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Excess Molar Volumes of Heptan-1-ol + Pentane, + Hexane, + Heptane, + Octane, and + 2,2,4-Trimethylpentane at T = 293.15 K

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Excess molar volumes, V_m^E, have been measured using a dilatometric technique for binary mixtures of heptan-1-ol (n-$C_7H_{15}OH$) + pentane (n-C_5H_{12}), + hexane (n-C_6H_{14}), + heptane (n-C_7H_{16}), + octane (n-C_8H_{18}), and + 2,2,4-trimethylpentane (2,2,4-TMP) at T = 293.15 K. V_m^E has been found to be negative throughout the entire range of composition for (x)n-$C_7H_{15}OH$ + (1 − x)n-C_5H_{12}, + (1 − x)n-C_6H_{14}, and + (1 − x)2,2,4-TMP. V_m^E has been found to be positive at lower mole fractions of n-$C_7H_{15}OH$ and negative at higher mole fractions of n-$C_7H_{15}OH$ for (x)n-$C_7H_{15}OH$ + (1 − x)n-C_7H_{16} and (x)n-$C_7H_{15}OH$ + (1 − x)n-C_8H_{18} with an inversion of sign from positive to negative values of V_m^E occurring at $x \sim 0.18$ and $x \sim 0.43$, respectively, for these mixtures. V_m^E has been fitted in a smoothing equation.

Introduction

Systematic studies of the thermodynamic excess properties of (alkane + alkanol) mixtures are important from the viewpoint of understanding the molecular liquid structure and the intermolecular interactions predominated by the self-association of the alkanol molecules due to hydrogen bonding and the prediction of thermodynamic properties of these mixtures of components of different shapes and sizes. The temperature dependence of the thermodynamic properties of these mixtures is also important from the viewpoint of understanding the extent of self-association of the alkanol molecules. Accordingly, Wagner and Heintz (1986) and Heintz et al. (1986) measured excess volumes, V_m^E, of mixtures of nonane and hexane with five different 1-alkanols at various temperatures. Fuente et al. (1992) determined V_m^E of (nonan-1-ol + decane or tetradecane) at different temperatures. Franzo et al. (1994) have measured V_m^E of x $CH_3(CH_2)_5OH$ + (1 − x)$CH_3(CH_2)_4CH_3$ at T = 298.15 K. Zielkiewicz (1994a,b) has measured total vapor pressures and V_m^E of mixtures of heptane with five different alkanols at 313.15 K. Although Nath and Pandey (1997a) have measured V_m^E for binary mixtures of butan-1-ol (n-C_4H_9OH) with pentane (n-C_5H_{12}), hexane (n-C_6H_{14}), heptane (n-C_7H_{16}), octane (n-C_8H_{18}), and 2,2,4-trimethylpentane (2,2,4-TMP) at 288.15 K and 298.15 K and also Nath and Pandey (1997b) have measured V_m^E for the binary mixtures of heptan-1-ol (n-$C_7H_{15}OH$) with the above hydrocarbons only at one temperature: for n-$C_7H_{15}OH$ + n-C_5H_{12} at 298.15 K and for n-$C_7H_{15}OH$ + n-C_6H_{14}, + n-C_7H_{16}, + n-C_8H_{18}, and + 2,2,4-TMP at 308.15 K, V_m^E of these mixtures of n-$C_7H_{15}OH$ at other temperatures has not been measured. In this work, V_m^E has been measured for n-$C_7H_{15}OH$ + n-C_5H_{12}, + n-C_6H_{14}, + n-C_7H_{16}, + n-C_8H_{18}, and + 2,2,4-TMP at T = 293.15 K, and the results obtained are reported and discussed in this paper.

Experimental Section

Materials. Pentane, hexane, heptane, octane, 2,2,4-trimethylpentane, and heptan-1-ol used in this work were of the same quality and were purified as described earlier (Nath and Pandey, 1997b).

Method. Excess molar volumes, V_m^E, were measured with an imprecision of the order of ±0.002 $cm^3{\cdot}mol^{-1}$, using a two-limbed Pyrex glass dilatometer that was similar to that used in earlier measurements (Nath and Saini, 1989; Nath and Chaudhary, 1992; Nath and Pandey, 1997a,b). Known amounts of the two liquid components were confined over mercury in the absence of air spaces in the two limbs of the dilatometer. The dilatometer (mounted on a stand) was immersed in a thermostat that was controlled to ±0.01 K. The mixing of the two liquid components was done by rocking the cell back and forth through a definite angle, and the mercury levels in the capillary of the dilatometer were noted before and after mixing, using a cathetometer that had the accuracy of ±0.001 cm, as described earlier (Nath and Pandey, 1997a,b).

