Densities and Excess Molar Volumes of Cyclopentane (1) + 1-Alkanol (2) Systems at (298.15 and 308.15) K

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Densities for binary mixtures of cyclopentane with 1-propanol, 1-pentanol, and 1-heptanol over the whole composition range have been measured at temperatures (298.15 and 308.15) K. From these densities, excess molar volumes were calculated. All the experimental excess molar volumes were fitted to the Redlich−Kister equation.

Introduction

Mixing of different organic liquids gives rise to solutions that generally do not behave ideally. Many thermodynamic properties are used to express the deviations for ideality, particularly excess or residual properties. Excess thermodynamic properties like excess molar volumes are useful in understanding the molecular interactions. In particular, they reflect the solute−solute, solvent−solvent, and solute−solvent interactions. Strong like interactions, as in alcohols, may give rise to positive excess molar volumes, and equally unlike interactions between molecules give rise to negative excess molar volumes. Binary mixtures are an important class of solvents and solutions, and changes occurring in their physical properties are still unclear.

As a part of our experimental program on thermodynamic and physicochemical properties of binary liquid mixtures, we report here measurements of the density, ρ, for binary mixtures of cyclopentane (1) + 1-propanol (2), + 1-pentanol (2), and 1-heptanol (2) at (298.15 and 308.15) K over the whole composition range. From these density measurements, we calculated the excess molar volumes V^E, and these were fitted to the Redlich−Kister polynomial equation.

Experimental Section

Materials. Cyclopentane, 1-propanol, 1-pentanol, and 1-heptanol were obtained from SD Fine Chemicals, India. All the liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen pressure. The estimated purities as per gas chromatographic analysis were better than 99.5 mol % for all liquid samples. Further, the purities of liquids were checked by comparing densities of pure solvents at desired temperatures, with their corresponding literature values.[1−8] These values are reported in Table 1.

Apparatus and Procedure. The densities of the pure liquids and their mixtures were measured using an Anton Paar DSA 5000 densimeter. As the densities are extremely sensitive to temperature, it was controlled to ± 0.01 K by a built-in solid state thermostat. Before each series of measurements, the apparatus was calibrated with double distilled and degassed water, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, and benzene. The reproducibility of density measurements was ± $1 \cdot 10^{-6}$ g·cm^{-3}, and uncertainties of these are assumed to be less than $5 \cdot 10^{-6}$ g·cm^{-3}

The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The

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Table 1. Experimental Densities (ρ) of the Pure Component Liquids at T = (298.15 and 308.15) K Together with Literature Values

		ρ/g·cm^{-3}	
solvent	T/K	exptl	lit.
cyclopentane	298.15	0.733634	0.73947[1]
			0.73969[2]
	308.15	0.726571	0.72942[1]
1-propanol	298.15	0.799813	0.799666[3]
			0.7995[4]
			0.79952[5]
			0.79958[6]
	308.15	0.791692	0.791765[3]
			0.79146[7]
1-pentanol	298.15	0.811037	0.811001[3]
			0.8109[4]
			0.81083[5]
	308.15	0.803683	0.803302[3]
			0.80345[8]
1-heptanol	298.15	0.818813	0.818789[3]
			0.81879[4]
	308.15	0.811730	0.812385[3]
			0.81239[8]

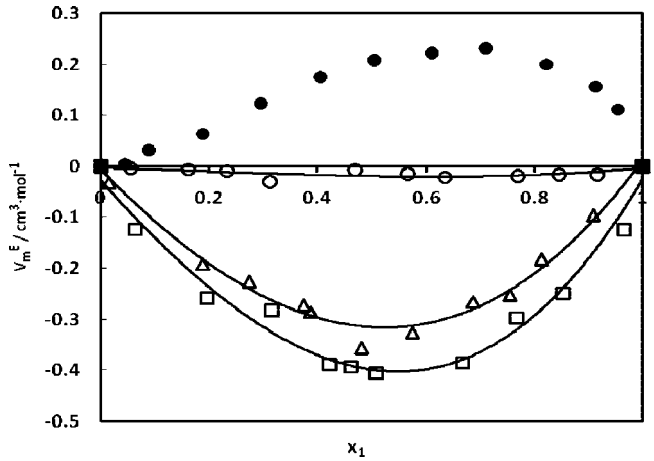

Figure 1. Excess molar volumes, V^E, at T = 298.15 K for cyclopentane (1) + 1-alkanol (2): ○, 1-propanol; ●, 1-propanol (ref 6); Δ, 1-pentanol; □, 1-heptanol. Solid lines have been obtained from eq 2.

