Excess Enthalpies of 2-Methyltetrahydrofuran + *n*-Alkane Binary Mixtures at 298.15 K

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Excess molar enthalpies, measured at 298.15 K in a microcalorimeter, are reported for the binary systems formed by mixing 2-methyltetrahydrofuran with hexane, heptane, octane, decane, or dodecane. Smooth representations of the results are described.

Introduction

Adverse concerns with regard to the use of methyl *tert*-butyl ether (MTBE) as a gasoline additive have provided an incentive to consider its replacement by other oxygenates. One possibility is 2-methyltetrahydrofuran (MTHF), which can be produced from agricultural waste. However, there have been relatively few studies of the thermodynamic properties of systems formed by mixing MTHF with various hydrocarbons. The present paper reports excess molar enthalpies, measured at 298.15 K, for binary mixtures composed of MTHF and either hexane (nC6), heptane (nC7), octane (nC8), decane (nC10), or dodecane (nC12).

Experimental Section

MTHF and nC6 were obtained from Aldrich; nC7, nC8, nC10, and nC12 were obtained from Sigma. In all cases, the purities stated by the manufacturers were at least 99 mol %. Apart from partial degassing, all of the components were used without further purification. Densities, ρ/kg·m^{-3}, measured at 298.15 K in an Anton−Paar digital densimeter, were 848.10, 655.39, 679.92, 698.73, 726.34, and 745.47 for MTHF, nC6, nC7, nC8, nC10, and nC12, respectively. The result for MTHF, which is ∼1% lower than the value given in the TRC Tables,[1] is fairly close to the more recent value reported by De Lorenzi et al.[2] The results for the alkanes are in reasonable agreement with values in the TRC Tables.[3]

An LKB flow microcalorimeter (model 10700-1), thermostated at (298.150 ± 0.003) K, was used to measure the excess molar enthalpies H_m^E. Details of the equipment and its operation have been described previously.[4,5] Over most of the mole fraction range, the errors of the excess molar enthalpies and the mole fractions of the mixtures are estimated to be $<0.005\cdot|H_m^E|$ and $<5 \times 10^{-4}$, respectively.

Results and Discussion

The experimental results for the excess molar enthalpies, H_m^E, of the five binary MTHF (1) + *n*-alkane (2) mixtures at 298.15 K are listed in Table 1 and plotted in Figure 1. The smoothing function

$$H_m^E/\mathrm{J\cdot mol^{-1}} = x_1(1-x_1)\sum_{k=1}^{n} h_k(1-2x_1)^{k-1} \qquad (1)$$

was fitted to the results by a least-squares method, with all points weighted equally. Values of the coefficients h_k are listed in Table 2, along with the standard deviation s for each of the representations. Curves calculated from these representations are plotted in Figure 1.

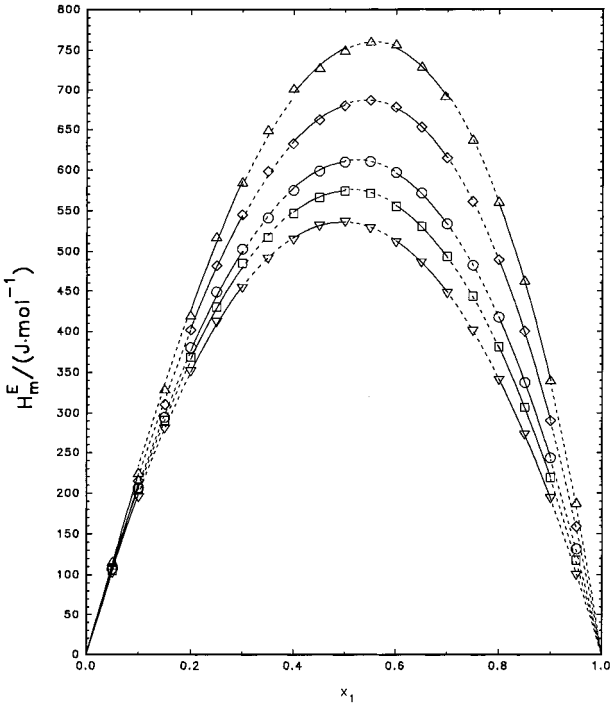

Figure 1. Excess molar enthalpies, H_m^E, for MTHF (1) + *n*-alkane (2) at 298.15 K. Experimental results: ▽, nC6; □, nC7; ○, nC8; ◇, nC10; △, nC12. Curves: —, calculated from the representations of the results by eq 1 with values of the coefficients given in Table 2; - - -, fit of results by the Liebermann−Fried model.

In all cases, the enthalpies are positive and, for a given x_1, H_m^E increases nearly linearly with increase in the chain length of the alkane. The curve for nC6 is nearly symmetric about $x_1 = 0.5$, but there is a slight tendency for the maxima of the curves to shift to higher mole fractions for the longer alkanes.

