Excess Enthalpies of Binary Mixtures of Methyl 1,1-Dimethylpropyl Ether with Hexane Isomers

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Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the three binary systems formed by mixing methyl 1,1-dimethylpropyl ether with 2-methylpentane, 3-methylpentane, or 2,2-dimethylbutane. Smooth representations of the results and analyses in terms of the Flory theory are presented.

Introduction

The thermodynamic properties of mixtures of methyl 1,1-dimethylpropyl ether (*tert*-amyl methyl ether or TAME) with hydrocarbons are of interest in view of the use of TAME as an oxygenating agent in some commercial gasolines. Previously (Zhu *et al.*, 1994a), we reported excess molar enthalpies H_m^E at 298.15 K for binary mixtures of TAME with hexane (nC6) and 2,3-dimethylbutane (23DMB). The present paper reports similar measurements for mixtures of TAME with each of the remaining hexanes, namely, 2-methylpentane (2MP), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB).

Experimental Section

TAME (Fluka, purum) had a stated purity exceeding 97 mol %. 2MP (Pure Grade) and 22DMB (Research Grade) were obtained from the Phillips Chemical Co. 3MP was obtained from the Aldrich Chemical Co. The alkanes had stated purities of at least 99 mol %. All of the components were used without further purification. Densities, measured at 298.15 K in an Anton-Paar digital densimeter, were 765.95, 648.71, 659.90, and 644.54 kg·m^{-3} for TAME, 2MP, 3MP, and 22DMB, respectively, in reasonable agreement with the literature values (*TRC Thermodynamic Tables*, 1988a,b).

The excess molar enthalpies were determined in an LKB flow microcalorimeter 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 H_m^E and the mole fraction x of TAME are estimated to be less than 0.5% and 5×10^{-4}, respectively.

Table 1. Experimental Excess Molar Enthalpies, H_m^E, at 298.15 K for Some Binary Mixtures of TAME with Hexane Isomers

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})
$x\ CH_3CH_2C(CH_3)_2OCH_3 + (1-x)\ (CH_3)_2CHCH_2CH_2CH_3$							
0.0500	50.7	0.2999	212.0	0.5500	238.5	0.8000	144.8
0.0999	94.9	0.3501	227.8	0.6002	230.4	0.8501	113.6
0.1499	132.2	0.4000	237.9	0.6500	217.3	0.9000	77.8
0.1999	164.5	0.4500	242.7	0.7000	198.1	0.9500	35.5
0.2446	189.6	0.5000	242.6	0.7521	170.9		
$x\ CH_3CH_2C(CH_3)_2OCH_3 + (1-x)\ CH_3CH_2CH(CH_3)CH_2CH_3$							
0.0501	53.0	0.2997	218.9	0.5503	246.2	0.8001	148.4
0.1000	98.1	0.3500	234.9	0.6001	234.4	0.8493	115.7
0.1500	137.0	0.3997	244.8	0.6499	221.5	0.9000	79.1
0.1999	170.3	0.4499	249.0	0.7002	202.8	0.9500	35.8
0.2498	197.4	0.5002	250.8	0.7502	178.2		
$x\ CH_3CH_2C(CH_3)_2OCH_3 + (1-x)\ (CH_3)_3CCH_2CH_3$							
0.0500	47.5	0.3000	194.3	0.5500	220.2	0.8000	133.9
0.1000	87.2	0.3502	208.7	0.5997	213.4	0.8501	104.7
0.1501	122.1	0.4002	219.2	0.6499	201.3	0.9000	71.1
0.1999	151.8	0.4497	223.6	0.6995	182.8	0.9500	35.9
0.2450	173.8	0.5001	224.1	0.7507	158.5		

Table 2. Coefficients, h_j, and Standard Deviations, s, for the Representation of H_m^E at 298.15 K for Binary Mixtures of TAME with Hexane Isomers (Eq 1)

	TAME +				
h_j	nC6[a]	2MP	3MP	22DMB	23DMB[a]
h_1	1078.26	973.07	999.82	898.77	953.94
h_2	100.98	73.32	99.80	58.31	105.78
h_3	76.11	32.69	40.92	−4.13	36.16
h_4	−110.97	85.14	−37.35	89.39	−104.13
h_5	−142.98	−111.78	−125.65	−35.09	−83.23
h_6	215.28		170.28		216.66
s	0.8	1.1	0.9	0.7	1.0

[a] Zhu *et al.* (1994a).

