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Excess Molar Volumes of 2-[2-(2-Alkoxyethoxy)ethoxy]ethanols with 2-Methoxyethanol at 298.15 K

Amalendu Pal* and Wazir Singh

Department of Chemistry, Kurukshetra University, Kurukshetra 132 119, India

The excess molar volumes V_m^E for binary liquid mixtures of 2-methoxyethanol, $CH_3O(CH_2)_2OH$ with 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, and 2-[2-(2-butoxyethoxy)ethoxy]-ethanol, have been measured using a continuous-dilution dilatometer at 298.15 K as a function of composition. The excess volumes are negative over the entire range of composition for 2-methoxyethanol with 2-[2-(2-methoxyethoxy)ethoxy]ethanol and 2-[2-(2-ethoxyethoxy)ethoxy]ethanol and are sigmoidal for 2-[2-(2-butoxyethoxy)ethoxy]ethanol. The results were used to estimate the excess partial molar volumes of the components.

Introduction

In our previous paper (Pal and Singh, 1996a) we have studied the excess molar volumes of $[xCH_3O(CH_2)_2OH +$ $x)H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH]$ for $\nu = 1$, 2, and 4 at 298.15 K. In continuation of these investigations of the excess thermodynamic properties of mixtures of an alkoxyethanol with an organic solvent (Pal and Singh, 1995b,c), the present paper reports the excess molar volumes for binary mixtures of $[xCH_3O(CH_2)_2OH + (1 - x)H(CH_2)_\nu$-$O(CH_2)_2\}_3OH]$ for $\nu = 1$, 2, and 4 at 298.15 K. No literature results are available for these mixtures.

Experimental Section

Materials. Materials were the same as used in earlier studies (Pal and Singh, 1996a, 1995c). Before the measurements, all liquids were stored in contact with molecular sieves type 4A to reduce the water content and were partially degassed under vacuum.

Apparatus and Procedure. Excess molar volumes, which are accurate to ± 0.003 $cm^3 \cdot mol^{-1}$, were measured directly by means of a continuous-dilution dilatometer described elsewhere (Dickinson et al., 1975). Details of its calibration and operational procedure have been described previously (Pal and Singh, 1994, 1995a). The composition of each mixture was obtained from the measured apparent masses of the components with an accuracy of 1×10^{-4}. All masses were corrected for buoyancy. Each run covered just over half of the range of x so as to give an overlap between two runs.

Densities of pure components, measured with a double-armed pycnometer, were reproducible to $\leq 3 \times 10^{-4}$ $g \cdot cm^{-3}$. Densities of 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, 2-[2-(2-butoxyethoxy)ethoxy]-ethanol, and 2-methoxyethanol at 298.15 K are reported in Table 1 along with the available literature data. All the measurements were carried out in a thermostatically controlled, well-stirred water bath whose temperature was controlled to ± 0.01 K.

Results and Discussion

The experimental results of excess molar volumes V_m^E of the binary mixtures at 298.15 K are listed as a function of mole fraction in Table 2. For each mixture, the excess quantities were fitted to the Redlich−Kister equation:

$$V_m^E/cm^3 \cdot mol^{-1} = x(1 - x) \sum_{j=1}^{n} a_j \, (2x - 1)^{j-1} \qquad (1)$$

The values of the parameters a_j were evaluated by the method of least squares and are summarized in Table 3 along with standard deviations $s(V_m^E)$. For all mixtures $s(V_m^E) < 0.003$ $cm^3 \cdot mol^{-1}$, showing the good accuracy attainable with the dilatometer used. The observed and calculated V_m^E values from eq 1 are plotted against the mole fraction x of 2-methoxyethanol. We have obtained the V_m^E values for mixtures of 2-methoxyethanol with 2-[2-(2-butoxyethoxy)ethoxy]ethanol within the limit of the dilatometer accuracy over the whole concentration range.

We have also calculated excess partial molar volumes $V_{m,1}^E = (V_{m,1} - V_{m,1}^*)$ and $V_{m,2}^E = (V_{m,2} - V_{m,2}^*)$ from V_m^E where $V_{m,1}^*$ and $V_{m,2}^*$ represent the molar volumes of the pure components. The partial molar volume $V_{m,1}$ and $V_{m,2}$ in their mixtures were evaluated (Davis, 1992) over the whole mole fraction range by using eqs 2 and 3.

$$V_{m,1}/cm^3 \cdot mol^{-1} = V_{m,1}^* + V_m^E + (1 - x)(\delta V_m^E/\delta x) \qquad (2)$$

$$V_{m,2}/cm^3 \cdot mol^{-1} = V_{m,2}^* + V_m^E - x(\delta V_m^E/\delta x) \qquad (3)$$

The derivatives of eqs 2 and 3 are obtained from differentiation of V_m^E data as obtained from eq 1. The results calculated for $V_{m,1}^E$ and $V_{m,2}^E$ are plotted against x in Figure 3.