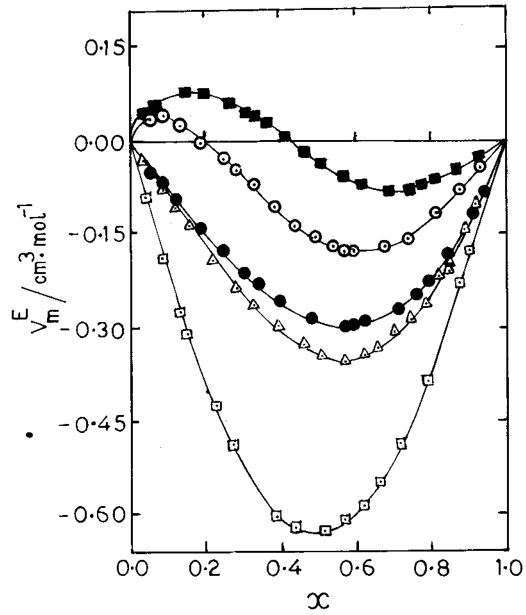

Figure 1. V_m^E plotted versus x for the following systems at T = 293.15 K: (⊡) (x)n-$C_7H_{15}OH$ + (1 − x)n-C_5H_{12}; (△) (x)n-$C_7H_{15}OH$ + (1 − x)n-C_6H_{14}; (⊙) (x)n-$C_7H_{15}OH$ + (1 − x)n-C_7H_{16}; (■) (x)n-$C_7H_{15}OH$ + (1 − x)n-C_8H_{18}; (●) (x)n-$C_7H_{15}OH$ + (1 − x)2,2,4-TMP.

Results and Discussion

The present experimental values of V_m^E for mixtures of n-$C_7H_{15}OH$ + n-C_5H_{12}, + n-C_6H_{14}, + n-C_7H_{16}, + n-C_8H_{18}, and + 2,2,4-TMP at T = 293.15 K are given in Table 1, where x refers to the mole fraction of n-$C_7H_{15}OH$ in the mixture. x has an uncertainty of ±0.0001. Values of V_m^E

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Table 1. Experimental Values of the Excess Molar Volumes, V_m^E, for n-$C_7H_{15}OH$ + n-C_5H_{12}, + n-C_6H_{14}, + n-C_7H_{16}, + n-C_8H_{18}, and + 2,2,4-TMP at T = 293.15 K

x	$V_m^E/cm^3 \cdot mol^{-1}$	x	$V_m^E/cm^3 \cdot mol^{-1}$	x	$V_m^E/cm^3 \cdot mol^{-1}$	x	$V_m^E/cm^3 \cdot mol^{-1}$
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_5H_{12}							
0.0509	−0.092	0.2275	−0.426	0.5151	−0.631	0.7216	−0.490
0.0928	−0.189	0.2741	−0.492	0.5748	−0.612	0.7959	−0.388
0.1341	−0.276	0.3906	−0.604	0.6225	−0.585	0.8843	−0.231
0.1521	−0.311	0.4394	−0.623	0.6631	−0.553	0.9113	−0.179
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_6H_{14}							
0.0393	−0.031	0.3315	−0.264	0.6605	−0.336	0.8558	−0.205
0.0892	−0.076	0.4022	−0.300	0.7156	−0.310	0.8985	−0.146
0.1271	−0.106	0.4651	−0.326	0.7531	−0.291	0.9313	−0.105
0.1662	−0.138	0.5147	−0.344	0.7923	−0.265		
0.2268	−0.192	0.5791	−0.354	0.8306	−0.227		
0.2849	−0.237	0.6280	−0.346	0.8488	−0.213		
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_7H_{16}							
0.0575	0.037	0.2895	−0.048	0.5390	−0.171	0.8185	−0.122
0.0922	0.040	0.3358	−0.072	0.5786	−0.178	0.8849	−0.083
0.1386	0.024	0.3897	−0.104	0.5959	−0.176	0.9396	−0.044
0.1907	−0.002	0.4472	−0.136	0.6795	−0.172		
0.2561	−0.028	0.5037	−0.156	0.7437	−0.158		
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_8H_{18}							
0.0486	0.044	0.3144	0.047	0.5118	−0.036	0.7812	−0.073
0.0789	0.058	0.3345	0.043	0.5670	−0.056	0.8172	−0.065
0.1551	0.077	0.3669	0.028	0.6245	−0.070	0.8731	−0.050
0.2062	0.075	0.4133	0.008	0.6902	−0.080	0.9366	−0.028
0.2737	0.061	0.4636	−0.017	0.7520	−0.079		
$(x)n$-$C_7H_{15}OH + (1 - x)$2,2,4-TMP							
0.0618	−0.052	0.3098	−0.212	0.5974	−0.296	0.8517	−0.187
0.0863	−0.068	0.3404	−0.229	0.6289	−0.294	0.9164	−0.121
0.1338	−0.101	0.4032	−0.258	0.7152	−0.272	0.9438	−0.087
0.1913	−0.140	0.4927	−0.285	0.7674	−0.251		
0.2531	−0.179	0.5777	−0.298	0.7961	−0.231		

