

Excess molar enthalpies of the ternary mixtures: (diisopropyl ether or 2-methyltetrahydrofuran) + cyclohexane + *n*-heptane at 298.15 K

Zhaohui Wang, George C. Benson*,
Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

Received 27 June 2002; received in revised form 10 September 2002; accepted 10 September 2002

Abstract

Microcalorimetric measurements of excess molar enthalpies, at 298.15 K, are reported for the two ternary systems formed by mixing either diisopropyl ether or 2-methyltetrahydrofuran with binary mixtures of cyclohexane and *n*-heptane. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams. It is shown that useful estimates of the ternary enthalpies can be obtained from the Liebermann and Fried model, using only the physical properties of the components and their binary mixtures.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diisopropyl ether; Cyclohexane; 2-Methyltetrahydrofuran; *n*-Heptane; Excess molar enthalpy; Ternary system; Liebermann–Fried model

1. Introduction

A recent paper [1], from our laboratory, reported excess molar enthalpies at 298.15 K for the ternary systems consisting of either diisopropyl ether (DIPE) or 2-methyltetrahydrofuran (MTHF), together with *n*-hexane (nC6) and *n*-hexadecane (nC16). As an extension of that investigation, similar measurements have been made for the analogous systems, in which the nC6 and nC16 were replaced by cyclohexane (cC6) and *n*-heptane (nC7), respectively.

2. Experimental

The DIPE and MTHF used for the present measurements, were obtained from Aldrich and had stated purities >99 mol%. The cC6 (HPLC grade) with purity >99.9% was also obtained from Aldrich. The nC7, obtained from Phillips, was research grade and had a purity of at least 99 mol%. Apart from partial degassing, all of the components were used as received from the manufacturer. Densities, measured at 298.15 K in an Anton–Paar digital densimeter, were 718.87, 848.10, 773.94 and 680.21 kg m⁻³ for DIPE, MTHF, cC6 and nC7, respectively. These are in reasonable agreement with values in the literature [2–4].

An LKB flow microcalorimeter (model 10700-1), maintained at 298.150 ± 0.003 K, was used to measure the excess molar enthalpies H_m^E . Details of the

* Corresponding author. Tel.: +1-613-562-5800/6118;
fax: +1-613-562-5172.
E-mail address: gbenson@eng.uottawa.ca (G.C. Benson).

equipment and the operating procedure have been described previously [5,6].

For the ternary systems $x_1(\text{C}_6\text{H}_{14}\text{O}$ or $\text{C}_5\text{H}_{10}\text{O}) + x_2\text{C}_6\text{H}_{12} + x_3\text{C}_7\text{H}_{16}$, the excess molar enthalpy $H_{m,1+23}^E$ was determined for several pseudo-binary systems in which DIPE or MTHF was added to a binary mixture of components 2 and 3, having a fixed mole ratio x_2/x_3 . For this purpose, binary mixtures with $x_2/x_3 \approx 0.3, 1.0$ and 3.0 were prepared by weighing. The excess molar enthalpy of the ternary system was obtained from the relation

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

where $H_{m,23}^E$ is the excess molar enthalpy of the particular binary mixture of cC6 and nC7. Over most of the mole fraction range of component 1, 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} .

3. Results and discussion

Excess molar enthalpies $H_{m,ij}^E$ ($i < j$), at $T = 298.15$ K, for three of the constituent binary systems of present interest, have been reported previously: DIPE(1) + nC7(3) [7], cC6(2) + nC7(3) [8], and MTHF(1) + nC7(3) [9]. The experimental values of x_1 and $H_{m,12}^E$, measured for DIPE(1) + cC6(2) and MTHF(1) + cC6(2) are listed in Table 1. Coefficients

h_k for the representations of those results by the smoothing function

$$H_{m,ij}^E (\text{J mol}^{-1}) = x_i(1 - x_i) \sum_{k=1}^m h_k (1 - 2x_i)^{k-1} \quad (i < j) \quad (2)$$

are listed in Table 2, along with the standard deviation s of the representation. Also included in Table 2 are the representations of $H_{m,ij}^E$ for the other constituent binaries [7–9].

Since the completion of our measurements, we have become aware of recently reported excess molar enthalpies of MTHF(1) + cC6(2) at 298.15 K, by Lafuente et al. [10]. At $x_1 = 0.5$ their curve falls above our curve, but the difference ($\sim 4 \text{ J mol}^{-1}$) is well within the combined uncertainties of the two investigations.

