where ϕ_K° and ϕ_v° are limiting apparent molar compressibility and limiting apparent molar volume, respectively. S_K and S_v are constants. The values of ϕ_K° and ϕ_v° and constants S_K and S_v have been obtained from the intercept and slope of the plots of ϕ_K vs $c^{1/2}$ and ϕ_v vs $c^{1/2}$ below the cmc and are recorded in Table II. The comparison of the data with that of electrolytes (*20*) shows that these soaps behave as simple electrolytes in dilute solutions.

The values of solvation number, S_n, of the solutions of manganese soaps in propan-1-ol decrease with increasing soap concentration (Table I). The plots of S_n vs c are characterized by a break at the cmc. The values of the solvation number exhibit a marked change above the cmc which may be attributed to more intake of solvent molecules above the cmc to reduce the repulsive forces acting between polar heads of ionic micelles.

Data on ultrasonic velocity show that the manganese soaps behave as simple electrolytes in solutions. The results confirm that there is a significant interaction between the soap–solvent molecules in dilute solutions, and the soap molecules do not aggregate appreciably above the cmc.

Registry No. Manganese caproate, 16571-42-9; manganese caprylate, 6819-13-2; manganese caprate, 7436-66-4; 1-propanol, 71-23-8.

Literature Cited

(1) Bossert, R. G. *J. Chem. Educ.* **1950**, *27*, 10–15.
(2) Reed, P. D. J. *Am. Perfum. Aromat.* **1961**, *76* (3), 49–50.
(3) Kambe, H. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1786–90.
(4) Mahendra, K. N.; Parashar, G. K.; Mehrotra, R. C. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11* (3), 187–96.
(5) Herron, R. C.; Pink, R. C. *J. Chem. Soc.* **1955**, 3948–52.
(6) Grunwald, E.; Coburn, W. C. *J. Am. Chem. Soc.* **1958**, *80*, 1322.
(7) Coggeshall, N. D.; Saier, E. L. *J. Am. Chem. Soc.* **1951**, *73*, 5414.
(8) Lin, W.; Tsay, S. J. *J. Phys. Chem.* **1970**, *74*, 1037.
(9) Schneider, W. G. In *Hydrogen Bonding*; Hadri, D., Ed.; Pergamon Press: London, 1959; p 55.
(10) Pimentel, G. C.; Maclellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco, 1960; p 67.
(11) Mehrotra, K. N.; Rawat, M. K. *Indian J. Pure Appl. Phys.* **1991**, *29*, 131–33.
(12) Mehrotra, K. N.; Tandon, K. *Monatsch. Chem.* **1990**, *121*, 577–84.
(13) Mehrotra, K. N.; Tandon, K. *Acoust. Lett.* **1990**, *13*, 205–8.
(14) Renand, P. *Chim. Anal. (Paris)* **1964**, *46* (5), 227.
(15) Pasynskii, A. *Acta physicochim. URSS* **1938**, *8*, 357; *Russ. J. Phys. Chem. (Engl. Transl.)* **1938**, *11*, 451.
(16) Garnsey, R.; Boe, R. J.; Mahoney, R.; Litovitz, T. A. *J. Chem. Phys.* **1969**, *50*, 5222.
(17) Prakash, S.; Icinaporia, F. M.; Pandey, J. D. *J. Phys. Chem.* **1964**, *58*, 3078.
(18) Bachem, C. Z. *Phys. A* **1936**, *101*, 541.
(19) Masson, D. O. *Philos. Mag.* **1929**, *8*, 218.
(20) Nigam, P. S.; Hasan, M. *Indian J. Pure Appl. Phys.* **1966**, *24*, 502.

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Excess Volumes of 1,2-Dibromoethane + 1-Propanol, + 1-Butanol, or + 1-Pentanol from 293.15 to 333.15 K

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Excess molar volumes V^E of 1,2-dibromoethane with 1-propanol, 1-butanol, and 1-pentanol have been measured at five temperatures, from 293.15 to 333.15 K. NMR shifts have also been reported for the mixtures of 1,2-dibromoethane with 1-butanol at 303.15 K. V^E is positive in all the mixtures studied over the whole range of compositions at all temperatures and increases in the order 1-pentanol > 1-butanol > 1-propanol. The temperature coefficient of V^E is positive. The positive excess molar volumes have been ascribed to deassociation of self-associated alcohol aggregates.

