Excess Molar Volumes of Binary Liquid Mixtures of 1-Propanol and of 2-Propanol + Propane-1,2-diol, 1-Methoxy-2-propanol, 1-Ethoxy-2-propanol, and 1-*tert*-Butoxy-2-propanol and Water + 1-Methoxy-2-propanol and 1-Ethoxy-2-propanol at 298.15 K

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Excess molar volumes (V_m^E), measured as a function of composition at 298.15 K using a dilution dilatometer, are reported for the 10 binary mixtures of 1-propanol and of 2-propanol with propane-1,2-diol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, or 1-*tert*-butoxy-2-propanol and water with 1-methoxy-2-propanol or 1-ethoxy-2-propanol. Excess volumes are negative over the whole mole fraction range and rather symmetrical for mixtures with 1-propanol. For the mixtures with 2-propanol and water, excess volumes are also negative over the whole mole fraction range but the curves are slightly unsymmetrical. The results are discussed on the basis of molecular interactions between the components of the mixtures.

Introduction

As a part of our systematic program of research on binary mixtures containing the oxy (−O−) and hydroxyl (−OH) functional groups (Pal and Singh, 1994, 1996a−c, 1997) we report here a new experimental data for excess molar volumes at 298.15 K and atmospheric pressure of mixtures containing 1-propanol or 2-propanol with propane-1,2-diol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, or 1-*tert*-butoxy-2-propanol and water with 1-methoxy-2-propanol or 1-ethoxy-2-propanol. The aim of this work is to provide a set of data for the characterization of the size, shape, and polarity of the ether on the thermodynamic properties of mixtures.

Experimental Section

HPLC grade 1-propanol, and 2-propanol, purchased from SRL, Bombay, were dried by refluxing over fused calcium oxide for 5 h and then fractionally distilled two to three times (Riddick et al., 1986; Perrin et al., 1980). Propane-1,2-diol (S.D. fine chemicals, AR grade), 1-methoxy-2-propanol (Merck-Schuchardt, FRG), 1-ethoxy-2-propanol (Acros, USA), and 1-*tert*-butoxy-2-propanol (Fluka, purum) were dried over anhydrous calcium chloride and fractionally distilled in an all-glass distillation apparatus. These operations were carried out under a nitrogen atmosphere. Estimated purities determined by gas chromatographic analysis were better than 99.5 mol % for all the liquid samples. The water content, measured for each sample by Karl−Fischer titration, was always found to be less than 0.002 mass %. The purities of the final samples were checked by measuring their densities at (298.15 ± 0.01) K with a calibrated double-armed pycnometer having a capacity of 15 cm^3. An average of triplicate measurements were taken into account, and the densities agreed to within $\pm 1 \times 10^{-4}$ g·cm^{-3} with the available literature values, as shown in Table 1. Before the measurements, all liquids were partially degassed under vacuum and stored over 0.4 nm molecular sieves (Fluka, AG). Water was deionized by means of ion-exchange resins and then distilled in glass. Its conductivity was always below 1.0×10^{-6} S cm^{-1}. The composition of each mixture was obtained with an accuracy of 1×10^{-4} from the measured apparent masses of the components. Correction were made for buoyancy. Each run covered just over half of the mole fraction range so as to give an overlap between two runs.

Table 1. Comparison of Experimental Densities of Pure Liquids with Literature Values at 298.15 K

component	ρ/g·cm^{-3} this work	literature	
water		0.997 048[a]	
1-propanol	0.7994	0.799 75,[b]	0.799 60[c]
2-propanol	0.7810	0.780 9,[d]	0.781 26[c]
propane-1,2-diol	1.0327	1.032 8[c]	
1-methoxy-2-propanol	0.9163	0.916 99,[e]	0.916 50[f]
1-ethoxy-2-propanol	0.8928		
1-*tert*-butoxy-2-propanol	0.8705		

[a] Kell (1967). [b] TRC Thermodynamic Tables (1994). [c] Riddick et al. (1986). [d] Aminabhavi and Bindu (1995). [e] Krishnaiah et al. (1993). [f] De Lorenzi et al. (1995).