The experimental results for $H_{m,1+23}^E$ and the corresponding values of $H_{m,123}^E$ are summarized in Tables 3 and 4 for $x_1(\text{C}_6\text{H}_{14}\text{O}$ or $\text{C}_5\text{H}_{10}\text{O}) + x_2\text{C}_6\text{H}_{12} + x_3\text{C}_7\text{H}_{16}$, respectively. The results for $H_{m,1+23}^E$ in Table 3 are plotted in Fig. 1 along with the values of $H_{m,1+23}^E$ given in Table 1 for the constituent binary DIPE(1) + cC6(2). The values of $H_{m,1+23}^E$ in Table 4 are plotted in Fig. 2 along with the values of $H_{m,12}^E$ given in Table 1 for the constituent binary MTHF(1) + cC6(2). Also plotted in both figures are curves for the cases $x_2 = 0$ and $x_3 = 0$, calculated from Eq. (2) with the coefficients given in Table 2.

Table 1

Experimental mole fractions x_1 and excess molar enthalpies $H_{m,12}^E$ for $x_1\text{C}_6\text{H}_{14}\text{O} + (1 - x_1)\text{C}_6\text{H}_{12}$ and $x_1\text{C}_5\text{H}_{10}\text{O} + (1 - x_1)\text{C}_6\text{H}_{12}$ binary mixtures at 298.15 K

x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$
DIPE(1) + cC6(2)							
0.0501	56.59	0.2487	268.53	0.4999	328.11	0.7499	226.58
0.1000	131.21	0.2998	295.80	0.5496	318.26	0.8007	188.77
0.1501	188.82	0.3505	315.08	0.6002	303.39	0.8501	150.64
0.1999	235.88	0.4007	327.07	0.6501	280.81	0.8999	105.14
0.2000	239.18	0.4496	330.59	0.7003	257.40	0.9500	56.98
MTHF(1) + cC6(2)							
0.0499	125.00	0.2500	460.87	0.5001	567.34	0.7504	404.53
0.0999	233.53	0.2998	504.02	0.5496	555.25	0.8001	342.67
0.1501	325.64	0.3502	537.96	0.5999	532.49	0.8500	274.85
0.2000	398.29	0.3996	559.41	0.6500	500.07	0.9000	189.93
0.2001	399.61	0.4504	568.71	0.6997	457.01	0.9500	100.08

Table 2

Coefficients h_k and standard deviations s for the representations of the excess molar enthalpies $H_{m,ij}^E$ of the constituent binary mixtures at 298.15 K by Eq. (2)

Component		h_1	h_2	h_3	h_4	h_5	h_6	s (J mol ⁻¹)
i	j							
DIPE	cC6	1305.68	207.86	157.80	345.90	-263.39	-676.10	2.61
DIPE	nC7 [7]	1016.36	1.09	28.44				0.81
cC6	nC7 [8]	964.88	-243.31	115.14	-139.02			1.03
MTHF	cC6	2268.58	289.20	146.20				1.08
MTHF	nC7 [9]	2298.97	-80.17	109.24				2.18

For both systems, the maximum values of $H_{m,1+23}^E$ and $H_{m,123}^E$ occur near $x_1 = 0.5$. However, in both the figures, the values of $H_{m,1+23}^E$ fall below the curves for the two constituent binaries and at constant x_1 , $H_{m,1+23}^E$ does not change monotonically with changes in x_2/x_3 .

Representation of the values of $H_{m,1+23}^E$ was based on the relation

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

Table 3

Experimental excess molar enthalpies $H_{m,1+23}^E$ at 298.15 K for the addition of DIPE to a binary mixture of cC6 and nC7 to form $x_1C_6H_{14}O + x_2C_6H_{12} + x_3C_7H_{16}$, and values of $H_{m,123}^E$ calculated from Eq. (1) using $H_{m,23}^E$ obtained from Eq. (2) with coefficients from Table 2