Introduction

We report new data on excess molar volumes, V^E, for three binary mixtures of 1,2-dibromoethane with 1-propanol, 1-butanol, and 1-pentanol as a function of temperature from 293.15 to 333.15 K. We also report NMR chemical shifts for the mixtures of 1,2-dibromoethane in 1-butanol at 303.15 K. The experimental results have been used to examine the effect of hydrogen bonding between like and unlike molecules of V^E. The results have also been used to study the effect of temperature on V^E.

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Table I. Normal Boiling Points, T_b, and Densities, ρ, of Pure Components

component	T_b/K this work	T_b/K lit. (2)	ρ(303.15 K)/(kg m^{-3}) this work	ρ(303.15 K)/(kg m^{-3}) lit. (3)
1,2-dibromoethane	404.15	404.51	2158.9	
1-propanol	370.10	370.301	795.36	795.61
1-butanol	390.65	390.875	802.51	801.91
1-pentanol	410.65	411.133	806.94	807.12

Experimental Section

Apparatus and Procedure. The batch dilatometers used for measuring V^E were similar to that described by Choudary and Naidu (*1*). The mixing cell contained two bulbs of different capacities that were connected through a U-tube with mercury separating the two compartments. One end of the first bulb was fitted with a capillary outlet, and the opposite end of the second bulb was closed with a Teflon stopper. Twelve dilatometers of this type were used to cover the whole range of compositions. The composition of each mixture was determined directly by weighing. After the experiment a few mixtures were analyzed on GC (Schimadzu GC, R1A, dual column gas chromatograph with flame ionization detector) to confirm the correctness of the compositions of mixtures. The measurements were made using a thermostatic bath controlled to

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Table II. Excess Molar Volumes, V^E, Coefficients, a_i, Equation 1, and Standard Deviations, $\sigma(V^E)$, Equation 2, for 1,2-Dibromoethane (1) + 1-Alkanols (2) as a Function of Mole Fraction x_1 at Temperature T