Table 2. Values of the Coefficients A_j of Eq 1 and the Standard Deviations, $\delta(V_m^E)$, for the Various Mixtures at T = 293.15 K

mixture	A_1[a]	A_2[a]	A_3[a]	A_4[a]	$\delta(V_m^E)$[a]
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_5H_{12}	−2.424 29	−0.754 56	1.240 41	−0.148 61	0.0046
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_6H_{14}	−1.030 56	−0.694 32	−0.389 72	0.419 20	0.0034
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_7H_{16}	0.059 46	−1.846 29	0.169 92	0.945 03	0.0029
$(x)n$-$C_7H_{15}OH + (1 - x)n$-C_8H_{18}	0.521 43	−1.446 20	−0.618 43	1.118 61	0.0022
$(x)n$-$C_7H_{15}OH + (1 - x)$2,2,4-TMP	−0.910 96	−0.284 36	−0.560 78	−0.016 51	0.0028

[a] In $cm^3 \cdot mol^{-1}$.

for the present mixtures have been plotted against x in Figure 1 and have been fitted by the method of least squares to the equation

$$V_m^E/x\,(1 - x) = \sum_{j=1}^{m} A_j Y \qquad (1)$$

where $Y = [(x - 1)/(1 + Dx)]^{j-1}$ and A_j are the coefficients characteristic of a system at a given temperature. As pointed out by Berro and Péneloux (1984), the calculations were performed for all these systems with $D = 25$. The values of the coefficients A_j of eq 1, along with the standard deviations, $\delta(V_m^E)$, for the various mixtures are given in Table 2.

V_m^E is positive at lower mole fractions of n-$C_7H_{15}OH$ for $(x)n$-$C_7H_{15}OH + (1 - x)n$-C_7H_{16} and $(x)n$-$C_7H_{15}OH + (1 - x)n$-C_8H_{18} and is negative at higher mole fractions of n-$C_7H_{15}OH$ for these mixtures at T = 293.15 K, with inversion of sign of V_m^E from positive to negative values occurring at $x \sim 0.18$ and $x \sim 0.43$, respectively, for the two systems. V_m^E is found to be negative throughout the entire range of composition for $(x)n$-$C_7H_{15}OH + (1 - x)n$-C_5H_{12}, $(x)n$-$C_7H_{15}OH + (1 - x)n$-C_6H_{14}, and $(x)n$-$C_7H_{15}OH + (1 - x)$2,2,4-TMP at T = 293.15 K. At x = 0.5, V_m^E for the present mixtures of n-$C_7H_{15}OH$ with alkanes follows the sequence

$$n\text{-}C_8H_{18} > n\text{-}C_7H_{16} > 2,2,4\text{-TMP} > n\text{-}C_6H_{14} > n\text{-}C_5H_{12}$$

The above (same) sequence is also found in the values of excess molar volumes V_m^E (Nath and Pandey, 1997a) and excess isentropic compressibilities K_S^E (Nath, 1997) at x = 0.5, for binary mixtures of butan-1-ol (n-C_4H_9OH) with n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, and 2,2,4-TMP. The above (same) sequence is also found (Nath and Pandey, 1997b) in the values of V_m^E at x = 0.5 for mixtures of n-$C_7H_{15}OH$ with n-C_5H_{12} at T = 298.15 K and for mixtures of n-$C_7H_{15}OH$ with n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, and 2,2,4-TMP at T = 308.15 K.

The values of V_m^E of the (alkanol + alkane) mixtures may be interpreted as the result of the contributions of the various types of intermolecular interactions operating between the alkane and alkanol molecules. Mainly three type of contributions, (i) physical, due to nonspecific interactions, (ii) chemical, due to hydrogen bonding, and (iii) structural, due to changes of interstitial accommodation and free volume, are important in determining the thermodynamic excess properties of the alkanol + alkane mixtures. The chemical contribution is important at low concentrations of alkanol where the breaking of self-association of the alkanol molecules due to H-bonds makes a positive contribution to V_m^E. The positive values of V_m^E for $(x)n\text{-}C_7H_{15}OH + (1 - x)n\text{-}C_7H_{16}$ and $(x)n\text{-}C_7H_{15}OH + (1 - x)n\text{-}C_8H_{18}$ at low values of x may thus be attributed to the predominance of the contributions to V_m^E from the breaking of self-association due to H-bonds in the heptan-1-ol molecules in these mixtures.

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