Excess Enthalpies of Binary Mixtures of Methyl *tert*-Butyl Ether with Di-*n*-alkyl Ethers

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Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for binary mixtures of methyl *tert*-butyl ether with diethyl ether and dipentyl ether. Smooth representations of the results are presented, and it is shown that the Flory theory provides a good basis for the correlation of the results with data for mixtures of methyl *tert*-butyl ether with other di-*n*-alkyl ethers.

Introduction

Previous papers from our laboratory have reported the excess enthalpies of binary mixtures of methyl *tert*-butyl ether (MTBE) with dipropyl ether (Liao *et al.*, 1997) and with dibutyl ether (Tong *et al.*, 1997). These earlier investigations have now been extended by measuring the excess molar enthalpies at 298.15 K for mixtures of MTBE with diethyl ether and dipentyl ether.

Experimental Section

The diethyl ether used in the present work was anhydrous ACS analytical reagent from BDH Chemicals. Dipentyl ether, with stated purity exceeding 99 mol %, was obtained from the Aldrich Chemical Co. Both of these ethers were stored over molecular sieve beads (Type 3A) and were used without further purification. The MTBE was the same as in our previous work (Liao *et al.*, 1997; Tong *et al.*, 1997). Densities, measured at 298.15 K in an Anton-Paar digital densimeter, were 707.91, 779.84, and 735.58 kg•m^{-3} for the diethyl ether, dipentyl ether, and MTBE, respectively.

Measurements of the excess enthalpies were carried out in an LKB flow microcalorimeter (Model 10700-1) at 298.15 K, maintained within ±0.002 K. Details of the equipment and its operation have been described previously (Tanaka *et al.*, 1975; Kimura *et al.*, 1983). Over most of the mole fraction range the errors of the excess molar enthalpy H_m^E and the mole fraction x are estimated to be less than 1.0% and 5×10^{-4}, respectively.

Results and Discussion

The experimental values of x and H_m^E at 298.15 K for $x(CH_3)_3COCH_3 + (1 - x)(C_\nu H_{2\nu+1})_2O$ with $\nu = 2$ and 5 are summarized in Table 1. Each set of data was fitted with the Redlich−Kister smoothing function

$$H_m^E/J\bullet mol^{-1} = x(1 - x)\sum_{k=1}^{m} h_k(1 - 2x)^{k-1} \qquad (1)$$

by the method of least squares with all points weighted equally. The results of these analyses are reported in the footnotes of Table 1, where the standard deviations s for the representations are also indicated.

Plots of the experimental data and their representations by eq 1 are shown in Figure 1. Also included in Figure 1 for comparison, are similar plots of the previous results for MTBE + dipropyl ether (Liao *et al.*, 1997) and MTBE + dibutyl ether (Tong *et al.*, 1997). The values of $H_m^E(x)$ for $x(CH_3)_3COCH_3 + (1 - x)(C_\nu H_{2\nu+1})_2O$ increase as the value of ν becomes larger. The curves are approximately symmetric about $x = 0.5$ but show a slight tendency to be skewed toward $x = 1$ for larger ν.

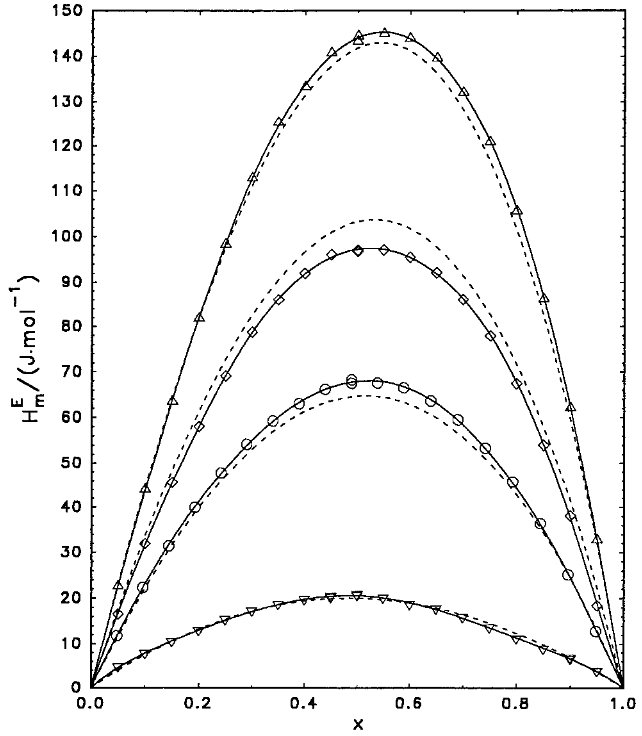

Figure 1. Excess molar enthalpies, H_m^E at 298.15 K for the binary mixtures $x(CH_3)_3COCH_3 + (1 - x)(C_\nu H_{2\nu+1})_2O$. Experimental results: (▽) $\nu = 2$; (○) $\nu = 3$; (◇) $\nu = 4$; (△) $\nu = 5$; (—) calculated from the Redlich−Kister forms; (- - -) calculated from the Flory theory with X_{12} from the last column of Table 2.

