temperature

0° C		25° C		50° C	
Molality	−1000Δd	Molality	−1000Δd	Molality	−1000Δd
0.0031021	0.3448	0.0028362	0.2863	0.0015646	0.1467
0.0038690	0.4299	0.0031585	0.3187	0.0017873	0.1675
0.0068191	0.7564	0.0035636	0.3593	0.0020841	0.1952
0.0076529	0.8496	0.0040879	0.4115	0.0024988	0.2339
0.0087190	0.9667	0.0047930	0.4827	0.0027721	0.2593
0.012087	1.3369	0.0057920	0.5830	0.0031123	0.2905
0.013467	1.4899	0.0064520	0.6489	0.0035482	0.3315
0.015204	1.6807	0.0072817	0.7323	0.0041257	0.3851
0.017456	1.9289	0.0083564	0.8400	0.0061426	0.5741
0.020490	2.2568	0.0098032	0.9847	0.0067908	0.6333
0.024800	2.7293	0.011856	1.1900	0.0068192	0.6361
0.027615	3.0402	0.013217	1.3256	0.0076632	0.7151
0.031151	3.4239	0.014930	1.4964	0.0077535	0.7241
0.035725	3.9224	0.017154	1.7186	0.0087456	0.8162
0.041893	4.5818	0.020157	2.0161	0.0090341	0.8422
0.048387	5.2773	0.024435	2.4400	0.010184	0.9503
0.048912	5.3402	0.027252	2.7173	0.010222	0.9504
0.050578	5.5171	0.030442	3.0287	0.010822	1.0070
0.061998	6.7368	0.030804	3.0677	0.012020	1.1192
0.069933	7.5741	0.035043	3.4837	0.012189	1.1336
0.070922	7.6748	0.035420	3.5228	0.013518	1.2582
0.082122	8.8597	0.041283	4.1007	0.013533	1.2582
0.082847	8.9296	0.041663	4.1388	0.015210	1.4141
0.099457	10.6640	0.047694	4.7238	0.015441	1.4384
		0.048387	4.7899	0.017362	1.6158
		0.050226	4.9786	0.018004	1.6607
		0.050578	5.0082	0.020222	1.8770
		0.053190	5.2542	0.021585	2.0023
		0.055069	5.4533	0.024211	2.2428
		0.060118	5.9407	0.026916	2.4914
		0.062626	6.1838	0.027235	2.5265
		0.069121	6.8029	0.030300	2.8073
		0.081294	7.9682	0.034658	3.2131
		0.098673	9.6172	0.039354	3.6470
				0.040479	3.7380
				0.048651	4.4892
				0.048912	4.5209
				0.054242	4.9959
				0.054454	5.0104
				0.056291	5.1915
				0.061285	5.6359
				0.061413	5.6484
				0.070410	6.4678
				0.082497	7.5363
				0.099592	9.0770

EXPERIMENTAL

The Ph_4AsCl used in this study was obtained from K & K Laboratories and recrystallized by the methods of Kalfoglou and Bowen (*5*). All of the solutions were made by weight with ion exchanged water (~8MΩ). The water was degassed before use, to prevent the formation of bubbles on the magnetic float during an experiment.

The magnetic float densitometer used to make the density measurements and a review of the development of the magnetic float method have been described in detail elsewhere (*10*). The densitometer consists of a 110-ml solution container which fits into a brass support containing a solenoid. The float (~32 cc) is made of borosilicate glass and contains a magnet. The densitometer was calibrated with ion exchanged water using the densities tabulated by Kell (*6*). The weight dilution method was used in all the density measurements. Duplicate density measurements on the same solution agreed to within ±1 ppm. The reproducibility of ±0.2 in the Φ_V's in the most dilute solutions (0.002*m*) indicates that the density precision, within a given experimental run, was ±0.3 ppm.

The temperature of the bath containing the densitometer was set to ±0.005° C with a Hewlett-Packard quartz crystal thermometer. The quartz crystal thermometer was calibrated with a platinum resistance thermometer (calibrated by the National Bureau of Standards to ±0.001° C) and a G-2 Mueller bridge. The bath was regulated to within ±0.001° with a Hallikainen Thermotrol. This temperature variation corresponds to a density uncertainty of ±0.3 ppm or ±0.2 in Φ_V in the most dilute solutions.

