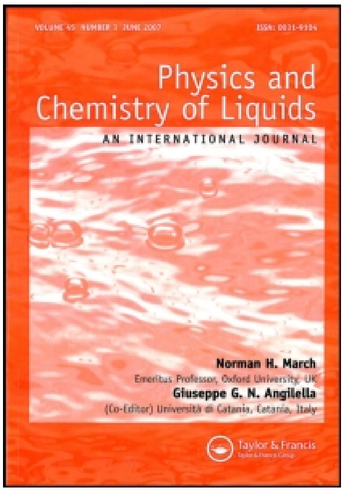

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Apparent Molar Volumes of Tetrabutylammonium Bromide and Tetrabutylammonium Lodide in 2-Methoxyethanol, 2-Ethoxyethanol, and 2-Butoxyethanol at Different Temperatures

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APPARENT MOLAR VOLUMES OF TETRABUTYLAMMONIUM BROMIDE AND TETRABUTYLAMMONIUM IODIDE IN 2-METHOXYETHANOL, 2-ETHOXYETHANOL, AND 2-BUTOXYETHANOL AT DIFFERENT TEMPERATURES

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The densities of tetrabutylammonium bromide and tetrabutylammonium iodide in 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol have been measured over the whole electrolyte concentration range at 288.15, 298.15, and 308.15 K. From these densities apparent molar volumes and partial molar volumes of the salts at infinite dilution have been evaluated. The infinite dilution partial molar expansibilities have been calculated from the temperature dependence of the limiting apparent molar volumes.

Keywords: Density; Apparent molar volume; Tetrabutylammonium bromide; Tetrabutylammonium iodide; 2-Alkoxyethanols

INTRODUCTION

Volumetric behavior of electrolyte solutions are of importance in elucidating the various interactions occurring in aqueous and nonaqueous solutions. The concentration and temperature dependence of the apparent and partial molar volume can be a very useful tool to obtain information on ion–ion, ion–solvent, and solvent–solvent interactions [1–3]. In the present article the densities of tetrabutylammonium bromide and tetrabutylammonium iodide solutions in 2-methoxyethanol (ME), 2-ethoxyethanol (EE), and 2-butoxyethanol (BE) have been measured over the whole concentration range at 288.15, 298.15, and 308.15 K. From these densities apparent molar volumes of both electrolytes in 2-alkoxyethanols have been calculated, and partial molar volumes at infinite dilution have been evaluated. The apparent and partial molar volumes of tetrabutylammonium salts have previously been studied in aqueous [4,5] and

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nonaqueous solvents [6–8] by several authors. The present work was therefore undertaken in order to determine the apparent and partial molar volumes of these electrolytes and to see their temperature dependence behaviors.

EXPERIMENTAL

2-Methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol were purchased from S.D. Fine Chemicals (Bombay) with purities greater than 99 mole percent. All the liquids were dried over ferrous sulphate (A.R., BDH) and then fractionally distilled under reduced nitrogen gas pressure [9]. Prior to measurements, all liquids were stored in contact with 0.4 nm molecular sieves to reduce water contents and were partially degassed under vacuum. The purities of the liquids were checked by measuring their densities (ρ_0), which are reported in Table I and compared with available literature data [9–15] at 298.15 ± 0.01 K.

Tetrabutylammonium bromide, and tetrabutylammonium iodide were of SDS analytical grade and used without further purification. They were dried under reduced pressure at elevated temperatures for 12 h. The salts were stored in vacuum desiccator over P_2O_5.

Solutions of the tetrabutylammonium salts for the density measurements were prepared by weight of the corresponding salt. All the preparations and manipulations involving anhydrous salts were carried out in dried boxes.

The densities were measured with a pycnometer (made of Borosil glass) having a total volume of about 10 cm^3 with a graduated stem of 0.05 cm^3 divisions. The pycnometer was calibrated at 288.15, 298.15, and 308.15 K with doubly distilled water which was filled to the marks on the stem. The mass of the dried pycnometer along with a teflon cap was first taken. Subsequently the test solution was introduced into it by means of a hypodermic syringe, taking care that no air bubble were entrapped. The limb of the pycnometer was then closed with teflon cap, and weighed. The apparatus was then immersed in the thermostat maintained at the desired temperature until no further change in the level of the solution in the capillary was observed. This level was noted and used in the calculation of density. Further readings on the same solution were taken at the other two lower temperatures, achieved by putting the pycnometer in two separate baths maintained at the required temperature. Care was taken to reduce evaporation during the measurements. An average of triplicate