Results and Discussion

The experimental values of x and H_m^E for the three binary mixtures are summarized in Table 1. The smoothing function

$$H_m^E/(\text{J·mol}^{-1}) = x(1-x)\sum_{j=1}^{m} h_j(1-2x)^{j-1} \quad (1)$$

was fitted to each set of results by the method of least squares with all points assigned equal weight. The values of the coefficients h_j obtained from the analyses are listed in Table 2, along with the standard deviation s for each representation. Plots of the experimental results and their representations by eq 1 are shown in Figure 1. Also included in Figure 1 are curves representing our previous results (Zhu *et al.*, 1994a) for TAME + nC6 and TAME + 23DMB. H_m^E is positive for all of the systems. The curves are nearly symmetric about $x = 0.5$, and fall in the order nC6 > 3MP > 2MP > 23DMB > 22DMB.

In a previous study of TAME + alkane systems (Zhu *et al.*, 1994b), the Flory theory (Flory, 1965; Abe and Flory, 1965) with an interchange-energy parameter X_{12} which depended quadratically on the chain length of the alkane, provided a good correlation of the H_m^E results. Application of the Flory theory to the present systems used the characteristic pressure p^*, molar volume V_m^*, and temperature T^* listed for each component in Table 3. The

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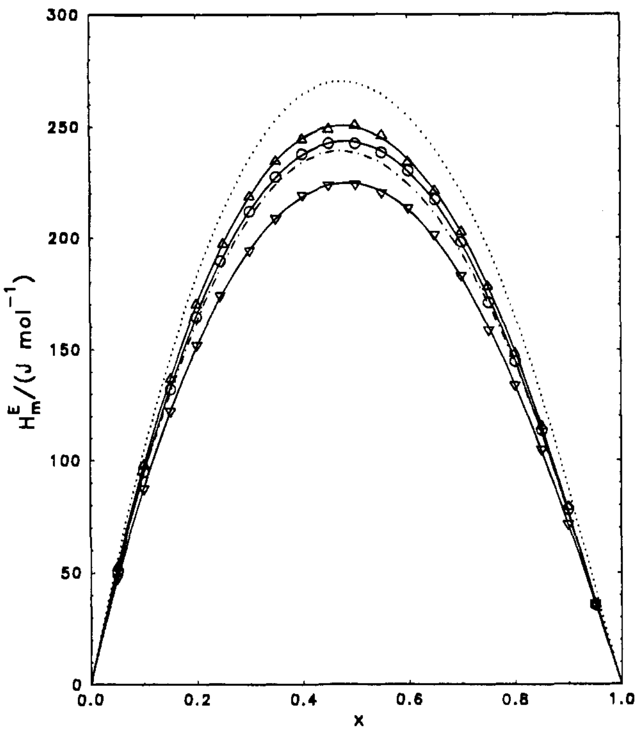

Figure 1. Excess molar enthalpies, H_m^E, of binary mixtures of TAME with hexane isomers at 298.15 K plotted against the mole fraction, x, of TAME. Experimental results: (○) 2MP; (△) 3MP; (▽) 22DMB. Curves (···) nC6 (Zhu *et al.*, 1994a); (-··-) 23DMB (Zhu *et al.*, 1994a); (—) calculated from eq 1 using the coefficients given in Table 2.

Table 3. Parameters Used in Calculations for Binary Mixtures of TAME with Hexane Isomers at 298.15 K by the Flory Theory

component	p^*/(J·cm^{-3})	V_m^*/(cm^3·mol^{-1})	T^*/K	s_{12}	X_{12}(fit)/(J·cm^{-3})	δ^2/(J·cm^{-3})	X_{12}(eq 3)/(J·cm^{-3})
TAME[a]	456.1	103.32	4714.8				
nC6[b]	424.2	99.52	4436.1	0.9876	10.146	220.906	9.946
2MP[b]	408.3	99.99	4380.8	0.9892	9.184	206.096	9.252
3MP[b]	424.2	98.68	4423.0	0.9848	9.426	212.807	9.567
22DMB[b]	389.0	100.07	4324.8	0.9894	8.566	188.535	8.430
23DMB[b]	405.3	99.16	4430.2	0.9864	8.988	203.151	9.115

[a] Flory parameters from Zhu *et al.* (1994b). [b] Flory parameters from Kimura and Benson (1983).

values of these parameters were taken from our previous investigations (Zhu *et al.*, 1994b; Kimura and Benson, 1983). Also listed in Table 3 is the ratio s_{12} of ether-to-alkane molecular surface areas of contact per segment, and the interchange-energy parameter X_{12} for each mixture. The values of s_{12} are based on the simple assumption that the molecules are spherical. The values of X_{12} in the sixth column of the table were obtained from least-squares analyses in which the Flory formula for H_m^E was fitted to the representation of the experimental results by eq 1.

