

Excess Enthalpies of Heptane + Ethanol + 1,2-Dimethoxyethane at 298.15 K

Ding-Yu Peng,[†] 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 ternary system heptane (1) + ethanol (2) + 1,2-dimethoxyethane (3). A smooth representation of the results is described and used to construct constant-enthalpy contours on a Roozeboom diagram. A relative maximum of the excess molar enthalpy (1585 J·mol⁻¹) is found where $x_1 = 0.4047$ and $x_2 = 0.1862$.

Introduction

Various ethers and short chain alkanols are added to gasoline to enhance the octane rating and to reduce pollution effects. A knowledge of the thermodynamic properties of mixtures comprising hydrocarbons and such materials is important for the efficient use of the latter as oxygenating agents in gasoline technology. A recent paper (Benson et al., 1998) from our laboratory described measurements of excess molar enthalpies at 298.15 K for the ternary system consisting of heptane (nC7), methyl 1,1-dimethylethyl ether (MTBE), and the diether 1,2-dimethoxyethane (DME). As an extension of that investigation, similar measurements have been made for the analogous system in which the second component is replaced by ethanol (EtOH).

Experimental Section

The nC7, Pure Grade from the Phillips Chemical Co., and the DME, HPLC Grade from Sigma-Aldrich, were the same as used in our previous work (Benson et al., 1998). Anhydrous EtOH, purchased from Commercial Alcohols Inc., was dried over molecular sieves type 3A. With that exception, the components were used as received from the suppliers. Densities, $\rho/\text{kg}\cdot\text{m}^{-3}$, measured at 298.15 K in an Anton-Paar digital densimeter, were 679.76, 785.33, and 861.29 for nC7, EtOH, and DME, respectively. These values are in reasonable agreement with values in the literature (TRC, 1988a,b; Riddick et al., 1986).

Excess molar enthalpies, H_m^E , were determined in an LKB flow microcalorimeter (model 10700-1), thermostated at 298.15 K, maintained within ± 0.003 K. Previous publications (Tanaka et al., 1975; Kimura et al., 1983) have described this equipment and the operating procedures. In studying the ternary system, the excess molar enthalpy $H_{m,1+23}^E$ was determined for several pseudo-binary mixtures in which component 1 (nC7) was added to binary mixtures of components 2 (EtOH) and 3 (DME), having fixed compositions. For this purpose, binaries with fixed mole ratios, x_2/x_3 , were prepared by mass. The excess

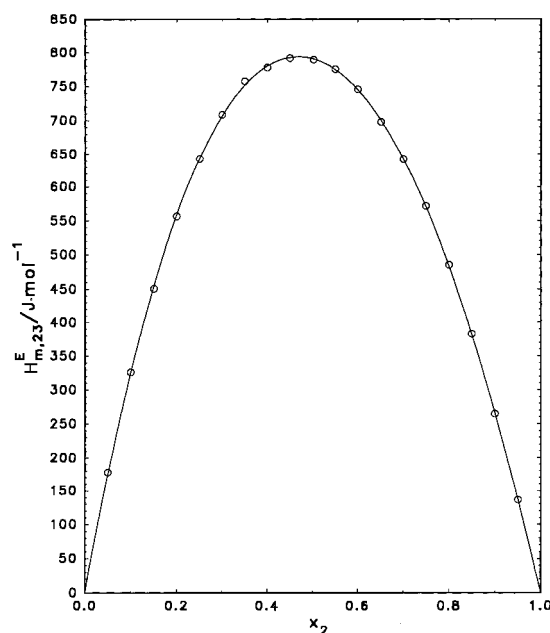


Figure 1. Excess molar enthalpies, $H_{m,23}^E$, for EtOH (2) + DME (3) at 298.15 K. Experimental results: \circ . Curves: —, calculated from the representation of the results by eq 2 using the coefficients given in Table 2.

molar enthalpy $H_{m,123}^E$ of the ternary mixture was then obtained from the relation

$$H_{m,123}^E = H_{m,1+23}^E + (1 - x_1)H_{m,23}^E \quad (1)$$

where x_1 is the mole fraction of nC7 and $H_{m,23}^E$ is the excess molar enthalpy of the particular binary mixture. Over most of the mole fraction range, the errors of $H_{m,1+23}^E$ are estimated to be less than 0.5%. Errors in the mole fractions of the final ternary mixtures are estimated to be less than 5×10^{-4} .

