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Excess molar volumes of some binary methyl *tert*-butyl ether + C_6-hydrocarbon mixtures at 298.15 K

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Abstract

Excess molar volumes V_m^E, derived from density determinations, are reported for binary mixtures of methyl *tert*-butyl ether with *n*-hexane, with 2,3-dimethylbutane, and with cyclohexane at 298.15 K. For each of these mixtures, V_m^E is positive and nearly symmetric over the entire mole-fraction range.

INTRODUCTION

The excess thermodynamic properties of methyl *tert*-butyl ether (MTBE) + hydrocarbon mixtures are of interest in view of the use of MTBE as a gasoline blending agent. This paper reports excess molar volumes V_m^E at 298.15 K for the binary mixtures MTBE + *n*-hexane, MTBE + 2,3-dimethylbutane, and MTBE + cyclohexane.

EXPERIMENTAL

Materials

MTBE (HPLC grade, stated purity 99.8 mol.%) was obtained from the Aldrich Chemical Co. The *n*-hexane, 2,3-dimehtylbutane and cyclohexane were Pure Grade materials (stated minimum purity 99.0 mol.%) from the Phillips Petroleum Co. All of these materials were used as received. In some cases, samples of the components from two different lots were utilized. The densities of the individual samples are indicated in the footnotes of Table 1.

Excess molar volumes

Mixtures of the components were prepared by weighing in "onion" cells [1] specially designed to minimize the effects of evaporation. The error of the mole fraction x of MTBE is estimated to be less than 1×10^{-4}.

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TABLE 1

Densities ρ and excess molar volumes V_m^E for MTBE + C_6-hydrocarbon mixtures at 298.15 K for various mole fractions x of MTBE

x	ρ/ (g cm^{-3})	V_m^E/ (cm^3 mol^{-1})	x	ρ/ (g cm^{-3})	V_m^E/ (cm^3 mol^{-1})
$x(CH_3)_3COCH_3 + (1-x)CH_3(CH_2)_4CH_3$					
0.0494 [a]	0.658318	0.0837	0.5500 [b]	0.695240	0.4201
0.0998 [a]	0.661672	0.1600	0.5992 [a]	0.699183	0.4110
0.1493 [a]	0.665045	0.2237	0.6499 [b]	0.703569	0.3869
0.1997 [a]	0.668564	0.2791	0.6992 [a]	0.707712	0.3560
0.2499 [a]	0.672152	0.3219	0.7500 [b]	0.712305	0.3132
0.2993 [a]	0.675726	0.3622	0.7993 [a]	0.716597	0.2686
0.3496 [b]	0.679512	0.3925	0.8502 [b]	0.721409	0.2100
0.3988 [a]	0.683187	0.4126	0.8993 [a]	0.725856	0.1491
0.4495 [b]	0.687168	0.4268	0.9498 [b]	0.730840	0.0768
0.4989 [a]	0.691014	0.4287			
$x(CH_3)_3COCH_3 + (1-x)(CH_3)_2CHCH(CH_3)_2$					
0.0498 [c]	0.660584	0.0634	0.5462 [d]	0.696657	0.3119
0.0966 [c]	0.663918	0.1187	0.5993 [c]	0.700884	0.3038
0.1497 [c]	0.667316	0.1692	0.6508 [d]	0.705118	0.2825
0.1995 [c]	0.670772	0.2109	0.6976 [c]	0.708971	0.2662
0.2511 [c]	0.674418	0.2455	0.7503 [d]	0.713462	0.2298
0.2995 [c]	0.677908	0.2722	0.7998 [c]	0.717675	0.2020
0.3508 [d]	0.681672	0.2932	0.8502 [d]	0.722135	0.1550
0.3994 [c]	0.685293	0.3083	0.8998 [c]	0.726520	0.1143
0.4503 [d]	0.689185	0.3129	0.9500 [d]	0.731098	0.0581
0.4997 [c]	0.692968	0.3203			
$x(CH_3)_3COCH_3 + (1-x)C_6H_{12}$					
0.0496 [e]	0.771461	0.0679	0.5495 [c]	0.749879	0.3199
0.0996 [e]	0.768991	0.1234	0.5997 [e]	0.748060	0.3099
0.1496 [c]	0.766558	0.1770	0.6496 [e]	0.746332	0.2900
0.1995 [e]	0.764246	0.2171	0.6991 [e]	0.744638	0.2696
0.2498 [e]	0.761975	0.2531	0.7506 [e]	0.742982	0.2345
0.3008 [e]	0.759743	0.2822	0.7997 [e]	0.741398	0.2036
0.3497 [e]	0.757689	0.3014	0.8499 [e]	0.739882	0.1578
0.3949 [e]	0.755832	0.3146	0.8998 [e]	0.738369	0.1154
0.4497 [e]	0.753670	0.3213	0.9500 [e]	0.736941	0.0597
0.4990 [c]	0.751767	0.3241			

Densities $\rho_i^{\ominus}$ (g cm^{-3}) of the component liquids used for the mixtures were: [a] $\rho_1^{\ominus} = 0.735555$, $\rho_2^{\ominus} = 0.655104$; [b] $\rho_1^{\ominus} = 0.735724$, $\rho_2^{\ominus} = 0.655104$; [c] $\rho_1^{\ominus} = 0.735724$, $\rho_2^{\ominus} = 0.657323$; [d] $\rho_1^{\ominus} = 0.735724$, $\rho_2^{\ominus} = 0.657333$; [e] $\rho_1^{\ominus} = 0.735555$, $\rho_2^{\ominus} = 0.774035$.