Excess volume versus composition plots in Figure 1 show that V_m^E is negative over the whole mole fraction range for mixtures with 2-[2-(2-methoxyethoxy)ethoxy]ethanol and 2-[2-(2-ethoxyethoxy)ethoxy]ethanol but the curves are unsymmetrical with minima at $x \gg 0.5$. Remarkably, V_m^E is mostly negative for the mixtures containing 2-[2-(2-butoxyethoxy)ethoxy]ethanol with expansion occurring at lower and higher values of x and contraction at the intermediate rich region. The unsymmetrical nature of V_m^E vs mole fraction curves in the binary systems appears to be primarily due to steric factors arising from a change in the proportion of different geometric forms of 2-methoxyethanol molecules with a change in its mole fraction. The behavior of these mixtures is very complex and the overall values of V_m^E are attributed to a resultant of several physical and chemical affects: breaking of liquid order on mixing and unfavorable interaction between

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* To whom correspondence should be addressed.

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Table 1. Densities ρ for the Pure Liquids at 298.15 K

component	ρ/g·cm^{-3}		ref
	this work	lit.	
2-methoxyethanol	0.9602	0.960 24	Riddick and Buner (1970)
2-[2-(2-methoxyethoxy)ethoxy]ethanol	1.0430	0.960 16	Roux et al. (1978)
2-[2-(2-ethoxyethoxy)ethoxy]ethanol	1.0161		
2-[2-(2-butoxyethoxy)ethoxy]ethanol	0.9868		

Table 2. Excess Molar Volumes, V_m^E, and Partial Molar Volumes, $V_{m,1}$ and $V_{m,2}$, for [xCH$_3$O(CH$_2$)$_2$OH + (1 − x)H(CH$_2$)$_\nu${O(CH$_2$)$_2$}$_3$OH] (ν = 1, 2, and 4), at T = 298.15 K

x	V_m^E/cm^3·mol^{-1}	$V_{m,1}$/cm^3·mol^{-1}	$V_{m,2}$/cm^3·mol^{-1}	x	V_m^E/cm^3·mol^{-1}	$V_{m,1}$/cm^3·mol^{-1}	$V_{m,2}$/cm^3·mol^{-1}
[xCH$_3$O(CH$_2$)$_2$OH + (1 − x)CH$_3${O(CH$_2$)$_2$}$_3$OH]							
Run I							
0.0358	−0.003	79.149	157.454	0.3494	−0.036	79.155	157.467
0.0767	−0.007	79.144	157.471	0.3976	−0.040	79.161	157.452
0.1162	−0.011	79.143	157.483	0.4444	−0.043	79.167	157.435
0.1667	−0.017	79.143	157.490	0.4935	−0.045	79.174	157.415
0.2117	−0.024	79.144	157.490	0.5346	−0.047	79.181	157.397
0.2600	−0.028	79.147	157.486	0.5828	−0.050	79.189	157.373
0.3042	−0.032	79.150	157.478	0.6256	−0.052	79.196	157.351
Run II							
0.6208	−0.052	79.196	157.353	0.8585	−0.034	79.238	157.202
0.6611	−0.052	79.203	157.331	0.9118	−0.023	79.244	157.161
0.7028	−0.051	79.211	157.306	0.9522	−0.016	79.248	157.128
0.7561	−0.048	79.220	157.273	0.9859	−0.009	79.249	157.100
0.8040	−0.041	79.229	157.241				
[xCH$_3$O(CH$_2$)$_2$OH + (1 − x)H(CH$_2$)$_2${O(CH$_2$)$_2$}$_3$OH]							
Run I							
0.0267	−0.002	79.146	175.402	0.3583	−0.037	79.153	175.414
0.0695	−0.006	79.146	175.403	0.3851	−0.039	79.157	175.410
0.0844	−0.009	79.145	175.403	0.4387	−0.043	79.166	175.399
0.1219	−0.012	79.145	175.407	0.4617	−0.045	79.171	175.392
0.1637	−0.018	79.145	175.411	0.4824	−0.046	79.175	175.386
0.1971	−0.022	79.144	175.414	0.5317	−0.048	79.186	175.369
0.2546	−0.207	79.145	175.418	0.6203	−0.050	79.207	175.332
0.2969	−0.031	79.147	175.418	0.6933	−0.047	79.223	175.299
0.3045	−0.032	79.148	175.418				
Run II							
0.6789	−0.048	79.220	175.305	0.8608	−0.026	79.246	175.231
0.7047	−0.046	79.225	175.294	0.8947	−0.021	79.248	175.221
0.7418	−0.042	79.232	175.277	0.9252	−0.016	79.249	175.214
0.7876	−0.036	79.239	175.258	0.9577	−0.008	79.249	175.208
0.8327	−0.030	79.244	175.240	0.9808	−0.005	79.249	175.203
[xCH$_3$O(CH$_2$)$_2$OH + (1 − x)H(CH$_2$)$_4${O(CH$_2$)$_2$}$_3$OH]							
Run I							
0.0133	0.003	79.336	209.040	0.3917	−0.010	79.229	209.007
0.0312	0.005	79.309	209.038	0.4589	−0.008	79.244	209.016
0.0867	0.006	79.248	209.028	0.5468	−0.007	79.257	209.030
0.1404	0.003	79.216	209.018	0.6195	−0.003	79.262	209.043
0.1996	−0.004	79.202	209.009	0.6783	−0.002	79.263	209.052
0.3033	−0.007	79.210	209.003	0.7299	−0.001	79.261	209.059
Run II							
0.7201	−0.001	79.261	209.058	0.9475	0.004	79.250	209.086
0.8121	0.001	79.257	209.068	0.9629	0.005	79.250	209.088
0.8557	0.002	79.254	209.073	0.9806	0.004	79.250	209.092
0.8983	0.003	79.252	209.078	0.9874	0.003	79.249	209.096
0.9263	0.004	79.251	209.082	0.9974	0.002	79.249	209.080