Results and Discussion

Excess molar enthalpies $H_{m,ij}^E$ ($i < j$), for two of the three constituent-binary mixtures of present interest, have been reported previously: nC7 (1) + EtOH (2) (Tong et al.,

[†] Visiting Professor on sabbatical leave from the Department of Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5C9.

Table 1. Experimental Mole Fractions, x_2 , and Excess Molar Enthalpies, $H_{m,23}^E$, for EtOH (2) + DME (3) at 298.15 K

x_2	$H_{m,23}^E/\text{J}\cdot\text{mol}^{-1}$	x_2	$H_{m,23}^E/\text{J}\cdot\text{mol}^{-1}$	x_2	$H_{m,23}^E/\text{J}\cdot\text{mol}^{-1}$	x_2	$H_{m,23}^E/\text{J}\cdot\text{mol}^{-1}$	x_2	$H_{m,23}^E/\text{J}\cdot\text{mol}^{-1}$
0.0500	177.7	0.2504	642.9	0.4498	791.8	0.6507	697.8	0.8493	382.5
0.1000	325.9	0.3000	708.3	0.5019	789.6	0.7003	642.3	0.8999	264.9
0.1501	450.8	0.3501	757.5	0.5498	775.4	0.7498	571.9	0.9501	136.5
0.2001	556.5	0.3995	777.5	0.5999	745.3	0.8000	485.1		

Table 2. Coefficients, h_k , and Standard Deviations, s , for the Representation of $H_{m,ij}^E$ ($i < j$) by Eq 2 for the Constituent Binary Mixtures at 298.15 K

component		h_0	h_1	h_2	h_3	h_4	h_5	$s/\text{J}\cdot\text{mol}^{-1}$
EtOH	DME	0.0	3163.21	368.49	353.38	70.33	-262.04	2.42
nC7	EtOH ^a	0.9566	2370.46	1736.60	525.89	906.38	469.43	1.30
nC7	DME ^b	0.0	5139.30	179.17	517.85			2.78

^a Tong et al. (1996). ^b Kumaran and Benson (1986).

Table 3. Experimental Excess Molar Enthalpies, $H_{m,1+23}^E$, Measured at 298.15 K, for the Addition of nC7 to EtOH + DME Mixtures To Form nC7 (1) + EtOH (2) + DME (3), and Values of $H_{m,123}^E$ Calculated from Eq 1

