Apparent Molal Volumes of Tetraalkylammonium Halides in Water at 25°C

Test of Redlich and Meyer Equation

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The densities of most of the tetraalkylammonium halides have been measured in water at 25°C. These results were combined with the literature data and plotted with the Redlich and Meyer equation, which holds to much higher concentrations than previously suspected.

In a recent study of the viscosity of aqueous electrolyte solutions (*5*), it was necessary to extend to higher concentrations some of the density data on the homologous salts R_4NX, since most of the precise work on these salts had been concerned with the determination of Φ_v^0 and its concentration dependence at low concentrations (*1, 2, 6, 9*). Since the solutions used for the viscosity measurements were available, the density measurements were also repeated down to 0.01m whenever some anomalies in the literature values were apparent. This note presents these data along with some of the literature data in a form that makes the density readily available.

One of the most convenient ways to represent the difference between the density of the solution and that of the solvent, $d - d_0$, is in terms of the apparent molal volume

$$\phi_v = \frac{M}{d_0} - 1000\,\frac{(d - d_0)}{c d_0} \tag{1}$$

where M is the solute molecular weight and c the molarity. For electrolyte solutions, Redlich and Meyer (*10*) have shown that ϕ_v can be fitted, over a fairly wide concentration range, with the equation

$$\phi_v = \phi_v^0 + Ac^{1/2} + hc \tag{2}$$

where A can be calculated from the Debye-Huckel limiting law and had the value 1.868 for aqueous 1:1 electrolytes at 25°C. Therefore from two parameters only, ϕ_v^0 and h, ϕ_v and con-

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Table I. Apparent Molal Volumes of Tetraalkylammonium Halides in Water at 25°C

Salt	c	ϕ_v	Salt	c	ϕ_v	Salt	c	ϕ_v
Me_4NCl	0.02415	107.44	n-Bu_4NCl	0.00439	293.61	n-Pr_4NBr	0.01068	239.49
	0.05415	107.63		0.01755	294.04		0.02703	239.45
	0.07622	107.66		0.02139	293.79		0.03256	239.49
	0.09708	107.78		0.03646	293.49		0.07254	239.28
	0.12768	107.76		0.06789	293.11		0.07540	239.07
	0.16591	107.88		0.07275	293.11		0.09493	239.14
	0.25416	107.89		0.08739	293.05		0.13479	238.87
	0.31560	107.90		0.13635	292.45		0.14803	238.89
	0.33314	107.90		0.14434	292.36		0.15410	238.57
	0.41574	107.93		0.16311	292.21		0.19173	237.84
	0.53068	107.92		0.21832	291.72		0.23639	238.07
	0.77797	107.90		0.24780	291.45		0.27328	237.92
							0.33511	237.68
Et_4NCl	0.01311	166.66	Et_4NI	0.01703	185.36		0.38479	237.22
	0.03737	166.89		0.02984	185.47		0.41884	236.90
	0.04641	166.70		0.05368	185.52		0.55403	236.04
	0.06457	166.74		0.06812	185.47		0.62977	235.70
	0.09011	166.71		0.09332	185.54			
	0.11782	166.64		0.12543	185.61	n-Bu_4NBr	0.03407	300.12
	0.13503	166.64		0.14315	185.57		0.04362	300.16
	0.21633	166.46		0.17862	185.55		0.05553	300.03
	0.23269	166.41		0.21544	185.54		0.06428	300.00
	0.25207	166.47		0.26324	185.57		0.07621	300.09
	0.29243	166.36					0.07627	300.02
	0.40479	166.05	n-Pr_4NI	0.00422	250.82		0.08634	300.00
	0.41921	166.01		0.02012	251.00		0.09023	299.99
	0.54943	165.54		0.02949	250.86		0.14045	299.57
				0.05684	250.87		0.21109	298.93
n-Pr_4NCl	0.01198	232.61		0.07584	250.85		0.26700	298.46
	0.02238	232.46		0.08540	250.89		0.32598	298.01
	0.03541	232.44		0.10647	250.81			
	0.06484	232.24		0.12912	250.72			
	0.08680	232.05		0.16383	250.60			
	0.16406	231.50						
	0.26041	230.81						
	0.36465	230.08						

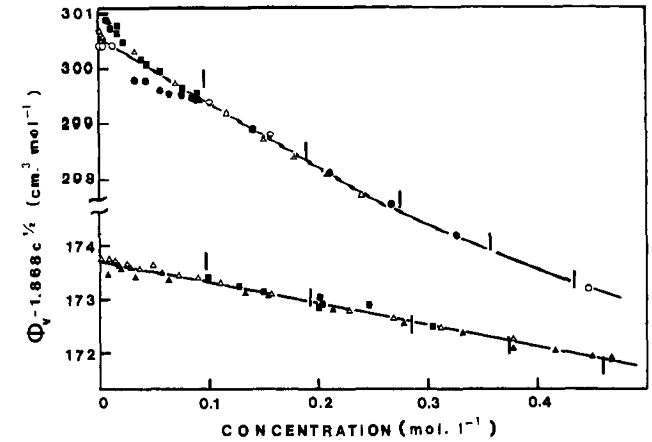

Figure 1. Apparent molal volumes of n-Bu_4NBr (top line) and Et_4NBr (bottom line) in water at 25°C