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Table 2. Densities (ρ) and Excess Molar Volume (V^E) for Cyclopentane (1) + 1-Alknaol (2) at T = (298.15 and 308.15) K

	ρ/g·cm^{-3}		V^E/cm^3·mol^{-1}	
x_1	298.15 K	308.15 K	298.15 K	308.15 K
Cyclopentane (1) + 1-Propanol (2)				
0.0553	0.795275	0.786980	−0.0047	0.0196
0.1627	0.786754	0.778045	−0.0059	0.0758
0.2341	0.781370	0.772538	−0.0089	0.0969
0.3137	0.775778	0.766718	−0.0315	0.1113
0.4691	0.764862	0.755363	−0.0081	0.2122
0.5666	0.758623	0.748897	−0.0161	0.2495
0.6338	0.754486	0.744566	−0.0215	0.2808
0.7688	0.746451	0.737144	−0.0201	0.2343
0.8446	0.742132	0.733210	−0.0170	0.2027
0.9167	0.738181	0.729510	−0.0173	0.1825
Cyclopentane (1) + 1-Pentanol (2)				
0.0155	0.810220	0.802763	−0.0322	−0.0183
0.1886	0.799340	0.791417	−0.1916	−0.1123
0.2742	0.793439	0.785673	−0.2262	−0.1661
0.3746	0.786395	0.778336	−0.2727	−0.1710
0.3884	0.785467	0.777389	−0.2863	−0.1819
0.4798	0.779082	0.770553	−0.3567	−0.1904
0.5738	0.771559	0.763458	−0.3262	−0.2131
0.6868	0.762096	0.754298	−0.2660	−0.1878
0.7543	0.756486	0.748638	−0.2526	−0.1648
0.8131	0.751070	0.743306	−0.1827	−0.1019
0.9079	0.742377	0.735151	−0.0963	−0.0811
Cyclopentane (1) + 1-Heptanol (2)				
0.0632	0.815837	0.808629	−0.1238	−0.1048
0.1965	0.808334	0.800856	−0.2579	−0.1976
0.3173	0.800287	0.792895	−0.2836	−0.2405
0.4244	0.793064	0.785675	−0.3883	−0.3493
0.4606	0.790282	0.782889	−0.3927	−0.3538
0.5084	0.786531	0.779091	−0.4054	−0.3601
0.6664	0.772628	0.764753	−0.3853	−0.2782
0.7675	0.762185	0.754805	−0.2971	−0.2611
0.8534	0.752769	0.745466	−0.2486	−0.2226
0.9644	0.739018	0.731663	−0.1262	−0.0901

Table 3. Standard Deviations (σ) and Parameters A_i in Equation 2 at T = (298.15 and 308.15) K

T/K	A_0	A_1	A_2	A_3	A_4	σ
Cyclopentane (1) + 1-Propanol (2)						
298.15	−0.0671	−0.0365	−0.0988			0.0094
308.15	0.8781	0.8677	0.3989			0.0244
Cyclopentane (1) + 1-Pentanol (2)						
298.15	−1.3419	−0.3618	0.9774	0.9667	−1.6793	0.0201
308.15	−0.8033	−0.0808	0.0148			0.0167
Cyclopentane (1) + 1-Heptanol (2)						
298.15	−1.6275	−0.3552	1.0603	0.1728	−3.0136	0.0284
308.15	−1.4205	−0.1061	1.4516	−0.4194	−3.2582	0.0253

weighings were done with an electronic balance with precision of ± 0.01 mg. The mole fraction of each mixture was obtained with an uncertainty of $1 \cdot 10^{-4}$ from the measured masses of the components. All molar quantities were based on the IUPAC relative atomic mass table.[9]

Results and Discussions

Experimental densities, ρ, for binary mixtures cyclopentane (1) + 1-propanol (2), + 1-pentanol (2), and + 1-heptanol (2) at (298.15 and 308.15) K are listed in Table 2. Excess molar volumes were calculated from our measurements according to the following equation

$$V^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

where x_1 and x_2 are mole fractions; M_1 and M_2 are molar masses; and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. ρ is the density of the binary mixtures.

