Volumetric Behavior of the Binary Mixtures of Methyl Ethyl Ketone with *n*-Hexane, Cyclohexane, and Benzene at $T = (303.15, 313.15, \text{and } 323.15)$ K

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Experimental values of density of binary liquid mixtures of methyl ethyl ketone (MEK) with *n*-hexane, cyclohexane, and benzene have been measured at a number of mole fractions at $T = (303.15, 313.15, \text{and } 323.15)$ K. The excess molar volumes V_m^E have been calculated from the density data. These quantities are further fitted to the appropriate polynomial equations. The sign and magnitude of the calculated excess values have been discussed in terms of the nature of the solvent−solvent interactions in binary mixtures.

Introduction

In the field of analytical chemistry, binary (or multicomponent) solvent systems suffice to think of conductometric, potentiometric, and electroanalytical techniques which work in mixed solvents, chromatographic applications, etc.[1−4] The nature and type of interactions in binary organic liquid mixtures are essential to understand their behavior in the analytical applications. These data are also useful in process engineering design applications and other related areas and have drawn considerable attention from many investigators.[5−12] We are concerned about the research on the accumulation of the binary physical property data of organic liquid mixtures,[8,11] and in continuation, the experimental density (ρ) data for the mixtures of methyl ethyl ketone (MEK) with *n*-hexane, cyclohexane, and benzene have been measured at a number of mole fractions at $T = (303.15, 313.15, \text{and } 323.15)$ K. Excess molar volumes, V_m^E, for the binary systems were calculated from the experimental data and fitted to the Redlich−Kister polynomial equation[13] to estimate the binary interaction parameters and standard errors. To analyze and interpret the experimental data and the derived quantities, some previous results for binary mixtures have been used.

Experimental

Materials. MEK (E. Merck, 0.98 mass fraction purity), *n*-hexane (E. Merck, 0.95 mass fraction purity), cyclohexane (BDH, 0.99 mass fraction purity), and benzene (BDH, 0.99 mass fraction purity) were used without further purification. Caution was taken to prevent evaporation of the solutions after preparation. The solvent purity was ascertained by comparing the densities of the liquids with the available literature data (Table 1). There is fairly good agreement between our data and the previously reported values.

Methods. All binary mixtures were prepared by mass on an analytical balance with an uncertainty of ± 0.0001 g, operating in a drybox and prepared just before use to ensure accuracy of the calculated mole fractions up to the fourth decimal place.

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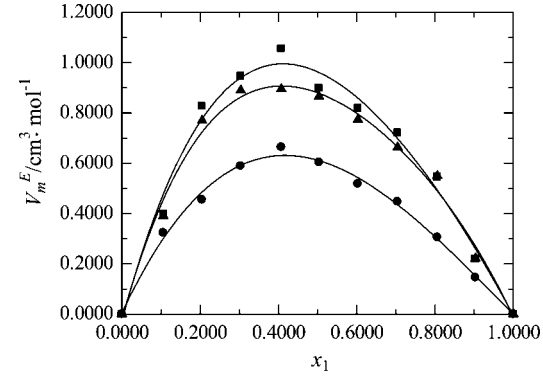

Figure 1. Excess molar volumes for MEK (1) + *n*-hexane (2): ●, 303.15 K; ▲, 313.15 K; ■, 323.15 K.

The densities of liquids and their mixtures were measured by a 25 mL specific gravity bottle, previously calibrated with redistilled water. The average uncertainty in the measured density was ± 0.0002 g·cm^{-3}. With the fluctuation of ± 0.05 K, temperature was controlled by a water thermostat. The V_m^E values are accurate to ± 0.05 cm^3·mol^{-1}. For all mixture compositions and pure solvents, triplicate measurements were performed, and the average of these values was considered in all calculations.