Table 3. Parameters a_j and Standard Deviations $s(V_m^E)$ for Least Squares Representations by Eq 1 of V_m^E for Studied Mixtures at T = 298.15 K

mixture	a_1	a_2	a_3	$s(V_m^E)$/cm^3·mol^{-1}
xCH$_3$O(CH$_2$)$_2$OH				
+(1 − x)CH$_3${O(CH$_2$)$_2$}$_3$OH	−0.1880	−0.1142	−0.0323	0.002
+(1 − x)H(CH$_2$)$_2${O(CH$_2$)$_2$}$_3$OH	−0.1888	−0.0772	0.0329	0.001
+(1 − x)H(CH$_2$)$_4${O(CH$_2$)$_2$}$_3$OH	−0.0351	0.0163	0.1141	0.002

unlike molecules produce positive V_m^E values; differences in molar volumes and free volumes between liquid components and possible association by hydrogen bonds produce negative V_m^E values, implying specific interactions. In fact we observe similar characteristics for V_m^E as in mixtures of 2-methoxyethanol with 2-alkoxyethanols and 2-(2-alkoxyethoxy)ethanols (Cobos et al., 1989; Pal and Singh, 1996a): a marked decrease in the algebraic value of V_m^E here. The V_m^E's pass through a minimum and then increase as the alkyl chain length of the alkoxyethanol increases for the two homologous series, as is shown in Figure 2 where we plot $V_m^E(x = 0.5)$ against ν, the number

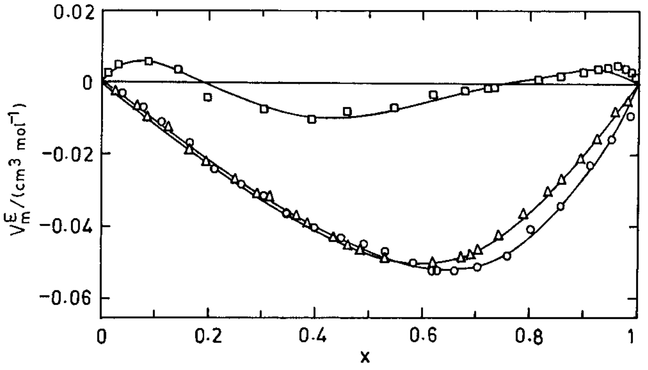

Figure 1. Excess molar volume V^E_m for [xCH$_3$O(CH$_2$)$_2$OH + (1 − x)H(CH$_2$)$_\nu${O(CH$_2$)$_2$}$_3$OH] at T = 298.15 K: (○) ν = 1; (△) ν = 2; (□) ν = 4. Solid curves were calculated from eq 1 using coefficients a_j of Table 3.