The excess molar volumes, which are accurate to ±0.003 cm^{-3}·mol^{-1}, were measured by means of a continuous dilution dilatometer similar to that described by Dickinson et al. (1975). Liquid components were introduced by mass, with a precision of ±0.05 mg, into the bulb of the dilatometer from a glass syringe. The dilatometer was clamped vertically into the water thermostat. Readings of the reference marks and those of liquid levels filling the dilatometer were measured with a cathetometer having a precision of ±0.001 cm. Details of its calibration, experimental setup, and operational procedure have been described elsewhere (Pal and Singh, 1994; Pal et al. 1994). All the measurements were carried out in a thermostatically controlled, well-stirred water bath with the temperature controlled to ±0.01 K.

Results and Discussion

The experimental excess volumes for binary mixtures of 1-propanol and of 2-propanol with propane-1,2-diol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, and 1-*tert*-butoxy-2-propanol and water with 1-methoxy-2-propanol and 1-ethoxy-2-propanol at 298.15 K are reported in Table 2 and graphically represented in Figures 1−3. The results

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Table 2. Experimental Results at 298.15 K

x_2	V_m^E/cm^3·mol^{-1}	x_2	V_m^E/cm^3·mol^{-1}	x_2	V_m^E/cm^3·mol^{-1}	x_2	V_m^E/cm^3·mol^{-1}	x_2	V_m^E/cm^3·mol^{-1}	x_2	V_m^E/cm^3·mol^{-1}
1-Propanol (1) + Propane-1,2-diol (2)											
0.0114	−0.005	0.1493	−0.063	0.3331	−0.113	0.5044	−0.126	0.6544	−0.114	0.8504	−0.066
0.0315	−0.015	0.1982	−0.082	0.3702	−0.118	0.5373	−0.124	0.6911	−0.105	0.9126	−0.038
0.0478	−0.025	0.2442	−0.093	0.3990	−0.121	0.5706	−0.121	0.7452	−0.095	0.9474	−0.024
0.0709	−0.033	0.2888	−0.101	0.4268	−0.123	0.6203	−0.115	0.7960	−0.081	0.9882	−0.006
0.1091	−0.048	0.3196	−0.109	0.4621	−0.124						
1-Propanol (1) + 1-Methoxy-2-propanol (2)											
0.0159	−0.009	0.1632	−0.076	0.3381	−0.115	0.4588	−0.125	0.5908	−0.118	0.7906	−0.087
0.0402	−0.027	0.2012	−0.093	0.3469	−0.116	0.4911	−0.124	0.6207	−0.117	0.8845	−0.058
0.0651	−0.040	0.2432	−0.101	0.3794	−0.117	0.5207	−0.122	0.7134	−0.107	0.9367	−0.036
0.0956	−0.056	0.2808	−0.108	0.4228	−0.120	0.5500	−0.121	0.7495	−0.099	0.9665	−0.021
0.1199	−0.063	0.3080	−0.111	0.4340	−0.123						
1-Propanol (1) + 1-Ethoxy-2-propanol (2)											
0.0033	−0.008	0.0963	−0.094	0.2432	−0.180	0.4292	−0.215	0.6095	−0.204	0.8078	−0.135
0.0225	−0.026	0.1131	−0.108	0.2720	−0.192	0.4613	−0.217	0.6431	−0.196	0.8426	−0.110
0.0345	−0.040	0.1293	−0.119	0.2980	−0.198	0.5024	−0.218	0.6725	−0.187	0.8740	−0.097
0.0454	−0.050	0.1534	−0.134	0.3252	−0.205	0.5309	−0.217	0.6997	−0.179	0.8952	−0.079
0.0621	−0.065	0.1785	−0.148	0.3475	−0.208	0.5604	−0.213	0.7315	−0.168	0.9221	−0.063
0.0737	−0.076	0.2094	−0.165	0.3760	−0.213	0.5857	−0.209	0.7691	−0.152	0.9660	−0.030
1-Propanol (1) + 1-*tert*-Butoxy-2-propanol (2)											
0.0117	−0.019	0.1083	−0.149	0.2378	−0.262	0.4027	−0.312	0.5900	−0.296	0.7937	−0.188
0.0247	−0.041	0.1284	−0.171	0.2642	−0.275	0.4290	−0.314	0.6328	−0.279	0.8609	−0.134