RESULTS AND DISCUSSIONS

The densities of dilute (0.002–0.1*m*) solutions of Ph_4AsCl have been determined at 0°, 25°, and 50° C. The differences ($\Delta d = d^\circ - d$) between the densities of the Ph_4AsCl solutions (d), and the density of water (d°) as a function of concentration and temperature are given in Table I. The apparent molal volumes, Φ_V, for these solutions were calculated from the equation

$$\Phi_V = 1000\ (d^\circ - d)/dd^\circ m + M/d \tag{1}$$

where m is the molality and M is the molecular weight of the Ph_4AsCl (418.79). The Φ_V's of these solutions are shown in Figure 1 as a function of the square root of molar concentration $(c)^{1/2}$. The Debye-Hückel limiting law slope (*13*) is approached at all the temperatures studied.

The infinite dilution partial molal volumes, $\Phi_V^0 = \bar{V}_2^0$, were obtained with the aid of the Redlich equation (*13*) (by a least-square best fit)

$$\Phi_V = \Phi_V^0 + S_V(c)^{1/2} + b_V c \tag{2}$$

where S_V is the theoretical slope (*13*) and b_V is an empirical deviation constant. Table II lists the $\bar{V}_2^0$'s and the b_V's for Ph_4AsCl solutions at 0°, 25°, and 50° C. Also given in Table II are the partial molal expansibilities, $\Phi_E^0 = \partial\Phi_V^0/\partial T = \bar{E}_2^0$, at infinite dilution at 12.5 and 37.5°.

The partial molal volumes, $\bar{V}_2$, of these solutions as a function of concentration have been calculated from the relation

$$\bar{V}_2 = \Phi_V + \left[\frac{1000 - c\Phi_V}{2000 + c^{3/2}\,(\partial\Phi_V/\partial c^{1/2})}\right] c^{1/2}\,(\partial\Phi_V/\partial c^{1/2}) \tag{3}$$

These $\bar{V}_2$'s were fit by a least-square best fit to the equation

$$\bar{V}_2 = \bar{V}_2^0 + 1.5\,S_V\,(c)^{1/2} + b'_V\,c \tag{4}$$

where $b'_V = 2\ b_V$ and $\bar{V}_2^0$ is given in Table II.

The deviations of the Φ_V's for the Ph_4AsCl solutions—i.e., b_V—are positive at 0°, and negative at 25° and 50° C. The negative deviations for the Ph_4AsCl solutions at 25° and 50° C are similar to deviations of the electrolytes $NaBPh_4$ (*8*) and Bu_4NCl (*1*). However, the effect of temperature on the b_V's for Ph_2AsCl solutions appears to be different from either $NaBPh_4$ or Bu_4NCl solutions in that $\partial b_V/\partial T$ is negative for Ph_4AsCl (like NaCl) (*2*, *9*) while the $\partial b_V/\partial T$ for $NaBPh_4$ and Bu_4NCl is positive (*8*). These results indicate the difficulties involved in interpreting the sign of the deviation constant b_V as being due to a specific type of ion-ion interaction—e.g., ion-pairing, salting-in effects, "ice-like" effects, etc. (*1*, *3*, *7*–*9*). For example, the large negative deviations of the Φ_V's for the Bu_4NX's have been attributed (*3*, *7*, *11*, *12*) to some type of cation-cation interaction—i.e., $Bu_4N^+ - Bu_4N^+$. By analogy one might attribute the negative deviations of the Ph_4AsCl solutions at 25° and 50° C to the same type of cation-cation interaction—i.e., $Ph_4As^+ - Ph_4As^+$. The temperature dependence of the b_V's for Ph_4AsCl and Bu_4NCl or the more similar $NaBPh_4$ indicates that the ion-ion interactions are different. The b_V's at 0° C for Ph_4AsCl and $NaBPh_4$ solutions have opposite signs. The cause of the differences between the ion-ion interactions for the Ph_4AsCl and