TABLE I Densities (ρ_0) of 2-alkoxyethanols at different temperatures

Solvent	ρ_0 (g cm^{-3})				
	288.15 K	*298.15 K*		*308.15 K*	
	This work	*This work*	*Literature*	*This work*	*Literature*
2-Methoxyethanol	0.96926	0.96032	0.96024 [9] 0.96016 [10] 0.96020 [11]	0.95129	0.95154 [12]
2-Ethoxyethanol	0.93478	0.92573	0.9258 [13] 0.92572 [14]	0.91674	0.91671 [12] 0.9163 [13]
2-Butoxyethanol	0.90448	0.89630	0.89623 [11] 0.89581 [15]	0.88810	0.88809 [12]

measurements were taken into account. The reproducibility of density measurements was $\pm 3 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$.

RESULT AND DISCUSSION

The density data obtained at different temperatures for the solutions of the tetrabutylammonium bromide and tetrabutylammonium iodide in ME, EE, and BE are given in Tables II and III. The respective values of the apparent molar volumes V_ϕ ($\mathrm{cm^3\,mol^{-1}}$) were calculated using the following equation

$$V_\phi = M/\rho - 1000 \cdot (\rho - \rho_0)/m \cdot \rho \cdot \rho_0 \qquad (1)$$

where m is molality (mol $\mathrm{kg^{-1}}$ of solvent) of the solution; ρ and ρ_0 are densities (g $\mathrm{cm^{-3}}$) of solute and solvent, respectively; and M is the molar mass of the solute (g $\mathrm{mol^{-1}}$). The Eq. (1) was used because the value of m is the experimental quantity obtained directly during preparation of the solution. The conversion of molality to molarity, that is the concentration in moles per unit volume, was done using the simple equation

$$C = \mathrm{m} \cdot \rho \qquad (2)$$

TABLE II Molal concentration (m), density (ρ) and apparent molar volumes (V_ϕ) for tetrabutylammonium bromide in 2-alkoxyethanols at 288.15, 298.15, and 308.15 K

m (mole $\mathrm{kg^{-1}}$)	*288.15 K*		*298.15 K*		*308.15 K*	
	ρ ($\mathrm{g\,cm^{-3}}$)	V_ϕ ($\mathrm{cm^3\,mol^{-1}}$)	ρ ($\mathrm{g\,cm^{-3}}$)	V_ϕ ($\mathrm{cm^3\,mol^{-1}}$)	ρ ($\mathrm{g\,cm^{-3}}$)	V_ϕ ($\mathrm{cm^3\,mol^{-1}}$)
			2-Methoxyethanol			
0.01292	0.96976	291.25	0.96082	293.57	0.95179	295.96
0.02136	0.97008	291.48	0.96114	293.81	0.95211	296.20
0.02831	0.97034	291.66	0.96140	293.99	0.95237	296.38
0.03419	0.97056	291.72	0.96162	294.06	0.95259	296.46
0.03960	0.97076	291.82	0.96182	294.16	0.95279	296.55
0.04537	0.97097	291.96	0.96203	294.30	0.95300	296.69
0.05027	0.97115	292.01	0.96221	294.34	0.95318	296.74
			2-Ethoxyethanol			
0.01329	0.93529	300.78	0.92624	303.29	0.91725	305.82
0.02123	0.93559	300.94	0.92654	303.45	0.91755	305.98
0.02791	0.93584	301.06	0.92679	303.57	0.91780	306.10
0.03328	0.93604	301.13	0.92699	303.64	0.91800	306.18
4.04033	0.93630	301.24	0.92725	303.76	0.91826	306.29
0.04572	0.93650	301.26	0.92745	303.77	0.91846	306.31
0.05018	0.93666	301.38	0.92761	303.90	0.91862	306.44
			2-Butoxyethanol			
0.01302	0.90504	303.65	0.89686	305.94	0.88866	308.26
0.02104	0.90538	303.82	0.89720	306.11	0.88900	308.44
0.02802	0.90567	304.10	0.89749	306.39	0.88929	308.73
0.03398	0.90592	304.13	0.89774	306.42	0.88954	308.76
0.04023	0.90617	304.42	0.89799	306.72	0.88979	309.05
0.04524	0.90638	304.44	0.89820	306.74	0.89000	309.08
0.05009	0.90658	304.46	0.89840	306.76	0.89020	309.10