0.0404	−0.064	0.1548	−0.197	0.2853	−0.287	0.4661	−0.315	0.6790	−0.259	0.8963	−0.100
0.0549	−0.087	0.1725	−0.214	0.3094	−0.297	0.4984	−0.313	0.7166	−0.237	0.9513	−0.047
0.0704	−0.106	0.1901	−0.229	0.3742	−0.309	0.5467	−0.307	0.7566	−0.211	0.9805	−0.018
0.0956	−0.137	0.2113	−0.245								
2-Propanol (1) + Propane-1,2-diol (2)											
0.0078	−0.005	0.0660	−0.050	0.2136	−0.141	0.3605	−0.198	0.5315	−0.226	0.7366	−0.189
0.0133	−0.012	0.0882	−0.065	0.2575	−0.162	0.3921	−0.209	0.5840	−0.223	0.8115	−0.152
0.0208	−0.018	0.1056	−0.077	0.2900	−0.176	0.4276	−0.214	0.6195	−0.220	0.8893	−0.103
0.0380	−0.029	0.1330	−0.096	0.3273	−0.189	0.4606	−0.219	0.6483	−0.217	0.9548	−0.048
0.0482	−0.040	0.1765	−0.120	0.3448	−0.197	0.4917	−0.225	0.6892	−0.205	0.9840	−0.018
2-Propanol (1) + 1-Methoxy-2-propanol (2)											
0.0067	−0.004	0.1177	−0.035	0.2777	−0.059	0.4671	−0.070	0.6712	−0.065	0.8779	−0.035
0.0211	−0.008	0.1479	−0.043	0.3093	−0.062	0.5128	−0.071	0.7087	−0.062	0.9057	−0.027
0.0325	−0.012	0.1814	−0.049	0.3458	−0.065	0.5619	−0.069	0.7542	−0.058	0.9488	−0.018
0.0576	−0.021	0.2143	−0.052	0.3821	−0.067	0.5992	−0.068	0.7880	−0.051	0.9824	−0.004
0.0824	−0.026	0.2451	−0.055	0.4255	−0.068	0.6432	−0.066	0.8136	−0.050		
2-Propanol (1) + 1-Ethoxy-2-propanol (2)											
0.0075	−0.006	0.1119	−0.063	0.3123	−0.120	0.5079	−0.125	0.6763	−0.106	0.8229	−0.072
0.0255	−0.016	0.1364	−0.074	0.3522	−0.124	0.5408	−0.123	0.7004	−0.103	0.8648	−0.061
0.0391	−0.024	0.1687	−0.085	0.3864	−0.125	0.5729	−0.122	0.7343	−0.095	0.9195	−0.037
0.0558	−0.035	0.1992	−0.094	0.4217	−0.126	0.6066	−0.118	0.7592	−0.093	0.9464	−0.026
0.0750	−0.046	0.2325	−0.102	0.4464	−0.128	0.6290	−0.116	0.7933	−0.081	0.9694	−0.014
0.0929	−0.053	0.2692	−0.110	0.4783	−0.127	0.6497	−0.113				
2-Propanol (1) + 1-*tert*-Butoxy-2-propanol (2)											
0.0069	−0.006	0.1042	−0.057	0.2391	−0.102	0.3846	−0.125	0.5863	−0.117	0.7992	0.074
0.0282	−0.019	0.1260	−0.067	0.2651	−0.107	0.4206	−0.127	0.6275	−0.108	0.8536	−0.057
0.0391	−0.024	0.1523	−0.077	0.2909	−0.111	0.4631	−0.126	0.6653	−0.103	0.8906	−0.049
0.0515	−0.032	0.1826	−0.088	0.3087	−0.116	0.4984	−0.125	0.7191	−0.092	0.9127	−0.036
0.0645	−0.039	0.2021	−0.092	0.3412	−0.119	0.5443	−0.124	0.7575	−0.083	0.9606	−0.014
0.0838	−0.047										
Water (1) + 1-Methoxy-2-propanol (2)											
0.0095	−0.069	0.1256	−0.751	0.3052	−1.299	0.5165	−1.225	0.7141	−0.815	0.8569	−0.447
0.0195	−0.140	0.1587	−0.899	0.3468	−1.339	0.5584	−1.146	0.7587	−0.703	0.8841	−0.365
0.0387	−0.267	0.2051	−1.075	0.4089	−1.335	0.6123	−1.044	0.7951	−0.612	0.9326	−0.229
0.0782	−0.501	0.2579	−1.211	0.4555	−1.305	0.6724	−0.919	0.8152	−0.559	0.9727	−0.095
0.0953	−0.602										
Water (1) + 1-Ethoxy-2-propanol (2)											
0.0115	−0.129	0.1273	−0.994	0.2899	−1.394	0.4457	−1.375	0.6073	−1.161	0.7894	−0.675
0.0245	−0.267	0.1627	−1.141	0.3204	−1.401	0.4922	−1.335	0.6629	−1.044	0.8361	−0.517
0.0487	−0.497	0.2193	−1.293	0.3695	−1.410	0.5254	−1.296	0.7172	−0.897	0.8953	−0.315
0.0713	−0.673	0.2501	−1.351	0.4036	−1.400	0.5655	−1.239	0.7480	−0.808	0.9737	−0.064
0.0951	−0.825										