Recent work[6] indicates that an extension of the model of Liebermann and Fried[7,8] can be useful in representing the excess enthalpies of binary mixtures and also has the potential for estimating the enthalpies of ternary mixtures from data for the pure components and their binary

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Table 1. Experimental Mole Fractions, x_1, and Excess Molar Enthalpies, H_m^E, for MTHF (1) + *n*-Alkane (2) Mixtures at 298.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
				MTHF (1) + nC6 (2)					
0.0500	103.23	0.2500	412.55	0.4500	532.52	0.6499	486.64	0.8499	273.98
0.1000	195.81	0.2997	454.84	0.5005	537.46	0.7004	448.19	0.9000	194.56
0.1500	281.37	0.3497	491.85	0.5501	529.70	0.7499	401.52	0.9500	100.79
0.2000	352.15	0.3999	515.65	0.6003	512.14	0.8005	341.43		
				MTHF (1) + nC7 (2)					
0.0501	105.42	0.2501	430.45	0.4503	566.38	0.6501	531.09	0.8500	307.36
0.1000	205.98	0.3000	485.11	0.5003	574.21	0.7002	493.84	0.9000	219.10
0.1500	291.12	0.3500	517.54	0.5502	571.49	0.7498	443.63	0.9499	117.85
0.2000	368.37	0.4001	547.24	0.6006	555.40	0.8004	381.25		
				MTHF (1) + nC8 (2)					
0.0500	107.67	0.2501	448.93	0.4504	599.12	0.6503	571.73	0.8501	337.78
0.1001	206.61	0.3001	503.05	0.5001	610.26	0.6999	534.15	0.9000	243.45
0.1500	294.67	0.3499	541.47	0.5500	610.97	0.7502	482.83	0.9500	131.69
0.2000	380.05	0.3996	575.01	0.6004	597.18	0.8000	417.75		
				MTHF (1) + nC10 (2)					
0.1001	215.14	0.3000	545.38	0.5001	680.16	0.6999	615.31	0.8500	400.40
0.1502	310.94	0.3501	598.55	0.5503	687.10	0.7496	561.39	0.9000	290.70
0.2000	402.01	0.3990	632.77	0.5999	678.30	0.8003	489.48	0.9500	159.18
0.2500	482.15	0.4500	662.44	0.6501	653.42				
				MTHF (1) + nC12 (2)					
0.0500	115.27	0.2499	517.69	0.4503	727.66	0.6502	729.67	0.8500	462.50
0.0999	224.30	0.2999	584.57	0.4997	749.34	0.6961	691.80	0.9000	339.43
0.1500	328.67	0.3499	648.98	0.5505	760.11	0.7501	637.23	0.9500	187.42
0.1999	419.31	0.4000	701.53	0.5999	756.72	0.8001	560.47		

Table 2. Coefficients, h_k, and Standard Deviations, *s*, for the Representation of H_m^E by Equation 1 for the Binary Mixtures of MTHF (1) with an *n*-Alkane (2) at 298.15 K

alkane	h_1	h_2	h_3	h_4	h_5	h_6	*s* J·mol^{-1}
nC6	2145.77	42.35	54.73				1.73
nC7	2298.97	−80.17	109.24				2.18
nC8	2443.43	−181.55	109.85	−98.50			2.49
nC10	2723.73	−429.51	284.04	99.02	−267.95	−432.04	1.88
nC12	3011.67	−565.87	190.76	−372.29			3.34

Table 3. Values of the Interaction Parameters, A_{ij} and A_{ji}, Standard Deviations, *s*, and Isobaric Thermal Expansivity, α_p, at 298.15 K for Liebermann−Fried Model Calculations

component					α_p (kK^{-1})	
i	*j*	A_{ij}	A_{ji}	*s*/J·mol^{-1}	*i*	*j*
MTHF	nC6	0.8155	0.8525	1.70	1.215[a]	1.387[b]
MTHF	nC7	0.8515	0.7946	2.62	1.215[a]	1.256[b]
MTHF	nC8	0.8884	0.7423	2.80	1.215[a]	1.164[b]
MTHF	nC10	0.9416	0.6652	3.38	1.215[a]	1.051[b]
MTHF	nC12	0.9804	0.6070	5.74	1.215[a]	0.960[b]

[a] Estimated from the density data of De Lorenzi et al.[2] [b] Benson et al.[9]

mixtures. It is therefore of interest to examine how well the Liebermann−Fried model can represent the enthalpies of the present binary systems.

The equations used in this application have been outlined by Wang et al.[6] Values of the Liebermann−Fried interaction parameters, A_{ij} and A_{ji}, for each of the binary mixtures are given in Table 3. These were obtained by fitting the Liebermann−Fried formula for $H_{m,ij}^E$ to the primary experimental results in Table 1. Also included in Table 3 are values of the standard deviations *s* achieved in the fitting process and values[2,9] of the isobaric thermal expansivities α_p of the components, used in evaluating the contributions due to different molecular sizes. The fits of the experimental results by the Liebermann−Fried model are plotted as broken lines in Figure 1. Although the standard deviations in Table 3 tend to be higher than those in Table 2, it can be seen from Figure 1 that the Liebermann−Fried model provides useful representations of the enthalpy data for the present systems.

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