	1-propanol		1-butanol		1-pentanol	
	x_1	$V^E/(10^{-6}$ m^3 mol$^{-1})$	x_1	$V^E/(10^{-6}$ m^3 mol$^{-1})$	x_1	$V^E/(10^{-6}$ m^3 mol)
			T = 293.15 K			
	0.1363	0.047	0.1343	0.096	0.1268	0.136
	0.2205	0.076	0.2279	0.154	0.2213	0.217
	0.3197	0.105	0.3524	0.230	0.3081	0.282
	0.4152	0.132	0.4666	0.269	0.3798	0.328
	0.5268	0.153	0.5662	0.287	0.4888	0.361
	0.6323	0.166	0.6683	0.271	0.6005	0.365
	0.7170	0.159	0.7340	0.242	0.7022	0.319
	0.8001	0.136	0.8221	0.183	0.7929	0.256
	0.8928	0.088	0.8926	0.117	0.8884	0.154
a_1		0.604		1.117		1.453
a_2		0.379		0.393		0.293
a_3		0.090		−0.167		−0.121
a_4		−0.074		−0.207		−0.126
$\sigma(V^E)/(10^{-6}$ m^3 mol$^{-1})$		0.002		0.002		0.003
			T = 303.15 K			
	0.1503	0.063	0.1066	0.082	0.1747	0.221
	0.2330	0.096	0.1590	0.125	0.2487	0.298
	0.3058	0.132	0.1641	0.136	0.3918	0.368
	0.3743	0.156	0.2441	0.194	0.4183	0.380
	0.4212	0.163	0.3525	0.256	0.5081	0.398
	0.5596	0.200	0.4836	0.309	0.6077	0.396
	0.6482	0.203	0.5850	0.338	0.6942	0.368
	0.7336	0.199	0.6475	0.324	0.7813	0.317
	0.8128	0.175	0.7634	0.285	0.8416	0.270
	0.8969	0.118	0.8342	0.217	0.9155	0.171
			0.9168	0.123		
a_1		0.754		1.291		1.583
a_2		0.442		0.519		0.192
a_3		0.186		−0.060		0.397
a_4		0.126		0.104		0.340
$\sigma(V^E)/(10^{-6}$ m^3 mol$^{-1})$		0.004		0.006		0.003
			T = 313.15 K			
	0.1309	0.079	0.1401	0.143	0.1367	0.201
	0.2235	0.129	0.2074	0.204	0.2340	0.299
	0.3071	0.174	0.2912	0.269	0.3265	0.372
	0.3757	0.209	0.3599	0.314	0.4293	0.420
	0.4702	0.238	0.4682	0.356	0.5204	0.443
	0.5345	0.251	0.5801	0.365	0.6225	0.426
	0.6487	0.258	0.6617	0.349	0.7300	0.386
	0.7236	0.243	0.7690	0.306	0.8483	0.290
	0.8061	0.202	0.8537	0.239	0.9097	0.204
	0.8913	0.123	0.9285	0.141		
a_1		0.996		1.435		1.730
a_2		0.518		0.304		0.220
a_3		0.008		0.225		0.507
a_4		−0.224		0.416		0.399
$\sigma(V^E)/(10^{-6}$ m^3 mol$^{-1})$		0.004		0.002		0.005
			T = 323.15 K			
	0.1693	0.155	0.1225	0.147	0.1362	0.240
	0.2428	0.197	0.2367	0.241	0.2139	0.320
	0.3076	0.241	0.3418	0.322	0.2730	0.372
	0.4362	0.286	0.4961	0.373	0.3211	0.406
	0.5419	0.304	0.5755	0.385	0.4971	0.469
	0.6385	0.308	0.6748	0.376	0.6140	0.463
	0.6975	0.290	0.7464	0.350	0.6918	0.437
	0.7814	0.243	0.8194	0.294	0.7823	0.377
	0.8725	0.176	0.9083	0.203	0.8454	0.322
					0.9085	0.234
a_1		1.205		1.492		1.836
a_2		0.321		0.342		0.155
a_3		0.225		0.546		0.849
a_4				0.479		0.442
$\sigma(V^E)/(10^{-6}$ m^3 mol$^{-1})$		0.004		0.008		0.008
			T = 333.15 K			
	0.1297	0.157	0.1552	0.202	0.1290	0.247
	0.2080	0.226	0.2329	0.281	0.2194	0.363
	0.3199	0.310	0.3415	0.359	0.3008	0.436
	0.4261	0.358	0.4545	0.418	0.4583	0.517
	0.5284	0.379	0.5532	0.449	0.5062	0.525
	0.6577	0.366	0.6775	0.430	0.6404	0.516
	0.7415	0.333	0.7406	0.403	0.7595	0.457

Table II (Continued)

	1-propanol		1-butanol		1-pentanol	
	x_1	$V^E/(10^{-6}$ m^3 mol$^{-1})$	x_1	$V^E/(10^{-6}$ m^3 mol$^{-1})$	x_1	$V^E/(10^{-6}$ m^3 mol)
			T = 333.15 K			
	0.8003	0.284	0.8095	0.347	0.8392	0.378
	0.8912	0.191	0.8991	0.241	0.9211	0.253
a_1	1.499		1.723		2.064	
a_2	0.305		0.430		0.120	
a_3	0.274		0.529		1.009	
a_4	0.111		0.448		0.904	
$\sigma(V^E)/(10^{-6}$ m^3 mol$^{-1})$	0.003		0.007		0.010	

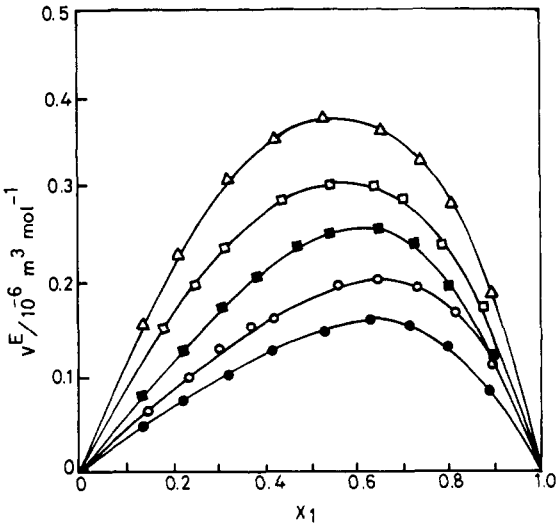

Figure 1. Excess molar volume V^E for 1,2-dibromoethane (1) + 1-propanol (2) as a function of the mole fraction, x_1, of 1,2-dibromoethane: ●, 293.15 K; ○, 303.15 K; ■, 313.15 K; □, 323.15 K; △, 333.15 K; calculated from eq 1 and parameters given in Table II.