Results and Discussion

Binary composition of the mixtures of MEK with *n*-hexane, cyclohexane, and benzene and the experimental densities at $T = (303.15, 313.15, \text{and } 323.15)$ K are summarized in Table 2. Excess molar volumes, V_m^E, for the mixtures of the solvent systems, as listed in Table 2, can be calculated using the formula

$$V_m^E = [(x_1M_1 + x_2M_2)/\rho_m - \{(x_1M_1)/\rho_1 + (x_2M_2)/\rho_2\}] \quad (1)$$

where x_1, M_1, and ρ_1 represent, respectively, mole fraction, molar mass, and density of MEK, and x_2, M_2, and ρ_2 are the corresponding quantities of other organic solvents (*n*-hexane, cyclohexane, and benzene). ρ_m is the density of the binary mixtures.

The calculated V_m^E of the systems were fitted by least-squares with a Redlich−Kister smoothing equation[13] of the form

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$$V_m^E = x_1 x_2 \sum_{i=0}^{n} a_i (x_2 - x_1)^i \quad (2)$$

The coefficients, a_i, of the polynomial equation with the standard deviations, σ, are listed in Table 3.

The trend of V_m^E for the binary mixtures of MEK with *n*-hexane, cyclohexane, and benzene as a function of the binary composition at $T =$ (303.15, 313.15, and 323.15) K is shown in Figures 1, 2, 3, and 4, respectively. As it shows, for the whole range of composition, the values of V_m^E are positive for the systems of MEK with *n*-hexane and cyclohexane (Figures 1 and 2), while it is negative for the system of MEK with benzene (Figure 3). It is also evident that the values of $\delta V_m^E/\delta T$, irrespective of sign of V_m^E, are positive for the binary systems

Table 1. Comparison of Experimental Densities, ρ (g·cm^{-3}), of Pure Liquids with Literature Values at $T =$ (303.15, 313.15, and 323.15) K

	T/K = 303.15		T/K = 313.15		T/K = 323.15	
liquid (s)	exp.	lit.[a]	exp.	lit.[a]	exp.	lit.[a]
MEK	0.7946	0.7948	0.7840	0.7844	0.7733	0.7738
n-hexane	0.6509	0.6503	0.6417	0.6411	0.6309	0.6317
cyclohexane	0.7689	0.7692	0.7592	0.7597	0.7487	0.7501
benzene	0.8681	0.8683	0.8574	0.8575	0.8466	0.8467

[a] TRC Databases for Chemistry and Engineering - TRC Thermodynamic Tables. Texas Engineering Experiment Station, Texas A&M University System, 1998.

Table 2. Composition, Experimental Densities, ρ, and Excess Molar Volumes, V_m^E, for the Binary Mixtures of MEK with *n*-Hexane, Cyclohexane, and Benzene at $T =$ (303.15, 313.15, and 323.15) K