A number of ways of characterizing the hexane isomers were investigated. These included the acentric factor ω, Riedel factor α_c, and solubility parameter δ (Reid and Sherwood, 1966), the molecular surface area A_w (Bondi, 1968), the number of gauche conformations Z_g (Mann *et al.*, 1967), and the molecular connectivity parameters $^1\xi$, $^2\xi$, and $^3\xi$ of the first, second, and third degrees (Singh *et al.*, 1981). Of these, the correlation coefficient of X_{12} with the Riedel factor was 0.923, and with the square of the Hildebrand solubility parameter δ was 0.963. Values of δ^2 at 298.15 K were calculated from the relation

$$\delta^2/(\mathrm{J{\cdot}cm^{-3}}) = [(H_m^v - RT)/V_m] \qquad (2)$$

using molar enthalpies of vaporization H_m^v from the *TRC Thermodynamic Tables* (1988b). These are listed in the seventh column of Table 3, and a plot of X_{12} against δ^2 is shown in Figure 2, where the least-squares line

$$X_{12}/(\mathrm{J{\cdot}cm^{-3}}) = -0.4001 + 0.04684\delta^2 \qquad (3)$$

is also plotted.

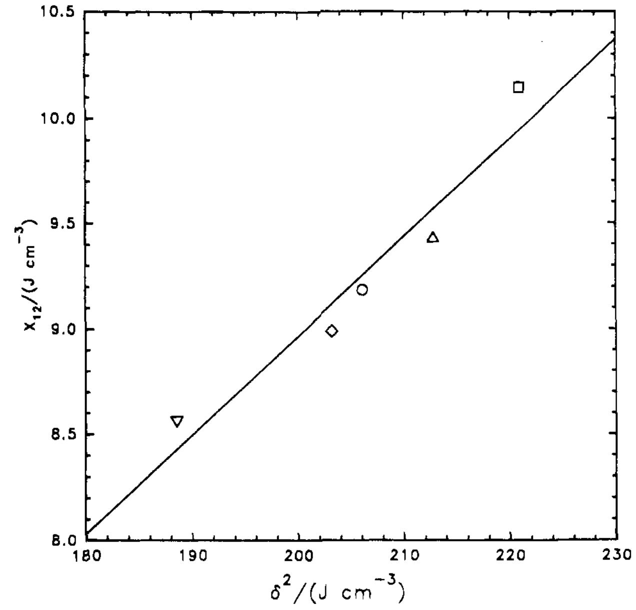

Figure 2. Flory interchange-energy parameter X_{12} for binary mixtures of TAME with hexane isomers at 298.15 K, plotted against δ^2, the square of the solubility parameter of the hexane isomer: (□) nC6; (○) 2MP; (△) 3MP; (▽) 22DMB; (◇) 23DMB; (—) plotted from eq 3.

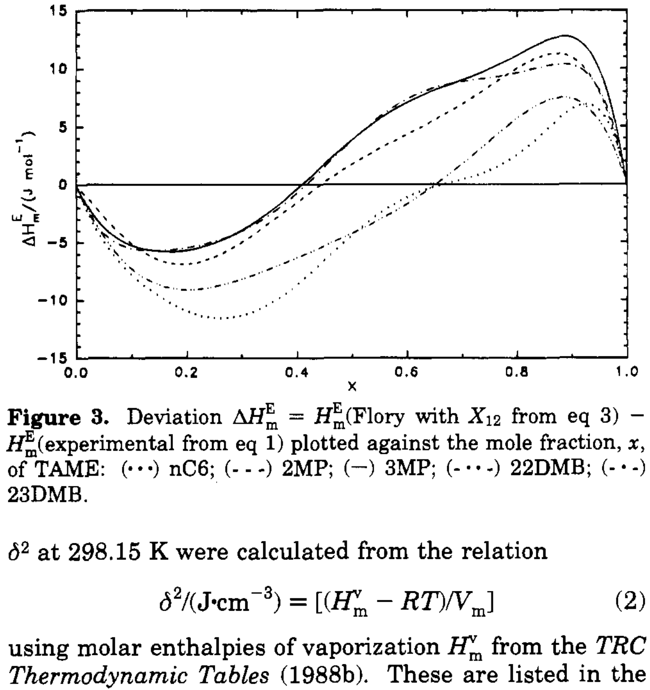

Figure 3. Deviation $\Delta H_m^E = H_m^E$(Flory with X_{12} from eq 3) − H_m^E(experimental from eq 1) plotted against the mole fraction, x, of TAME: (···) nC6; (- - -) 2MP; (—) 3MP; (-···-) 22DMB; (-··-) 23DMB.

Values of X_{12} for the five hexane isomers, calculated from eq 3, are listed in the last column of Table 3. Deviations of the values of H_m^E, estimated by the Flory theory using these X_{12}, from those calculated with the representations of the experimental results by eq 1, are plotted in Figure 3. It is evident from this that the Flory theory with X_{12} from eq 3 underestimates H_m^E for small values of x, and overestimates it for larger x. The mean absolute relative deviations between the estimated and experimental curves are all in the range of 4.0−6.0%.

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