In the past, the Flory theory (Flory, 1965; Abe and Flory, 1965) has frequently proven to be useful in representing and correlating the excess enthalpies of systems containing ethers and alkanes. Accordingly, that approach was investigated for the present systems. The parameters used in the calculations are summarized in Table 2.

Values of the characteristic pressures p^*, molar volumes V_m^* and temperature T^* for MTBE, diethyl ether, and dipentyl ether were taken from our previous publications, as indicated in the footnotes of the table. In evaluating s_1/s_2, the ratio of the molecular surface areas of contact per segment for MTBE (1) + di-*n*-alkyl ether (2), it was assumed that the molecules were spherical. The values of the interchange-energy parameters X_{12} were obtained

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Table 1. Experimental Mole Fractions, x, and Excess Molar Enthalpies, H_m^E, at 298.15 K for $x(CH_3)_3COCH_3$ + $(1 - x)(C_\nu H_{2\nu+1})_2O$ with $\nu = 2$ and $\nu = 5$

x	H_m^E/J•mol^{-1}	x	H_m^E/J•mol^{-1}	x	H_m^E/J•mol^{-1}	x	H_m^E/J•mol^{-1}	x	H_m^E/J•mol^{-1}
$\nu = 2$[a]									
0.0500	4.73	0.3002	17.25	0.4997	20.76	0.6498	17.70	0.8498	8.87
0.1000	7.80	0.3504	18.66	0.4998	20.63	0.6998	15.85	0.8999	6.88
0.1499	10.53	0.3999	19.69	0.5496	20.08	0.7499	13.65	0.9000	6.56
0.2000	12.96	0.4498	20.19	0.5998	18.67	0.7999	11.20	0.9499	3.78
0.2498	15.33	0.4500	20.36						
$\nu = 5$[b]									
0.0500	22.74	0.3000	112.96	0.4995	143.38	0.5994	143.96	0.7998	105.66
0.0998	44.13	0.3496	125.41	0.4998	143.38	0.6502	139.66	0.8499	86.35
0.1499	63.60	0.4005	133.47	0.5008	144.52	0.6998	132.19	0.8999	62.23
0.1999	81.93	0.4497	140.80	0.5499	145.04	0.7497	121.03	0.9499	32.93
0.2497	98.40								

[a] $h_1 = 82.11$; $h_2 = 8.20$; $h_3 = -34.00$; $h_4 = 1.29$; $h_5 = 49.59$; $s = 0.19$. [b] $h_1 = 576.26$; $h_2 = -98.33$; $h_3 = 49.89$; $h_4 = -109.07$; $h_5 = -48.55$; $h_6 = 104.97$; $s = 0.43$.

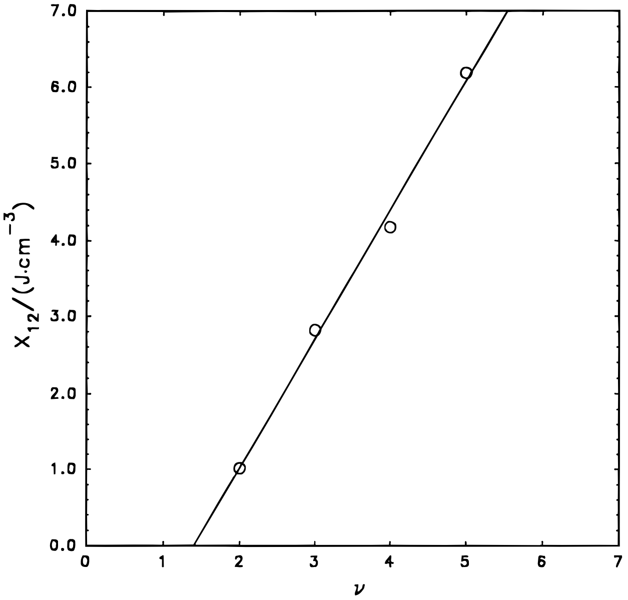

Figure 2. Flory interchange-energy parameters X_{12} for binary mixtures of MTBE with some di-*n*-alkyl ethers $(C_\nu H_{2\nu+1})_2O$ at 298.15 K, plotted against the value of ν: (○) X_{12}(fit) from column 6 of Table 2; (—) calculated from eq 2.