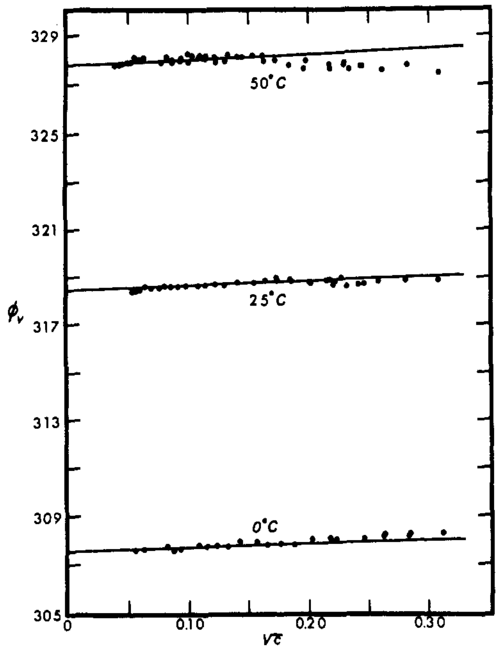

Figure 1. The apparent molal volumes, Φ_V's, of aqueous Ph_4AsCl solutions as a function of $(c)^{1/2}$ at 0°, 25°, and 50° C. The straight lines are the theoretical limiting law slopes (*13*)

Table II. Partial Molal Volumes of Ph_4AsCl in Water at Infinite Dilution and Deviation Constants from Limiting Law at 0°, 25°, and 50° C[a]

Temp, °C	$\Phi_V^0 = \bar{V}_2^0$	$\Phi_E^0 = \bar{E}_2^0$	b_V	RMS
0.0	307.5_7		3.16	0.09
12.5		0.436		
25.0	318.4_8		−1.75	0.10
37.5		0.378		
50.0	327.9_4		−13.24	0.14

[a] Units are ml mol^{-1} for $\bar{V}_2^0$, ml mol^{-1} deg^{-1} for $\bar{E}_2^0$, and ml l. mol^{-1} for b_V.

$NaBPh_4$ solutions may be caused by the differences in the ion-ion interactions of the Na^+ and Cl^- ions—i.e., $Ph_4As^+ - Cl^-$ and $Na^+ - BPh_4^-$ interactions—or higher order triplet interactions ($Ph_4As^+ - Cl^- - Ph_4As^+$). Further physical-chemical measurements must be made on these systems before these causes can be fully elucidated.

The partial molal expansibilities of the Ph_4AsCl solutions at infinite dilution, $\bar{E}_2^0$, are similar to $NaBPh_4$ (*8*) or NaCl (*2, 9*) solutions in that $\partial \bar{E}_2^0 / \partial T$ is negative. By extrapolating the $\bar{E}_2^0$'s for Ph_4AsCl solutions to zero, the temperature where $\bar{V}_2^0$ goes through a maximum is found to be ~200° C compared to ~138° C for $NaBPh_4$ (*8*).

The cause of the decrease in the $\bar{E}_2^0$ of Ph_4AsCl with increasing temperature or the maximum in the $\bar{V}_2^0$ can be attributed to the decrease in volume due to the increase in electrostriction with increasing temperature—i.e., $\bar{V}^0$(elect) and $\bar{E}^0$(elect). Using Hepler's (*4*) or Millero's (*11, 12*) methods, the Ph_4AsCl and $NaBPh_4$ electrolytes would be classified as "structure breaking" or "negative hydrating" solutes.

The cause of the differences (*7, 8*) between the ion-water interactions of electrolytes with an aromatic (Ph_4As^+ or BPh_4^-) or alkane (Bu_4N^+) hydrocarbon groups may be due to differences in the structure of the benzene ring compared to the alkane group or due to differences in the packing of water molecules around the benzene ring compared to the alkane group. We prefer the explanation based on packing effects—i.e., the water molecules may be able to fill the void spaces around the Bu_4N^- ion, while for the BPh_4^- and Ph_4As^+ ions, this filling up or penetration is not possible.

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