x_1	$H_{m,1+23}^E/\text{J}\cdot\text{mol}^{-1}$	$H_{m,123}^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_{m,1+23}^E/\text{J}\cdot\text{mol}^{-1}$	$H_{m,123}^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_{m,1+23}^E/\text{J}\cdot\text{mol}^{-1}$	$H_{m,123}^E/\text{J}\cdot\text{mol}^{-1}$
$x_2/x_3 = 0.3444, H_{m,23}^E/\text{J}\cdot\text{mol}^{-1} = 651.7$								
0.0499	266.8	885.9	0.4003	1185.6	1576.4	0.6995	1048.4	1244.3
0.0998	487.5	1074.2	0.4501	1214.7	1573.0	0.7492	950.1	1113.5
0.1497	685.2	1239.3	0.4995	1224.3	1550.5	0.7994	838.6	969.3
0.1999	827.6	1349.0	0.5516	1206.0	1498.2	0.8499	690.1	788.0
0.2500	957.0	1445.8	0.5992	1179.3	1440.5	0.8998	511.3	576.6
0.3007	1060.1	1515.8	0.6495	1123.2	1351.6	0.9499	295.5	328.2
0.3497	1131.2	1555.0						
$x_2/x_3 = 0.9866, H_{m,23}^E/\text{J}\cdot\text{mol}^{-1} = 791.4$								
0.0500	240.5	992.4	0.4001	1023.3	1498.1	0.6992	928.1	1166.2
0.0998	440.0	1152.5	0.4496	1049.2	1484.8	0.7494	852.8	1051.1
0.1502	613.3	1285.9	0.4978	1062.8	1460.2	0.7993	756.0	914.8
0.1999	736.1	1369.3	0.4984	1062.1	1459.1	0.8496	635.5	754.6
0.2500	839.9	1433.5	0.5496	1053.2	1409.6	0.8996	490.1	569.6
0.2995	922.5	1476.9	0.5992	1026.1	1343.3	0.9498	317.8	357.5
0.3495	984.5	1499.3	0.6497	984.5	1261.8			
$x_2/x_3 = 2.9501, H_{m,23}^E/\text{J}\cdot\text{mol}^{-1} = 575.4$								
0.0499	200.1	746.8	0.3993	813.6	1159.2	0.6995	766.3	939.2
0.0998	363.7	881.7	0.4490	836.3	1153.3	0.6996	765.8	938.6
0.1498	489.0	978.2	0.4498	836.3	1152.9	0.7493	717.2	861.4
0.1998	595.0	1055.4	0.4999	846.3	1134.1	0.7994	645.1	760.5
0.2500	670.7	1102.2	0.5487	839.1	1098.8	0.7997	651.1	766.4
0.2506	670.6	1101.8	0.5497	841.8	1100.9	0.8495	567.8	654.4
0.2993	734.6	1137.8	0.5995	830.1	1060.6	0.8996	456.4	514.2
0.3492	780.5	1155.0	0.6494	801.6	1003.3	0.9499	319.0	347.8
0.3499	785.0	1159.0	0.6494	802.6	1004.3	0.9499	322.7	351.5
0.3992	814.4	1160.1						

^a Ternary term for representation of $H_{m,1+23}^E$ by eqs 2 and 3: $H_{m,1+23}^E/\text{J}\cdot\text{mol}^{-1} = \{x_1x_2x_3/(1-x_1-x_2)\} (3412.60 + 2546.74x_1 + 355.49x_2 - 9564.48x_1^2 - 7060.32x_1x_2 + 4762.92x_2^2 + 8122.74x_1^3)$, $s = 3.8 \text{ J}\cdot\text{mol}^{-1}$.

1996) and nC7 (1) + DME (3) (Kumaran and Benson, 1986). Experimental values for the binary mixture EtOH (2) + DME (3) at 298.15 K are summarized in Table 1. The smoothing function

$$H_{m,ij}^E/\text{J}\cdot\text{mol}^{-1} = x_jx_i[1 + h_0(x_j - x_i)]^{-1} \sum_{k=1}^n h_k(x_j - x_i)^{k-1} \quad (2)$$

was fitted to these results by the method of least-squares, with all points weighted equally. Values of the coefficients h_k are listed in Table 2, along with the standard deviation s of the representation. For convenience, the coefficients and the standard deviations for the two other binary mixtures are also included in Table 2. The results for EtOH (2) + DME (3) and their representation by eq 2 are plotted in Figure 1. The curve is slightly skewed toward

$x_2 = 0$ with a maximum value of $H_{m,23}^E \approx 794 \text{ J}\cdot\text{mol}^{-1}$ occurring near $x_2 = 0.47$.