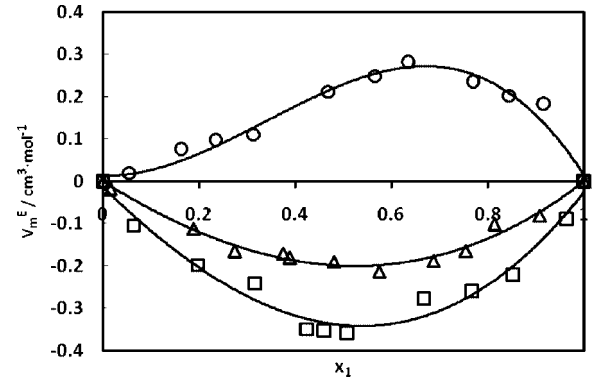

Figure 2. Excess molar volumes, V^E, at T = 308.15 K for cyclopentane (1) + 1-alkanol (2): ○, propanol; Δ, 1-pentanol; □, 1-heptanol. Solid lines have been obtain from eq 2.

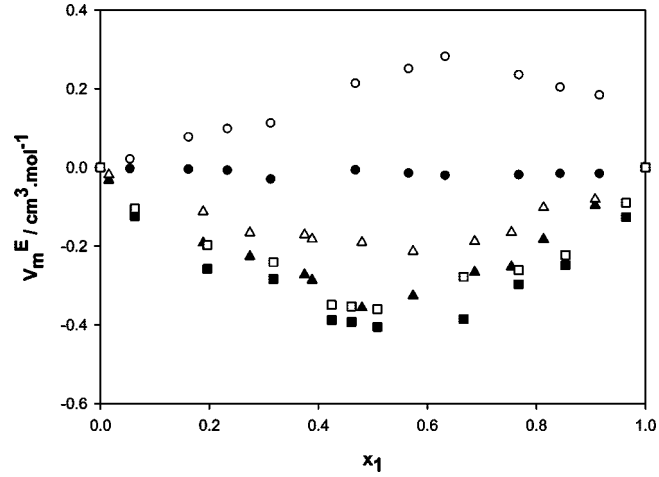

Figure 3. Excess molar volumes, V^E, for cyclopentane (1) + 1-alkanol (2): (1-propanol, ●, 298.15 K; ○, 308.15 K); (1-pentanol, ▲, 298.15 K; Δ, 308.15 K); (1-heptanol, ■, 298.15 K; □, 308.15 K).

The calculated values of V^E of the binary mixtures, at each investigated temperature, were fitted to a Redlich−Kister[10] type polynomial equation.

$$V^E = x_1x_2\sum_{i=0}^{n} A_i(x_1 - x_2)^i \qquad (2)$$

The coefficients A_i of eq 2 for the correlation of V^E−composition data, evaluated using the least-squares method, are given in Table 3 along with the resulting standard deviations in excess molar volume $\sigma(V^E)$. The standard deviation was calculated by

$$\sigma(V^E) = \left[\sum_{1}^{n} (V^E_{\text{exptl}} - V^E_{\text{calcd}})^2/(n-m)\right]^{1/2} \qquad (3)$$

where n and m are the number of experimental points and parameters, respectively.

It is observed from Table 2 and Figures 1 and 2 that the excess molar volumes for all the mixtures at (298.15 and 308.15) K are negative over the whole composition range except for the system cyclopentane (1) + 1-propanol (2) at 308.15 K for which it shows positive deviations. The negative excess molar volumes can be attributed to strong unlike interactions between molecules. The excess molar volumes increase with the decrease in the chain length of 1-alkanol at both studied temperatures, which imply that the dipole−dipole interactions are weak in lower 1-alkanols owing to the decrease in their polarizability

with decreasing chain length.[11] For comparison, we have shown the excess molar volumes for cyclopentane (1) + 1-propanol (2) at 298.15 K reported earlier.[6] Also, excess molar volumes increase with the increase in temperature for all the mixtures studied, with a change in sign for the cyclopentane (1) + 1-propanol (2) mixture, as shown in Figure 3, which implies a weaker unlike interaction between molecules at higher temperature.

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