TABLE III Molal concentration (m), density (ρ) and apparent molar volumes (V_ϕ) for tetrabutylammonium iodide in 2-alkoxyethanols at 288.15, 298.15, and 308.15 K

m (mole kg^{-1})	*288.15 K*		*298.15 K*		*308.15 K*	
	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
2-Methoxyethanol						
0.01269	0.97016	305.32	0.96122	307.45	0.95219	309.63
0.02025	0.97069	305.48	0.96175	307.61	0.95272	309.79
0.02740	0.97119	305.51	0.96225	307.65	0.95322	309.83
0.03474	0.97170	305.56	0.96276	307.70	0.95373	309.89
0.03835	0.97195	305.58	0.96301	307.72	0.95398	309.91
0.04433	0.97236	305.68	0.96342	307.82	0.95439	310.01
0.04945	0.97271	305.74	0.96377	307.88	0.95474	310.07
2-Ethoxyethanol						
0.01294	0.93577	307.27	0.92672	309.41	0.91773	311.56
0.02125	0.93640	307.37	0.92735	309.51	0.91836	311.66
0.02788	0.93690	307.43	0.92785	309.57	0.91886	311.73
0.03334	0.93731	307.48	0.92826	309.62	0.91927	311.77
0.04002	0.93781	307.51	0.92876	309.65	0.91977	311.81
0.04579	0.93824	307.54	0.92919	309.68	0.92020	311.84
0.05050	0.93859	307.56	0.92954	309.70	0.92055	311.86
2-Butoxyethanol						
0.01276	0.90549	311.29	0.89731	313.23	0.88911	315.21
0.02133	0.90616	311.53	0.89798	313.49	0.88978	315.46
0.02801	0.90668	311.62	0.89850	313.58	0.89030	315.56
0.03397	0.90714	311.76	0.89896	313.71	0.89076	315.70
0.03943	0.90756	311.84	0.89938	313.80	0.89118	315.79
0.04479	0.90797	311.94	0.89979	313.90	0.89159	315.89
0.05016	0.90838	312.00	0.90020	313.97	0.89200	315.96

Derived values of the apparent molar volumes (V_ϕ), and the molal concentrations (m) of the electrolyte solutions in 2-alkoxyethanols at 288.15, 298.15, and 308.15 K are given in Tables II and III.

It has been established that for both the salts studied the plots of the apparent molar volume against the square root of its molar concentration are linear at all temperatures over the whole concentration range studied and the Masson's equation is valid [16,17]

$$V_\phi = V_\phi^0 + S_V^* \cdot C^{1/2} \tag{3}$$

where V_ϕ^0 is the limiting value of the apparent molar volume (equal to the partial molar volumes at infinite dilution) and S_V^* is the experimental slope. The values of V_ϕ^0 and S_V^* obtained by least-squares fitting of the V_ϕ values to the Eq. (3) are reported in Tables IV and V alongwith the corresponding values of average standard deviations.

The partial molar volumes of a solute at infinite dilution reflect the effects of ion–solvent interactions while the magnitude of the slope is related to the ion–ion interactions. As can be seen from Figs. 1 and 2 and also from Tables IV and V that the slopes are positive for both the salts in three solvents studied suggesting ion–ion interactions (ionic association) occurring in the system. The lowest positive value of the slope is observed for EE, i.e., for the solvent having the highest value of dielectric constant. The literature value of the dielectric constant at 298.15 K for the studied solvents are $\varepsilon_r = 16.9$ for ME [9], $\varepsilon_r = 29.6$ for EE [9], and $\varepsilon_r = 9.30$ for BE [9]. As expected the slope increases with increasing temperature in these solvents for

TABLE IV Limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_V^*) for tetrabutylammonium bromide in 2-alkoxyethanols at 288.15, 298.15, and 308.15 K

Solvent		V_ϕ^0 ($cm^3\,mol^{-1}$)	S_V^* ($cm^3\,L^{1/2}\,mol^{-3/2}$)	*Standard deviation*
2-Methoxyethanol	288.15 K	290.48	6.96	0.035
	298.15 K	292.78	7.13	0.033
	308.15 K	295.17	7.23	0.029
		(290.94 [18])	(7.81 [18])	
2-Ethoxyethanol	288.15 K	300.17	5.44	0.035
.	298.15 K	302.67	5.54	0.040
	308.15 K	305.19	5.67	0.038
2-Butoxyethanol	288.15 K	302.71	8.46	0.129
	298.15 K	304.98	8.61	0.107
	308.15 K	307.29	8.81	0.103

TABLE V Limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_V^*) for tetrabutylammonium iodide in 2-alkoxyethanols at 288.15, 298.15, and 308.15 K