	T/K = 303.15		T/K = 313.15		T/K = 323.15	
x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
			MEK (1) + *n*-Hexane (2)			
0.0000	0.6509	0.0000	0.6417	0.0000	0.6309	0.0000
0.1057	0.6600	0.3236	0.6504	0.3905	0.6396	0.3988
0.2048	0.6700	0.4550	0.6590	0.7694	0.6480	0.8263
0.3035	0.6806	0.5891	0.6695	0.8901	0.6585	0.9462
0.4071	0.6929	0.6642	0.6820	0.8950	0.6704	1.0548
0.5035	0.7060	0.6037	0.6947	0.8659	0.6838	0.8985
0.6029	0.7207	0.5182	0.7092	0.7728	0.6982	0.8186
0.7042	0.7368	0.4473	0.7253	0.6631	0.7142	0.7212
0.8059	0.7549	0.3057	0.7429	0.5499	0.7322	0.5449
0.9033	0.7740	0.1453	0.7630	0.2221	0.7523	0.2198
1.000	0.7946	0.0000	0.7840	0.0000	0.7733	0.0000
			MEK (1) + Cyclohexane (2)			
0.0000	0.7689	0.0000	0.7592	0.0000	0.7487	0.0000
0.1066	0.7680	0.4497	0.7583	0.4498	0.7474	0.5191
0.2093	0.7683	0.7130	0.7574	0.8845	0.7465	0.9625
0.3084	0.7695	0.8538	0.7582	1.0664	0.7473	1.1462
0.4042	0.7713	0.9052	0.7599	1.1183	0.7492	1.1681
0.5064	0.7736	0.9192	0.7624	1.0900	0.7513	1.1908
0.6055	0.7762	0.8965	0.7651	1.0385	0.7544	1.0795
0.7007	0.7798	0.7489	0.7692	0.8080	0.7578	0.9325
0.8015	0.7840	0.5978	0.7727	0.6937	0.7617	0.7912
0.9070	0.7896	0.2544	0.7778	0.4185	0.7672	0.4204
1.000	0.7946	0.0000	0.7840	0.0000	0.7733	0.0000
			MEK (1) + Benzene (2)			
0.0000	0.8681	0.0000	0.8574	0.0000	0.8466	0.0000
0.1010	0.8612	−0.079	0.8506	−0.0583	0.8399	−0.0706
0.1999	0.8542	−0.0864	0.8435	−0.0854	0.8329	−0.1090
0.2988	0.8471	−0.1151	0.8366	−0.1349	0.8259	−0.1480
0.3969	0.8399	−0.1339	0.8293	−0.1413	0.8187	−0.1653
0.4996	0.8327	−0.1525	0.8221	−0.1583	0.8115	−0.1819
0.5988	0.8252	−0.1388	0.8146	−0.1419	0.8039	−0.1525
0.6993	0.8175	−0.1021	0.8069	−0.1017	0.7964	−0.1333
0.7931	0.8099	−0.0768	0.7994	−0.0847	0.7889	−0.1144
0.8961	0.8022	−0.0391	0.7917	−0.0432	0.7811	−0.0584
1.000	0.7946	0.0000	0.7840	0.0000	0.7733	0.0000

Table 3. Coefficients, a_i, of the Redlich−Kister Equation (Equation 2), Expressing V_m^E and Standard Deviation, σ, for the Binary Mixtures of MEK with *n*-Hexane, Cyclohexane, and Benzene at $T =$ (303.15, 313.15, and 323.15) K

system	T/K	a_0	a_1	a_2	a_3	σ/cm^3·mol^{-1}
MEK (1) + *n*-hexane (2)	303.15	2.4483	−0.8861	0.0251	−0.0218	0.0266
	313.15	3.5275	−1.3377	0.7198	0.6716	0.0530
	323.15	3.8621	−1.7849	0.2764	1.3058	0.0648
MEK (1) + cyclohexane (2)	303.15	3.7233	−0.1768	0.5892	−1.2545	0.0228
	313.15	4.4176	−1.6267	0.7976	2.5114	0.0373
	323.15	4.7222	−1.2770	1.2845	1.4935	0.0358
MEK (1) + benzene (2)	303.15	−0.5777	0.0389	0.1986	0.0525	0.0065
	313.15	−0.6009	0.1132	0.1421	−0.0765	0.0099
	323.15	−0.6800	0.0768	−0.0316	−0.0746	0.0087

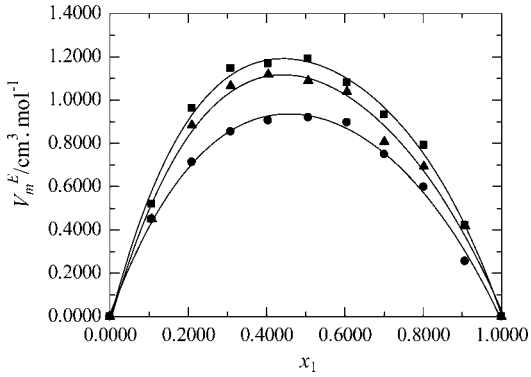

Figure 2. Excess molar volumes for MEK (1) + cyclohexane (2): ●, 303.15 K; ▲, 313.15 K; ■, 323.15 K.