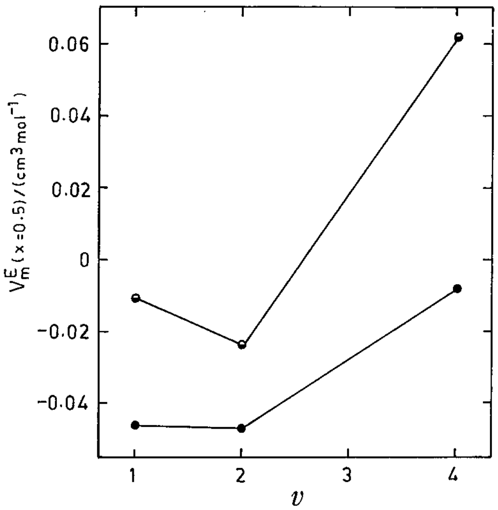

Figure 2. Plot of V^E_m(x=0.5) against number ν: (◒) [0.5CH$_3$O-$_2$)$_2$OH + 0.5H(CH$_2$)$_\nu${O(CH$_2$)$_2$}$_2$OH], (Pal and Singh, 1996a);) [0.5CH$_3$O(CH$_2$)$_2$OH + 0.5H(CH$_2$)$_\nu${O(CH$_2$)$_2$}$_3$OH], this work at 298.15 K.

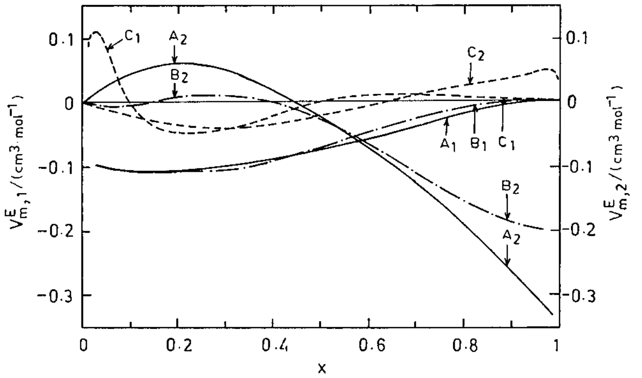

Figure 3. Partial molar excess volumes $V^E_{m,1}$ and $V^E_{m,2}$ for [xCH$_3$O(CH$_2$)$_2$OH + (1 − x)H(CH$_2$)$_\nu${O(CH$_2$)$_2$}$_3$OH] at T = 298.15 K: A (—), ν = 1; B (—•—), ν = 2; C (- - -), ν = 4.

of carbon atoms in the aliphatic chain of the alkoxyethanol. This behavior is consistent with that of the V^E_m of 2-[2-(2-alkoxyethoxy)ethoxy]ethanols with ether (Pal and Singh, 1996b) at a low mole fraction range of x but with opposite trend.

The algebraic values of V^E_m at x < 0.55 for all the binary systems with 2-methoxyethanol are in the order (ν = 2) < 1) < (ν = 4). The negative contribution to the V^E_m of 2-[2-(2-ethoxyethoxy)ethoxy]ethanol caused by the formation of intermolecular hydrogen bonds yields higher nega- V^E_m values compared with those of the other two mixtures.

Figure 3 shows that in accordance with the sign of , there is a monotonic decrease and increase in $V^E_{m,2}$(ν = 4) and $V^E_{m,1}$(2-methoxyethanol) with increasing x as compared with the behavior in 2 methoxyethanol with ν = 1 and 2. The decrease in partial molar volume of nonelectrolyte solute 2-methoxyethanol in the very 2-[2-(2-alkoxyethoxy)ethoxy]ethanol-rich region is due to the difference in molecular size between the solute and the solvent and to the packing density of the solvent. The larger the size ratio of the solute to the solvent, the smaller the partial molar volume of the solute. The first molecule of 2-[2-(2-alkoxyethoxy)ethoxy]ethanols, after breaking away from its self-associated hydrogen-bonded structural environment, is now surrounded by much smaller 2-methoxyethanol molecules, which tend to fill in gaps that were present in the pure solvent environment. As x increases, the packing density of the solvent as well as the excess partial molar volume $V^E_{m,1}$ of 2-methoxyethanol decreases. According to this, if the packing density of the pure solvent is lowered, by forming a hydrogen bond, for instance, the resulting partial molar volume after mixing would be larger than that determined by the size difference alone; that is, in the case of {2-methoxyethanol + 2-[2-(2-ethoxyethoxy)-ethoxy]ethanol or +2-[2-(2-butoxyethoxy)ethoxy]ethanol} compared with that of {2-methoxyethanol + 2-[2-(2-methoxyethoxy)ethoxy]ethanol}. This reflects the structural changes of 2-methoxyethanol introduced by 2-[2-(2-alkoxyethoxy)ethoxy]ethanols, as supported by the behavior of V^E_m. However, further studies are required to confirm this postulate.

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