Values of V_m^E were derived from densities ρ measured at 298.150 ± 0.005 K in an Anton Paar densimeter (Model DMA 48) using the relation

$$V_m^E = [xM_1 + (1-x)M_2]/\rho - [xM_1/\rho_1^\ominus + (1-x)M_2/\rho_2^\ominus] \quad (1)$$

where M_i and $\rho_i^\ominus$ are respectively the molar mass and density of component i (1 for MTBE and 2 for the C_6-hydrocarbon). The error of V_m^E is estimated to be less than 1×10^{-3} cm^3 mol^{-1}.

RESULTS AND DISCUSSION

The experimental values of the densities and the corresponding values of V_m^E calculated from eqn. (1) are listed in Table 1 for the three systems. Plots of V_m^E against the mole fraction x of MTBE are shown in Fig. 1.

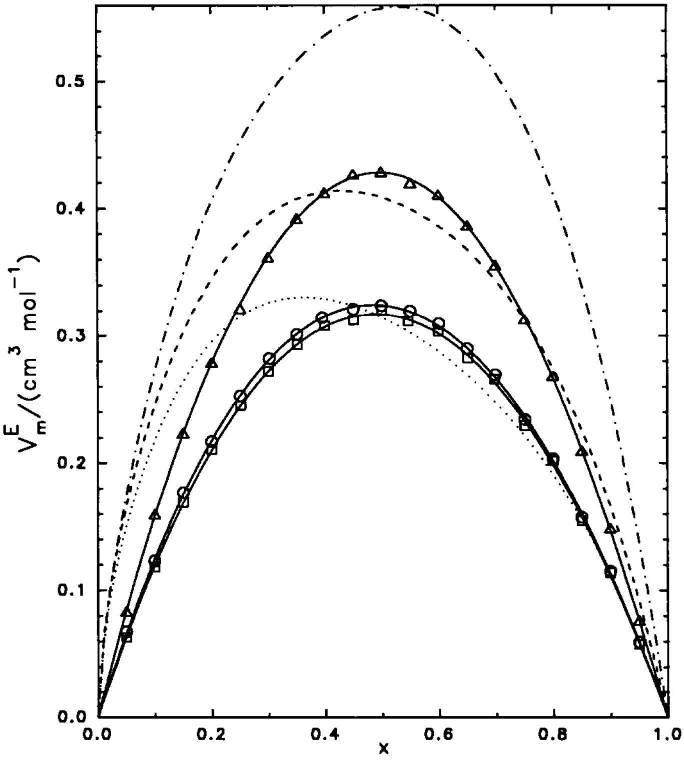

Fig. 1. Excess molar volumes V_m^E at 298.15 K for binary mixtures of MTBE or ethanol with some C_6-hydrocarbons plotted against the mole fraction x of MTBE or ethanol. Results for MTBE mixtures: △, *n*-hexane; □, 2,3-dimethylbutane; ○, cyclohexane. Curves calculated from eqn. (2) with coefficients from Table 2. Literature data for ethanol mixtures: ---, *n*-hexane [2]; ···, 2,3-dimethylbutane [3]; ·–·–, cyclohexane [2].

TABLE 2

Coefficients v_j and standard deviations s for least-squares representations of V_m^E at 298.15 K for binary mixtures of MTBE with some C_6-hydrocarbons (eqn. (2))

Component 2	v_0	v_1	v_2	v_3	s
n-Hexane	1.7128	0.0332	−0.0183	0.0802	0.0015
2,3-Dimethylbutane	1.2689	0.0604	0.0276		0.0022
Cyclohexane	1.2976	0.0842	0.0436		0.0016

The equation

$$V_m^E/(\mathrm{cm^3\,mol^{-1}}) = x(1-x)\sum_{j=0}^{n} v_j(1-2x)^j \tag{2}$$

was fitted to the results for each mixture. Values of the coefficients v_j, determined by the method of least squares with all points weighted equally, are given in Table 2, together with the standard deviations s of the representations.

Curves calculated from eqn. (2) with coefficients from Table 2 are included in Fig. 1. We are not aware of any comparable previous studies of these mixtures.

All three curves are nearly symmetrical about $x = 0.5$. The maximum value of V_m^E for the *n*-hexane system is ≈0.428 $\mathrm{cm^3\,mol^{-1}}$. The differences between the curves for the 2,3-dimethylbutane and cyclohexane systems are relatively small, and their maxima are about 25% less than for the *n*-hexane system. The larger values of V_m^E for the latter system are attributable in part to the destruction of the orientational order of the *n*-hexane molecules when the mixture is formed.

Because ethanol is also used as a gasoline oxygenating agent, it is of interest to compare the present results with those for the corresponding ethanol + C_6-hydrocarbon mixtures. Curves representing V_m^E at 298.15 K for binary mixtures of ethanol with *n*-hexane [2], cyclohexane [2], and 2,3-dimethylbutane [3] are plotted in Fig. 1. The curves for the ethanol mixtures are more asymmetric than those for the MTBE mixtures. In particular, the curves for *n*-hexane and 2,3-dimethylbutane are markedly skewed toward $x = 0$; that for cyclohexane is slightly skewed toward $x = 1$. The maxima of V_m^E are similar in magnitude for mixtures of *n*-hexane with methanol and with MTBE; the same is true for 2,3-dimethylbutane. However, the maximum for ethanol + cyclohexane is almost 75% larger than that for MTBE + cyclohexane, and as a consequence, the order of the curves for the three ethanol mixtures differs from that for the three MTBE mixtures. In the case of the ethanol mixtures, these differences reflect changes in the hydrogen bonding of the alcohol when mixed with C_6-molecules of different shape.

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