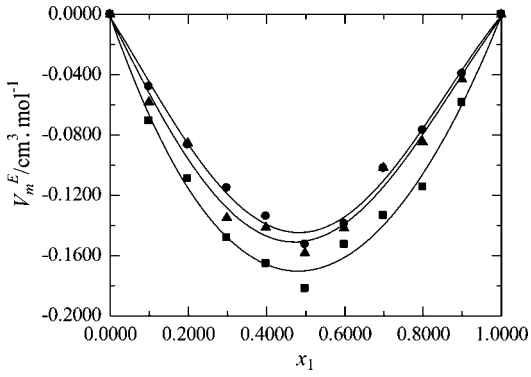

Figure 3. Excess molar volumes for MEK (1) + benzene (2): ●, 303.15 K; ▲, 313.15 K; ■, 323.15 K.

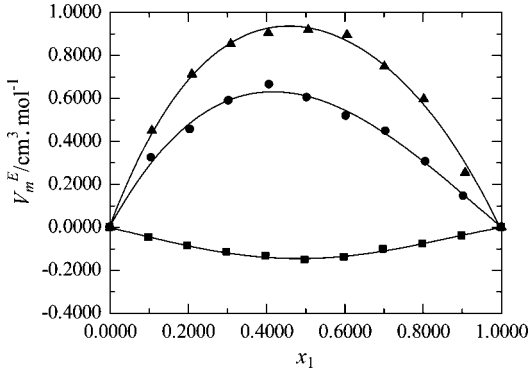

Figure 4. Comparison of the excess molar volumes for the binary mixtures at $T = 303.15$ K: ●, MEK (1) + *n*-hexane (2); ▲, MEK (1) + cyclohexane (2); ■, MEK (1) + benzene (2).

of MEK with *n*-hexane and cyclohexane, while it is negative for the system of MEK with benzene.

Comparison of the V_m^E curves shows that, throughout the whole range of composition, the V_m^E values for the binary system of MEK with cyclohexane are only slightly greater than that obtained for the system of MEK with *n*-hexane (Figure 4). However, the values of V_m^E are negative for the system of MEK with benzene. The sign of V_m^E depends upon the resultant of the factors contributing to expansion and contraction of volume. Dissociation of associated MEK in solution systems, particularly in the hydrocarbon-rich region, and dispersive force in MEK may be responsible for the expansion of volume in the present systems. For volume contraction, probable reasons to be considered are: donor−acceptor interaction between π-electrons of aromatic ring and ketone and possible inclusion of benzene at least partially into the structural network of ketone. In the hydrocarbon-rich region, disintegration of multimers of ketone into smaller units through disruption of H-bonding in ketone takes place causing the volume to expand. The contribution of dispersive force in volume expansion is clearly indicated by the more positive V_m^E obtained for *n*-hexane and cyclohexane than that for benzene. For MEK with the benzene system, the combined effect for volume contraction (i.e., donor−acceptor interaction and inclusion of benzene into the structural network of ketone, as mentioned earlier) exceeds the effects responsible for volume expansion indicated by the observed negative V_m^E. Chowdhury et al.[8] and Singh et al.[12] suggested a similar explanation for the volumetric properties of the systems of 1-hexanol with *n*-hexane and 1-propanol with xylenes, respectively.

The calculated values of V_m^E and volumetric behavior for the system of MEK with *n*-hexane are comparable with the results of Baraldi et al.[10] at $T = (303.15, 313.15, \text{and } 323.15)$ K. Volumetric behavior of MEK with cyclohexane at $T = (298.15 \text{ and } 303.15)$ K was reported by Lee et al.,[14] while data at $T = 298.15$ K were available from Ramallo et al.[15] However, no literature data are available with which to compare the present results for MEK with cyclohexane at $T = (313.15 \text{ and } 323.15)$ K. Grolier et al.[16] and Grguric et al.[17] reported experimental density data for the solvent mixture of MEK with benzene at $T = 298.15$ K, but no data are available in the literature with which we can compare the present results.

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