Excess Enthalpies of Methyl 1,1-Dimethylpropyl Ether + a C_6 Hydrocarbon at 298.15 K

Shemin Zhu, Shubao Shen, George C. Benson,* and Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the four binary systems formed by mixing methyl 1,1-dimethylpropyl ether with hexane, 2,3-dimethylbutane, cyclohexane, or benzene. Smooth representations of the results are presented.

Introduction

The use of methyl 1,1-dimethylpropyl ether (*tert*-amyl methyl ether or TAME) in "oxygasoline" technology has stimulated interest in the thermodynamic properties of TAME + hydrocarbon mixtures. This paper reports measurements of excess molar enthalpies H_m^E at 298.15 K for binary mixtures of TAME with each of the C_6 hydrocarbons: hexane, 2,3-dimethylbutane, cyclohexane, and benzene.

Experimental Section

TAME and HPLC grade benzene were obtained from the Aldrich Chemical Co. Hexane, 2,3-dimethylbutane (both pure grade reagents), and cyclohexane (research grade) were obtained from the Phillips Chemical Co. The sample of TAME had a low stated minimum purity of 94 mol %, but it was the only material readily available within the time frame of our investigation. Since its density was close to the literature value (*1*), it was deemed to be adequate for the present measurements of technological interest. The other components had stated purities exceeding 99 mol %. All of the components were used without further purification. Their densities, measured at 298.15 K in an Anton-Paar digital densimeter, were 765.91, 655.04, 657.13, 773.94, and 873.63 kg m^{-3} for TAME, hexane, 2,3-dimethylbutane, cyclohexane, and benzene, respectively. These results agree reasonably with the literature values (*1*, *2*).

The measurements of H_m^E at 298.150 ± 0.002 K used the same equipment and operating procedure as in our previous work (*3*, *4*). 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.

Results and Discussion

The experimental values of H_m^E for the four systems are listed in Table 1, where in all cases x is the mole fraction of TAME. Plots of the results are shown in Figure 1. The equation

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

was fitted to each set of results by the method of least squares with all points weighted equally. Values of the coefficients, h_j, and the standard deviations, s, for these representations are given in Table 2. Curves calculated from eq 1 are included in Figure 1.

Table 1. Experimental Excess Molar Enthalpies, H_m^E, at 298.15 K for Some TAME + C_6 Hydrocarbon Mixtures

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})
			$x\ C_2H_5C(CH_3)_2OCH_3 + (1-x)\ CH_3(CH_2)_4CH_3$				
0.0500	55.9	0.3001	235.7	0.5001	268.2	0.7503	195.1
0.1000	104.6	0.3500	252.7	0.5501	265.7	0.8000	165.9
0.1500	147.2	0.3999	264.4	0.6007	253.0	0.8500	129.4
0.2000	182.7	0.4500	270.0	0.6500	241.3	0.9000	87.1
0.2499	211.6	0.5001	270.2	0.7001	220.7	0.9500	43.3
			$x\ C_2H_5C(CH_3)_2OCH_3 + (1-x)\ (CH_3)_2CHCH(CH_3)_2$				
0.0500	50.5	0.3000	207.8	0.5002	238.1	0.7500	170.3
0.1000	93.7	0.3500	224.2	0.5499	233.3	0.8000	143.6
0.1500	131.7	0.4000	234.2	0.5999	223.9	0.8500	111.8
0.2001	163.4	0.4501	240.2	0.6501	211.1	0.9000	77.3
0.2501	187.6	0.5000	238.9	0.6999	193.4	0.9500	35.5
			$x\ C_2H_5C(CH_3)_2OCH_3 + (1-x)\ C_6H_{12}$				
0.0500	87.1	0.3001	357.4	0.5500	386.6	0.8000	233.0
0.1000	163.0	0.3501	381.4	0.6001	369.9	0.8500	183.4
0.1500	230.4	0.3998	395.2	0.6498	345.6	0.9000	126.1
0.2000	283.0	0.4499	399.7	0.7000	316.4	0.9500	65.5
0.2498	324.2	0.5001	398.6	0.7500	277.4		
			$x\ C_2H_5C(CH_3)_2OCH_3 + (1-x)\ C_6H_6$				
0.0500	56.6	0.3499	209.4	0.5502	193.4	0.7999	101.6
0.1000	104.2	0.4001	211.4	0.6000	180.6	0.8500	73.0
0.1501	141.6	0.4500	208.0	0.6501	164.3	0.8500	71.9
0.1999	168.1	0.5001	201.7	0.7002	143.0	0.8997	48.2
0.2500	188.6	0.5002	203.0	0.7491	122.4	0.9499	16.5
0.3000	202.2						