Solvent		V_ϕ^0 ($cm^3\,mol^{-1}$)	S_V^* ($cm^3\,L^{1/2}\,mol^{-3/2}$)	*Standard deviation*
2-Methoxyethanol	288.15 K	304.95	3.49	0.031
	298.15 K	307.06	3.61	0.040
	308.15 K	309.23	3.75	0.025
2-Ethoxyethanol	288.15 K	306.99	2.69	0.007
	298.15 K	309.12	2.70	0.007
	308.15 K	311.27	2.82	0.005
2-Butoxyethanol	288.15 K	310.58	6.71	0.026
	298.15 K	312.50	6.93	0.028
	308.15 K	314.46	7.13	0.024

both electrolytes. This is reflected to accommodation of more and more solute molecules in the empty space left in the packing of associated solvent molecules resulting in an increased ion pairing (ion–ion interactions). The highest slope for BE and the lowest slope for EE are characteristic for solvent showing the lowest and highest value of dielectric constant. Moreover, Tables IV and V show that the values of the slope for tetrabutylammonium bromide solutions in these solvents are markedly higher than the corresponding values found for the tetrabutylammonium iodide in the same solvents. It is interesting to note that the difference in magnitude of the slope observed for the salts is due to difference in nature of anions. The smaller bromide ion shows a strong affinity toward the ionic association, while the larger iodide ion seems to be responsible for the inability to ion-pair formation.

Tables IV and V show that the limiting apparent molar volumes (V_ϕ^0) are large and positive for both electrolytes, and the values increase with increasing size of the anions. The V_ϕ^0 value for tetrabutylammonium bromide available only at 308.15 K compares well the literature data [18]. The large V_ϕ^0 values for the tetrabutylammonium iodide suggest the strong solute–solvent interactions in these solvents.

Further discussion is possible after splitting of the limiting values into ionic contribution. Various methods for obtaining individual limiting ionic partial molar volumes were reviewed by different authors [5,19]. However, in the present studies, the splitting

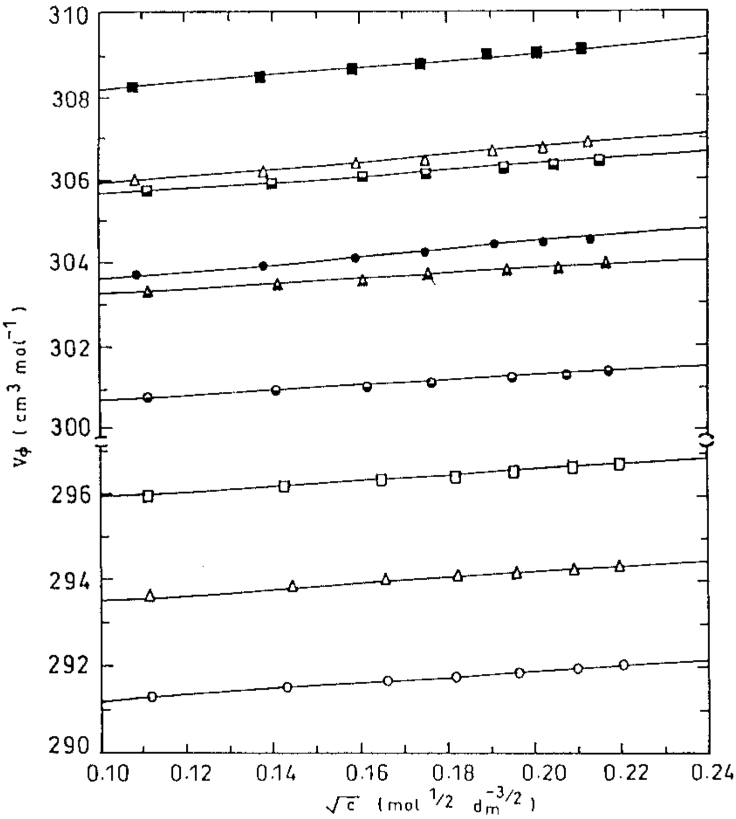

FIGURE 1 Apparent molar volumes as a function of $\sqrt{c}$ for tetrabutylammonium bromide in 2-methoxyethanol {288.15 K (○); 298.15 K(△); 308.15 K (□)}; in 2-ethoxyethanol {288.15 K (◒); 298.15 K (◭); 308.15 K (⬓)}; and in 2-butoxyethanol {288.15 K (●); 298.15 K (▲); 308.15 K (■)}.

of the limiting partial molar volume for $(C_4H_9)_4NBr$ into its ionic components has been made using values available for the ionic volumes of Br^- ion ($-5.08\,cm^3\,mol^{-1}$) [18] in ME at 308.15 K. The ionic limiting partial molar volume of $(C_4H_9)_4N^+$ were calculated as the difference in the values for $(C_4H_9)_4NBr$ and for the Br^- anion. The obtained values of V_ϕ^0 for tetrabutylammonium cation in ME at 308.15 K is $300.25\,cm^3\,mol^{-1}$. The large positive value for $(C_4H_9)_4N^+$ indicates that this ion is scarcely solvated in ME solvent media at 308.15 K, thereby indicating a positive change in volume.