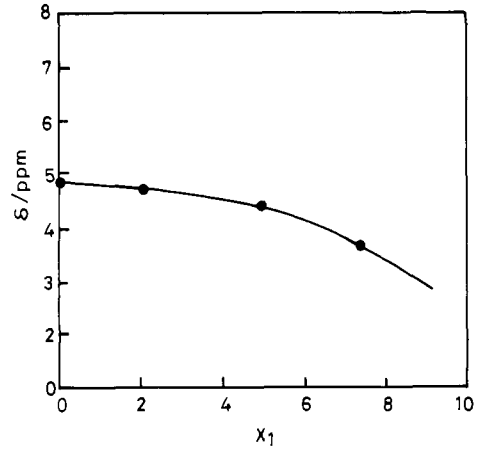

Figure 2. Chemical shifts, δ, for 1,2-dibromoethane (1) + 1-butanol (2) as a function of the mole fraction, x_1, of 1,2-dibromoethane at 303.15 K.

within ±0.001 K. The V^E's were reproducible to ±0.003 × 10^{-6} m^3 mol^{-1}.

NMR data were obtained on a Varian XL 100 nuclear magnetic resonance spectrometer. This instrument gives a spectrum on precalibrated chart paper. The studies were carried out under optimum ambient conditions. The samples were checked against an external reference (3% tetramethylsilane in $CDCl_3$) as well as against the tetramethylsilane used internally. The reference compound and its position did not affect the shifts being measured.

Materials. 1,2-Dibromoethane (Riedel) was purified by the method described by Riddick and Bunger (*2*). 1-Propanol (IDPL, India), 1-butanol (IDPL, India), and 1-pentanol (Riedel) were further purified as described by Choudary and Naidu (*1*). The purified substances were checked for purity by GC and were found to be better than 99.9 mol % and also by measuring the density, ρ, and normal boiling point, T_b (Table I).

Results and Discussion

The experimental V^E data for the three binary mixtures are given in Table II. The values of V^E may be expressed by an empirical equation of the form given below:

$$V^E/(10^{-6}\text{ m}^3\text{ mol}^{-1}) = x_1x_2[a_1 + a_2(x_1 - x_2) + ...] \quad (1)$$

where a_1, a_2, etc., are adjustable parameters. The values of parameters a_i obtained by least-squares analysis of n experimental points along with standard deviation $\sigma(V^E)$ calculated using eq 2 are also given in Table II.

$$\sigma(V^E) = \left[\frac{(V^E_{\text{calcd}} - V^E_{\text{exptl}})^2}{(n-p)}\right]^{1/2} \quad (2)$$

The experimental data are also graphically presented for the mixtures of 1,2-dibromoethane with 1-propanol in Figure 1. The graphs of the other two systems are similar to Figure 1.

V^E is positive over the whole range of composition in the three mixtures and increases in the order 1-pentanol > 1-butanol > 1-propanol. The temperature coefficient of V^E is positive. These results show that the main contribution to V^E is the expansion in volume due to deassociation of the alcohols. The same conclusion is also reached by the NMR study. The NMR chemical shifts (Figure 2) reveal that the proton absorption of hydroxylic proton moves upfield by the addition of dibromoethane; i.e., the electron density around the proton increases due to the decrease in hydrogen bonding (*4*).

Registry No. PrOH, 71-23-8; BuOH, 71-36-3; 1,2-dibromoethane, 106-93-4; 1-pentanol, 71-41-0.

Literature Cited

(1) Choudary, N. V.; Naidu, P. R. *Can. J. Chem.* **1981**, *59*, 2210.
(2) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; John Wiley & Sons: New York, 1986.
(3) Hales, J. L.; Ellender, J. H. *J. Chem. Thermodyn.* **1976**, *8*, 1177.
(4) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981; p 194.

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