Table 2. Parameters Used in Flory Calculations at T = 298.15 K for MTBE (1) + Di-*n*-alkyl Ether (2)

component	p^*/ J•cm^{-3}	V_m^*/ cm^3•mol^{-1}	T^*/K	s_1/s_2	X_{12}/J•cm^{-3} fit	eq 2
MTBE	442.9[a]	90.20[a]	4385.0[a]			
diethyl ether	462.5[b]	77.07[b]	4168.8[b]	0.9489	1.0151	1.0186
dipropyl ether	441.5[c]	106.03[c]	4639.2[c]	1.0554	2.8202[c]	2.7072
dibutyl ether	450.7[d]	133.93[d]	4909.8[d]	1.1409	4.1801[d]	4.3958
dipentyl ether	450.8[e]	162.02[e]	5155.4[e]	1.2163	6.1905	6.0844

[a] Wang *et al.* (1993). [b] Luo *et al.* (1988). [c] Liao *et al.* (1997). [d] Tong *et al.* (1997). [e] Wang *et al.* (1989).

by fitting the Flory formula for H_m^E to the smooth representations of the experimental results by eq 1, using the coefficients given in the footnotes of Table 1. The values of s_1/s_2 and X_{12}, obtained in these calculations are listed in the fifth and sixth columns of Table 2. Also listed in that table are the parameters and results from our previous applications of the Flory theory to MTBE + dipropyl ether (Liao *et al.*, 1997) and MTBE + dibutyl ether (Tong *et al.*, 1997).

In Figure 2, the values of X_{12} are plotted against the value of ν for the di-*n*-alkyl ether. It can be seen that X_{12} varies nearly linearly with ν. The coefficient of linear correlation is 0.998, and the form

$$X_{12}/\text{J•cm}^{-3} = -2.3587 + 1.6886\nu \qquad (2)$$

provides a good representation. Values of X_{12}, calculated from this equation are listed in the last column of Table 2. The largest deviation from linearity (0.2157 J•cm^{-3}), occurring for dibutyl ether, is only slightly larger than the standard deviation of the linear fit (0.19 J•cm^{-3}). The broken curves in Figure 1 were calculated from the Flory theory, using the values of X_{12} from the last column of Table 2. The mean absolute relative deviations between the estimated and experimental curves in Figure 1 are all in the range 2.3−6.6%.

Literature Cited

Abe, A.; Flory, P. J. The Thermodynamic Properties of Mixtures of Small, Nonpolar Molecules. *J. Am. Chem. Soc.* **1965**, *87*, 1838−1846.

Flory, P. J. Statistical Thermodynamics of Liquid Mixtures. *J. Am. Chem. Soc.* **1965**, *87*, 1833−1838.

Kimura, F.; Benson. G. C.; Halpin, C. J. Excess Enthalpies of Binary Mixtures of *n*-Heptane with Hexane Isomers. *Fluid Phase Equilib.* **1983**, *11*, 245−250.

Liao, D.; Tong, Z.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies of (*n*-Heptane or *n*-Decane) + Methyl *tert*-Butyl Ether + Di-*n*-Propyl Ether Ternary Mixtures at 298.15 K. *Fluid Phase Equilib.* **1997**, in press.

Luo, B.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies for (Diethyl Ether + *n*-Alkane) at 298.15 K. *J. Chem. Thermodyn.* **1988**, *20*, 267−271.

Tanaka, R.; D'Arcy, P. J.; Benson, G. C. Application of a Flow Microcalorimeter to Determine the Excess Enthalpies of Binary Mixtures of Non-electrolytes. *Thermochim. Acta* **1975**, *11*, 163−175.

Tong, Z.; Liao, D.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies of Ternary Mixtures of an *n*-Alkane with Methyl *tert*-Butyl Ether and Di-*n*-Butyl Ether. *Can. J. Chem.* **1997**, in press.

Wang, L.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies of Binary Mixtures of Di-n-Pentyl Ether with n-Alkanes at 298.15 K. *Fluid Phase Equilib.* **1989**, *46*, 211−221.

Wang, L.; Benson, G. C.; Lu, B. C.-Y. Excess Molar Enthalpies of Methyl *tert*-Butyl Ether + *n*-Hexane + (*n*-Decane or *n*-Dodecane) Ternary Mixtures at 298.15 K. *Thermochim. Acta* **1993**, *213*, 83−93.

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