● Present results. ○ Dunn (6). ■ Conway et al, (2). △ Conway and Lalberté (1). ▲ Wirth (12). | Wen and Saito (11)

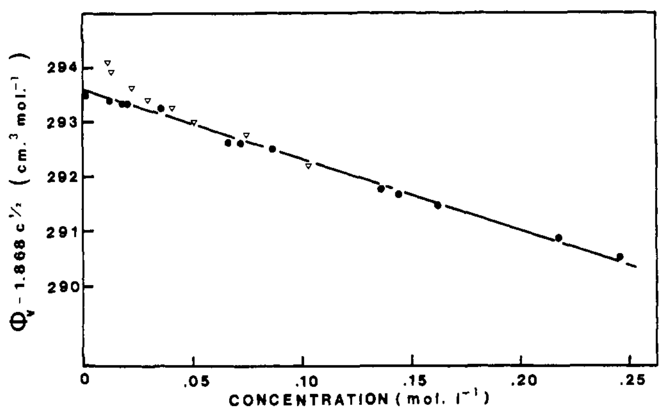

Figure 2. Apparent molal volumes of n-Bu_4NCl in water at 25°C

● Present results. ▽ Conway et al. (2)

sequently d may be calculated at any concentration in the region where the Redlich and Meyer equation holds.

The techniques for density measurements (*3*) and salt purification (*2*, *5*) have been described elsewhere. All solutions were prepared in molalities and the concentrations converted to molarities from the density data. The present results are given in Table I.

A few typical examples of plots of $\phi_v - 1.868\, c^{1/2}$ vs. c are shown in Figures 1 and 2. With Et_4NBr, all authors were in excellent agreement over the whole concentration range, and it was not necessary to repeat any measurements. In the case of n-Bu_4NCl, n-Bu_4NBr, and most other salts, important discrepancies are observed at low concentrations; most of the deviations amount to errors of at most 4×10^{-6} g cm^{-3}. Still, once all the data are compared on the same figure, it is evident that the Redlich and Meyer equation is obeyed to a much larger extent than it was previously suspected. The only salt that presented serious difficulties was n-Bu_4NI. Depending on the method of preparation and purification, different families of lines of $\phi_v - 1.868\, c^{1/2}$, with similar slopes, were obtained, but none of the extrapolated ϕ_v^0 were acceptable from the additivity test.

Table II. Parameters of Redlich and Meyer Equation for Apparent Molal Volumes of Tetraalkylammonium Halides in Water at 25°C

Salt	ϕ_v^0	h	Max concn	Ref.
Me_4NCl	107.30	−1.40	0.8	*2*
Et_4NCl	166.59	−4.35	0.6	*2*
n-Pr_4NCl	232.39	−9.75	0.4	*2*
n-Bu_4NCl	293.60	−12.89	0.25	*2*
Me_4NBr	114.35	−1.01	2.5	*2, 11*
Et_4NBr	173.74	−4.12	1.0	*2, 11, 12*
n-Pr_4NBr	239.36	−8.77	0.50	*1, 2, 11*
n-Bu_4NBr	300.59	−11.85	0.30	*1, 2, 6, 11*
Me_4NI	125.78	−0.02	0.25 sat	*2, 8*
Et_4NI	185.18	−2.21	0.27 sat	
n-Pr_4NI	250.77	−5.71	0.17 sat	*2*
n-Bu_4NI	311.97[a]	−7.7	0.05 sat	

[a] Value estimated from additivity.

The parameters ϕ_v^0 and h of Equation 2, obtained from a least-square fit of the linear region of our data, and all of the available literature data (*1*, *2*, *6*, *9*, *11*, *12*), are given in Table II. In the case of n-Bu_4NI, h is the average slope of the family of lines of the $\phi_v - 1.868\, c^{1/2}$ vs. c plot, but ϕ_v^0 was estimated by additivity principles. The maximum concentrations for the linear region of the Redlich and Meyer equation or the highest concentration studied is also given.

The derived ϕ_v^0 are all additive to ± 0.05 cm^3 mol^{-1}, showing the self-consistency of the data. The present study stresses the need for accurate density measurements over a wide region of concentrations if reliable extrapolations to infinite dilution of apparent molal quantities are desired.

These ϕ_v^0 are in general fairly close to previously published values (*1*, *2*, *6*, *7*, *9*), but some of the parameters, h, are significantly different. However, the trends have not been changed and the conclusions reached previously (*4*) are still valid.

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