Table 3. Smoothing Coefficients A_i and Standard Deviations of $\sigma(V_m^E)$ for Eq 1 for Binary Mixtures at 298.15 K

	A_0	A_1	A_2	A_3	$\sigma(V_m^E)$/cm^3·mol^{-1}
1−propanol + propane-1,2-diol	−0.4997	0.0108	−0.0038	−0.0142	0.001
1-propanol + 1-methoxy-2-propanol	−0.4911	0.0141	−0.1708	0.0191	0.002
1-propanol + 1-ethoxy-2-propanol	−0.8723	0.1015	−0.1596	0.0596	0.002
1-propanol + 1-*tert*-butoxy-2-propanol	−1.2536	0.2453	−0.1358	0.0966	0.002
2-propanol + propane-1,-2-diol	−0.8980	−0.1310	−0.0590	−0.0166	0.001
2-propanol + 1-methoxy-2-propanol	−0.2797	−0.0150	−0.0979	0.0428	0.001
2-propanol + 1-ethoxy-2-propanol	−0.5057	0.0765	−0.1068	0.0045	0.001
2-propanol + 1-*tert*-butoxy-2-propanol	−0.4961	0.1024	−0.0589	−0.0052	0.002
water + 1-methoxy-2-propanol	−5.0085	2.8093	−0.4380	−1.1487	0.004
water + 1-ethoxy-2-propanol	−5.3041	2.2614	−1.7044	2.5510	0.003

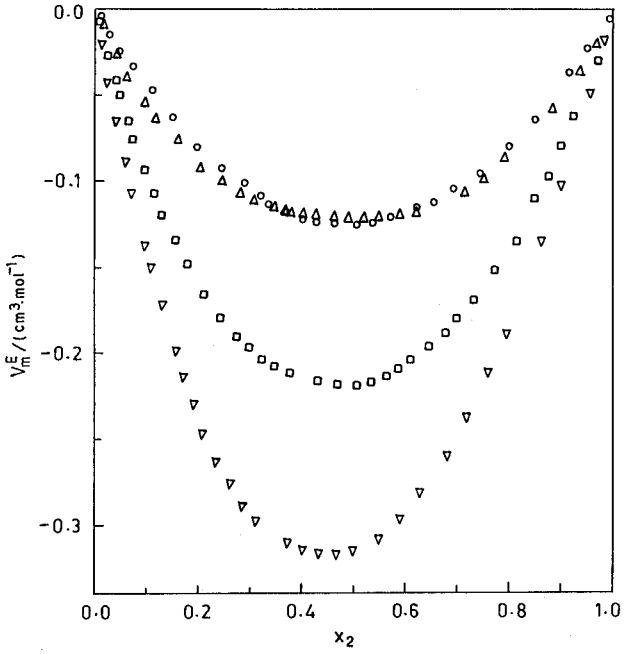

Figure 1. Excess molar volume V_m^E for 1-propanol (1) + propane-1,2-diol (2) (○), + 1-methoxy-2-propanol (2) (△), 1-ethoxy-2-propanol (2) (□), and + 1-*tert*-butoxy-2-propanol (2) (▽) at 298.15 K.