The variation of V_ϕ^0 with temperature can be expressed as

$$V_\phi^0 = a + b \cdot T + c \cdot T^2 \tag{4}$$

where T is the temperature in degrees Kelvin.

The partial molar expansibility at infinite dilution can be obtained by differentiating Eq. (4) with respect to temperature

$$\phi_E^0 = (\partial V_\phi^0/\partial T)_p = b + 2 \cdot c \cdot T \tag{5}$$

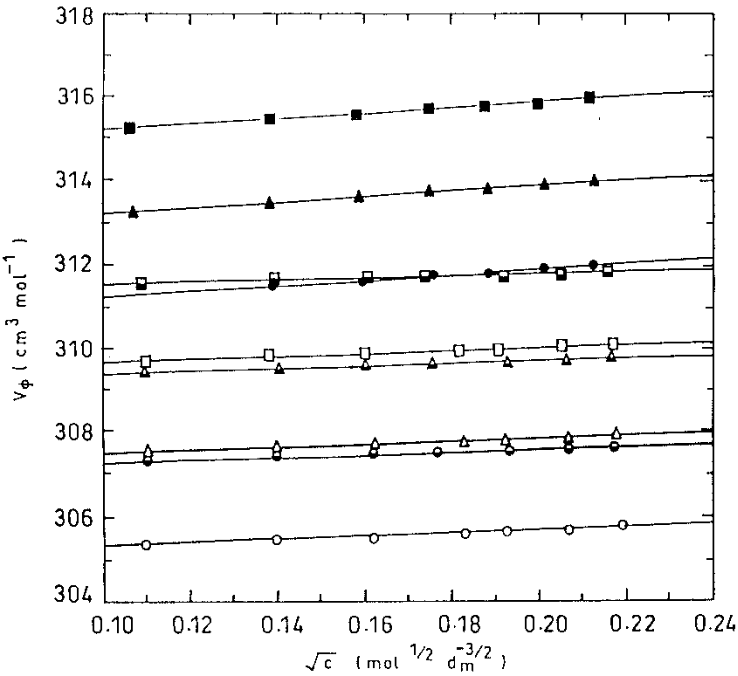

FIGURE 2 Apparent molar volumes as a function of $\sqrt{c}$ for tetrabutylammonium iodide in 2-methoxyethanol {288.15 K (○); 298.15 K (△); 308.15 K (□)}; in 2-ethoxyethanol {288.15 K (⊖); 298.15 K (⧋), 308.15 K(⊟)}; and in 2-butoxyethanol (288.15 K (●); 298,15 K (▲); 308.15 K (■))}.

TABLE VI Limiting partial molar expansibilities (ϕ_E^0) for tetrabutylammonium halides in 2-alkoxyethanols at 288.15, 298.15, and 308.15 K

Salt		ϕ_E^0 ($cm^3\,mol^{-1}\,K^{-1}$)		
		288.15 K	298.15 K	308.15 K
$(C_4H_9)_4NBr$	2-Methoxyethanol	0.226	0.234	0.243
	2-Ethoxyethanol	0.249	0.251	0.253
	2-Butoxyethanol	0.225	0.229	0.233
$(C_4H_9)_4NI$	2-Methoxyethanol	0.208	0.214	0.220
	2-Ethoxyethanol	0.211	0.213	0.215
	2-Butoxyethanol	0.190	0.194	0.198

The ϕ_E^0 values of the studied electrolytes at 288.15, 298.15, and 308.15 K are determined and recorded in Table VI. It may be noted that the ϕ_E^0 values of each salt increase with rising temperature. This may be considered as an indication of the fact that the structure of solvent is weakened by the elevation of temperature, that is, some solvent molecules may be released from the loose solvation layers of the solutes. The effect is that the removal of solvent molecules favor ion–ion interaction causing less electrostriction around the ions as evidenced by the higher S_V^* values with rising temperature.

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