The experimental results for the ternary mixtures are reported in Table 3, where values of $H_{m,1+23}^E$ are listed against the mole fraction x_1 of nC7. Also included in the table are the corresponding values of $H_{m,123}^E$, calculated from eq 1. The values of $H_{m,1+23}^E$ are plotted in Figure 2, along with curves for the constituent-binary mixtures having $x_2 = 0$ (Kumaran and Benson, 1986) and $x_1 + x_2 = 1$ (Tong et al., 1996). The latter were calculated from eq 2 using values of the coefficients given in Table 2. In all cases, the maximum values of $H_{m,1+23}^E$ and $H_{m,123}^E$ occur near $x_1 = 0.5$, and at constant x_1 , the enthalpies increase with increase in the relative content of the diether in the mixture.

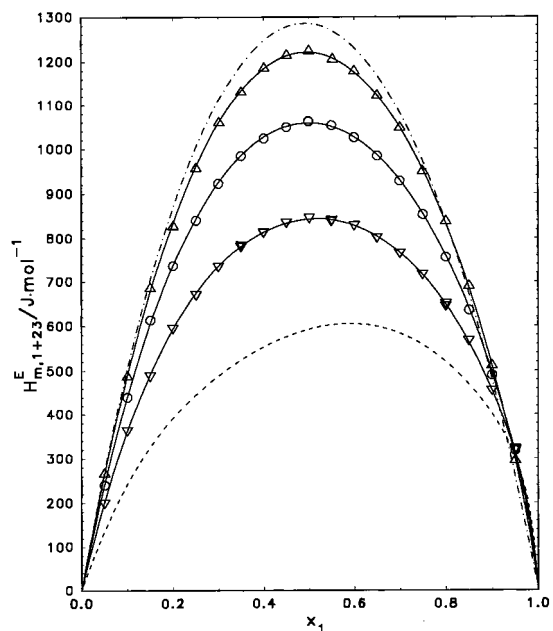


Figure 2. Excess molar enthalpies, $H_{m,1+23}^E$, for nC7 (1) + EtOH (2) + DME (3) at 298.15 K. Experimental results: Δ , $x_2/x_3 = 0.3444$; \circ , $x_2/x_3 = 0.9866$; ∇ , $x_2/x_3 = 2.9501$. Curves: \cdots , $x_2 = 0$, Kumaran and Benson (1986); $---$, $x_1 + x_2 = 1$, Tong et al. (1996); $-$, calculated from the representation of the results by eqs 2–4, using the ternary term $H_{m,T}^E$ given in the footnote of Table 3.

As in our previous work (Benson et al., 1998), the values of $H_{m,1+23}^E$ were represented as a sum of binary terms

(Tsao and Smith, 1953) with an added ternary contribution

$$H_{m,1+23}^E = [x_2/(1-x_1)]H_{m,12}^E + [x_3/(1-x_1)]H_{m,13}^E + H_{m,T}^E \quad (3)$$

where values of the $H_{m,ij}^E$ were calculated from the appropriate smoothing functions. The form

$$H_{m,T}^E/\text{J}\cdot\text{mol}^{-1} = [x_1x_2x_3/(1-x_1-x_2)](c_0 + c_1x_1 + c_2x_2 + c_3x_2^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + \dots) \quad (4)$$

which was adopted for the ternary contribution, is similar to that used by Morris et al. (1975) with an extra skewing factor $(1-x_1-x_2)^{-1}$ inserted. Values of the parameters c_i were obtained from least-squares analyses in which eqs 3 and 4 were fitted to the experimental values in Table 3. The resulting representation of $H_{m,T}^E$ is given in the footnote of the table, along with the standard deviation s of the fit. The solid curves for $H_{m,1+23}^E$ in Figure 2 were calculated from eq 3 using this representation.