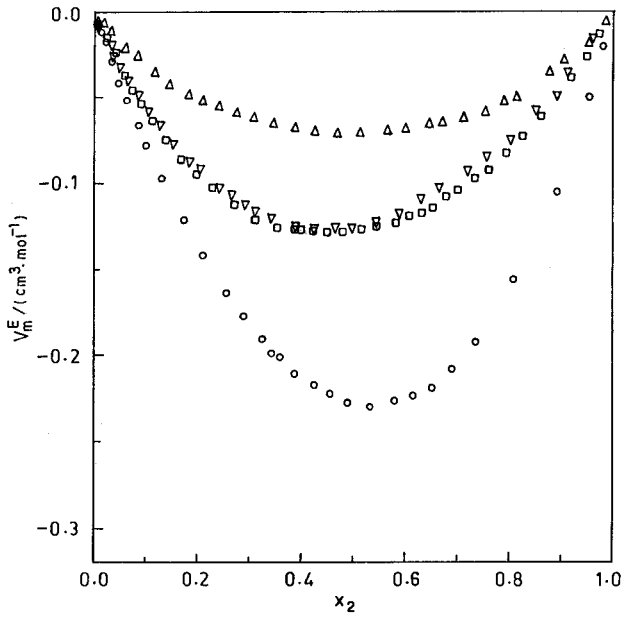

Figure 2. Excess molar volume V_m^E for 2-propanol (1) + propane-1,2-diol (2) (○), + 1-methoxy-2-propanol (2) (△), + 1-ethoxy-2-propanol (2) (□), and + 1-*tert*-butoxy-2-propanol (2) (▽) at 298.15 K.

for all the mixtures were fitted to the equation (Redlich and Kister, 1948)

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2[A_0 + A_1(x_2 - x_1) + A_2(x_2-x_1)^2 + A_3(x_2 - x_1)^3] \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively. A_0, A_1, A_2, and A_3 are the adjustable parameters obtained by the method of least squares and are given in Table 3 along with standard deviations $\sigma(V_m^E)$. For all the mixtures $\sigma(V_m^E) \leq 0.004$ cm^3·mol^{-1}, showing the good accuracy attainable with the dilatometer used. We were unable to measure water + 1-*tert*-butoxy-2-propanol due to immiscibility.

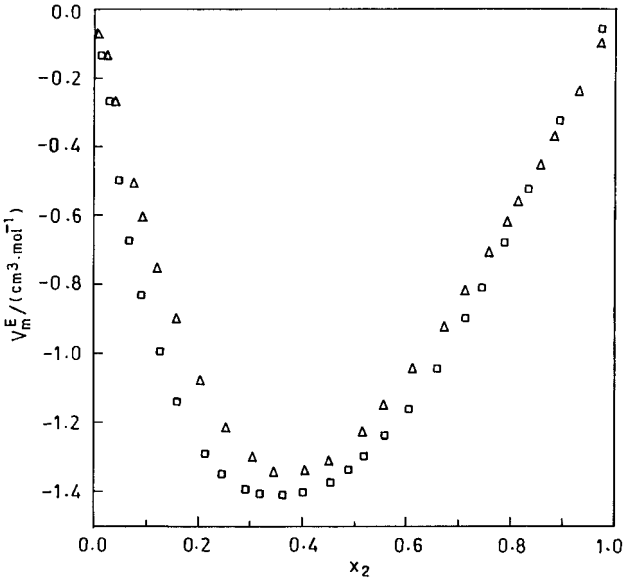

Figure 3. Excess molar volume V_m^E for water (1) + 1-methoxy-2-propanol (2) (△) and + 1-ethoxy-2-propanol (2) (□) at 298.15 K.

Table 2 and Figures 1−3 show that the excess volumes are negative for all the mixtures over the entire composition range. For the mixtures with 1-propanol, the V_m^E curves are symmetrical but the curves are slightly unsymmetrical toward the region of low mole fraction of 2-propanol or high mole fraction of water. Remarkably, V_m^E is more negative for the mixtures with 1-propanol as compared to 2-propanol. But in the case of propane-1,2-diol, V_m^E is more negative with 2-propanol. The large negative value indicates a reasonably strong association between the 2-propanol and the diol. There is a substantial decrease in the excess molar volume in all the cases from primary to secondary alcohol except with propane-1,2-diol.

The magnitude of the excess molar volume decreases with the size and shape of the ether in mixtures containing 1-propanol, but with 2-propanol the trend is 1-methoxy-2-propanol < 1-*tert*-butoxy-2-propanol < 1-ethoxy-2-propanol. At mole fractions $x_2 \leq 0.70$, for the water + 1-ethoxy-2-propanol system excess molar volumes are the more negative. It is simple to note that the addition of a CH_2 group introduces a negative group contribution to V_m^E. At higher ether mole fractions, the difference in excess molar volumes of water + 1-ethoxy-2-propanol and water + 1-methoxy-2-propanol are less significant. The experimental results suggest that the volume behaviors of these mixtures are the result of several opposing effects accompanying the differences in the size and the shape of the components, in the interaction energy between like and unlike molecules, and with structural changes.

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