0021-9568/94/1739-0302$04.50/0 © 1994 American Chemical Society

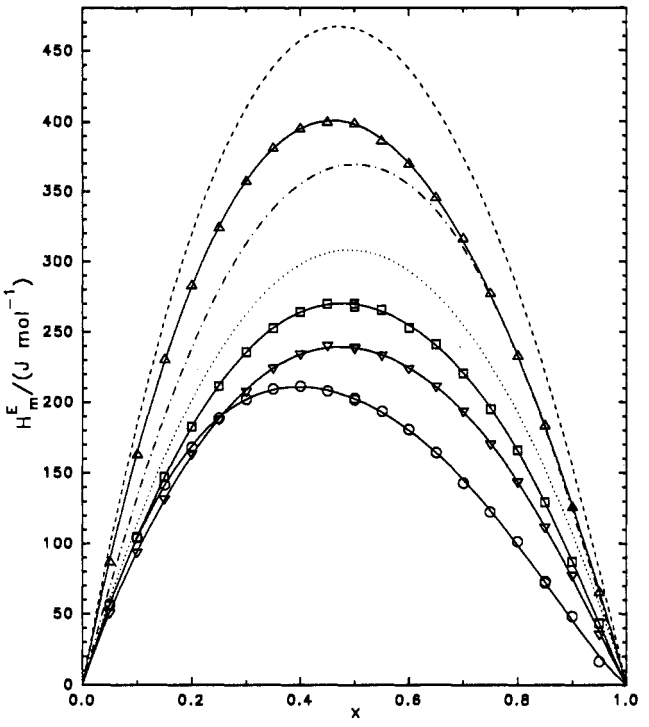

Figure 1. Excess molar enthalpies, H^E_m, of some TAME + C_6 hydrocarbon systems at 298.15 K plotted against the mole fraction, x, of TAME. Experimental results: (□) hexane; (▽) 2,3-dimethylbutane; (△) cyclohexane; (○) benzene. Curves: (—) calculated from eq 1 using the coefficients given in Table 2; (---) MTBE + hexane (*6*); (···) MTBE + 2,3-dimethylbutane (*7*); (- - -) MTBE + cyclohexane (*8*).

H^E_m is positive for all of the systems, and maxima fall in the order cyclohexane > hexane > 2,3-dimethylbutane > benzene. The curves are all skewed toward $x = 0$, but the skew of the benzene curve is more pronounced, and as a consequence the benzene and 2,3-dimethylbutane curves cross near $x = 0.25$.

We are not aware of any directly comparable previous studies of these systems. A few measurements of H^E_m at 293.15 K have been reported for methyl amyl ether + benzene by Kehiaian *et al.* (*5*). These indicate a maximum of ~220 J mol^{-1} near $x = 0.4$. This compares reasonably with our findings for TAME.

Methyl *tert*-butyl ether (MTBE) is also used as a gasoline oxygenating additive. Previously, we have reported values of H^E_m at 298.15 K for binary mixtures of MTBE with hexane (*6*), 2,3-dimethylbutane (*7*), and cyclohexane (*8*). Curves calculated from the smooth representations of these data are shown in Figure 1 for comparison with the TAME systems. The curves for MTBE fall in the same order as those for TAME, but in all cases the values of H^E_m are larger. At $x = 0.5$ the differences are 100, 69, and 67 J mol^{-1} for hexane, 2,3-dimethylbutane, and cyclohexane, respectively.

Table 2. Coefficients, h_j, and Standard Deviations, s, for the Representation of H^E_m at 298.15 K for Some TAME + C_6 Hydrocarbon Systems by Eq 1

	TAME +			
h_j	hexane	2,3-dimethylbutane	cyclohexane	benzene
h_1	1078.26	953.94	1592.81	809.31
h_2	100.98	105.78	256.45	316.47
h_3	76.11	36.16	45.40	137.47
h_4	−110.97	−104.13		136.27
h_5	−142.98	−83.23		−165.96
h_6	215.28	216.66		
s	0.8	1.0	1.1	1.6

Literature Cited

(1) *TRC—Thermodynamic Tables—Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1988; 1963, loose-leaf data sheet 23-2-1-[1.2121]-a.
(2) Riddick, J. A.; Bunger, W. B.; Sakano, T.K. In *Organic Solvents*, 4th ed.; Weissberger, A., Ed.; John Wiley and Sons: New York, 1986; Techniques of Chemistry, Vol. II, pp 90, 92, 99, and 135.
(3) Tanaka, R.; D'Arcy, P. J.; Benson, G. C. *Thermochim. Acta* **1975**, *11*, 163.
(4) Kimura, F.; Benson, G. C.; Halpin, C. J. *Fluid Phase Equilib.* **1983**, *11*, 245.
(5) Kehiaian, H. V.; Sosnkowska-Kehiaian, K.; Hryniewicz, R. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 922.
(6) Wang, L.; Benson, G. C.; Lu, B. C.-Y. *Thermochim. Acta* **1993**, *213*, 83.
(7) Wang, L.; Benson, G. C.; Lu, B. C.-Y. *J. Chem. Thermodyn.* **1992**, *24*, 1305.
(8) Zhu, S.; Shen, S.; Benson, G. C.; Lu, B. C.-Y. *Thermochim. Acta*, in press.

Received for review June 23, 1993. Revised November 15, 1993. Accepted November 30, 1993.• The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

• Abstract published in *Advance ACS Abstracts*, February 1, 1994.