Eqs 1–4 were also used to calculate the constant $H_{m,123}^E$ contours plotted on the Roozeboom diagram in Figure 3. It can be seen that there is a relative maximum of $H_{m,123}^E = 1585 \text{ J}\cdot\text{mol}^{-1}$, located inside the triangle where $x_1 = 0.4047$ and $x_2 = 0.1862$. This differs from our previous findings for the analogous system in which component 2 was MTBE (Benson et al., 1998). In that case, there was no indication of an internal maximum. The present behavior is similar to that found for other ternary systems

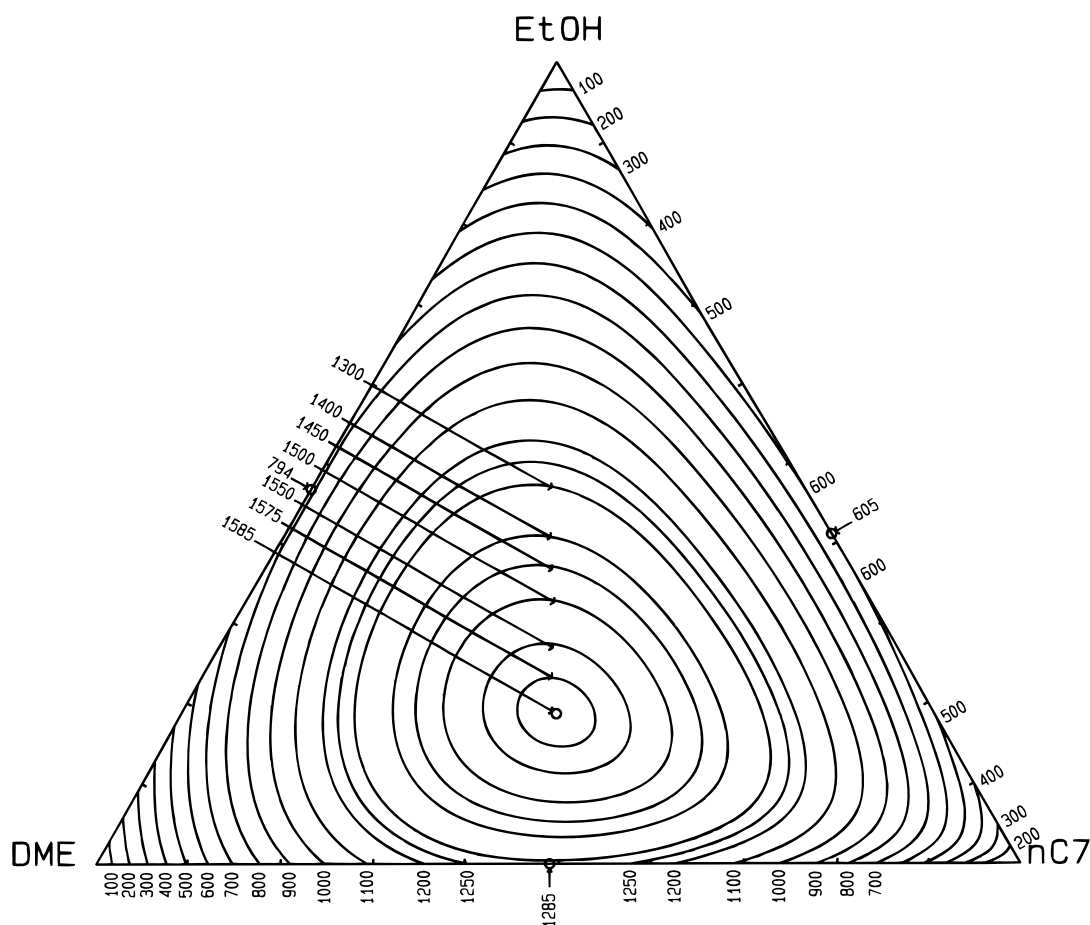


Figure 3. Contours for constant values of $H_{m,123}^E/\text{J}\cdot\text{mol}^{-1}$ for nC7 (1) + EtOH (2) + DME (3) at 298.15 K, calculated from the representation of the experimental results by eqs 1–4 with $H_{m,T}^E$ from the footnote of Table 3.

containing EtOH as a component (Zhu et al., 1993a,b, 1994; Tong et al., 1996).

Acknowledgment

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