x_1	$H_{m,1+23}^E$ ^a (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)	x_1	$H_{m,1+23}^E$ ^a (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)	x_1	$H_{m,1+23}^E$ ^a (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)
$x_2/x_3 = 0.3332$, $H_{m,23}^E$ (J mol ⁻¹) = 160.21								
0.0500	37.87	190.07	0.3998	215.49	311.65	0.6997	188.68	236.79
0.1000	78.91	223.10	0.4501	220.75	308.85	0.7498	168.61	208.69
0.1500	114.15	250.33	0.5000	225.42	305.52	0.8001	144.56	176.58
0.2000	144.51	272.68	0.5498	220.16	292.29	0.8504	116.57	140.55
0.2501	168.21	288.35	0.6001	214.42	278.48	0.9000	81.42	97.44
0.2999	189.12	301.28	0.6501	203.91	259.96	0.9500	45.26	53.27
0.3506	204.75	308.79						
$x_2/x_3 = 0.9996$, $H_{m,23}^E$ (J mol ⁻¹) = 241.21								
0.0500	39.78	268.93	0.4001	207.72	352.42	0.7004	177.53	249.80
0.1000	79.32	296.41	0.4497	213.45	346.19	0.7502	157.67	217.92
0.1500	113.67	318.70	0.4996	214.60	335.30	0.8000	134.46	182.71
0.2000	142.08	335.05	0.5502	211.37	319.86	0.8501	108.26	144.42
0.2498	163.93	344.89	0.6002	204.93	301.36	0.9000	75.63	99.74
0.2996	183.05	352.00	0.6502	193.03	277.41	0.9500	39.99	52.05
0.3504	197.48	354.17						
$x_2/x_3 = 2.9989$, $H_{m,23}^E$ (J mol ⁻¹) = 212.41								
0.0500	47.86	249.66	0.4001	232.09	359.51	0.7002	192.67	256.36
0.0999	93.06	284.24	0.4501	237.29	354.09	0.7495	170.85	224.05
0.1498	130.07	310.67	0.5001	237.70	343.88	0.7998	144.83	187.35
0.2000	161.86	331.79	0.5498	233.17	328.79	0.8500	114.81	146.66
0.2498	186.62	345.97	0.6001	224.11	309.06	0.9000	81.00	102.23
0.3002	207.02	355.65	0.6496	210.87	285.29	0.9500	42.47	53.09
0.3500	221.89	359.95						

^a Ternary term for representing $H_{m,1+23}^E$ by Eqs. (3) and (4): $H_{m,T}^E$ (J mol⁻¹) = $x_1x_2x_3(-1930.05 - 2523.87x_1 + 4356.04x_2 + 19368.54x_1^2 - 13455.65x_1x_2 - 3984.93x_2^2 - 25763.37x_1^3)$; s (J mol⁻¹) = 3.23.

Table 4

Experimental excess molar enthalpies $H_{m,1+23}^E$ at 298.15 K for the addition of MTHF to a binary mixture of cC6 and nC7 to form $x_1\text{C}_5\text{H}_{10}\text{O} + x_2\text{C}_6\text{H}_{12} + x_3\text{C}_7\text{H}_{16}$, and values of $H_{m,123}^E$ calculated from Eq. (1) using $H_{m,23}^E$ obtained from Eq. (2) with coefficients from Table 2

x_1	$H_{m,1+23}^E$ ^a (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)	x_1	$H_{m,1+23}^E$ ^a (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)	x_1	$H_{m,1+23}^E$ ^a (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)
$x_2/x_3 = 0.3332$, $H_{m,23}^E$ (J mol ⁻¹) = 160.21								
0.0499	99.93	252.14	0.4008	514.89	610.89	0.7005	452.77	500.75
0.1011	200.24	344.25	0.4549	531.49	618.82	0.7501	405.90	445.93
0.1499	280.93	417.12	0.5009	536.58	616.54	0.8000	348.13	380.18
0.2001	351.90	480.05	0.5498	531.28	603.41	0.8500	279.08	303.11
0.2501	409.38	529.52	0.6003	515.62	579.66	0.9000	199.40	215.42
0.2998	456.34	568.52	0.6503	489.49	545.51	0.9500	106.55	114.56
0.3525	490.24	593.97						
$x_2/x_3 = 0.9996$, $H_{m,23}^E$ (J mol ⁻¹) = 241.21								
0.0499	104.93	334.10	0.4003	489.14	633.80	0.6997	421.92	494.35
0.1000	191.62	408.71	0.4503	502.65	635.24	0.7504	376.37	436.58
0.1500	268.63	473.65	0.5002	505.45	626.00	0.8000	322.02	370.25
0.2001	336.66	529.61	0.5498	499.58	608.17	0.8500	256.71	292.88
0.2500	390.70	571.61	0.5999	482.92	579.44	0.9001	181.69	205.79
0.2995	431.80	600.76	0.6497	457.30	541.80	0.9500	96.66	108.73
0.3499	466.15	622.97						
$x_2/x_3 = 2.9989$, $H_{m,23}^E$ (J mol ⁻¹) = 212.41								
0.0500	102.21	304.00	0.4014	488.47	615.61	0.7003	412.85	476.51
0.1000	190.15	381.31	0.4511	500.74	617.34	0.7498	367.59	420.73
0.1500	274.89	455.44	0.5001	502.11	608.29	0.7999	313.01	355.52
0.2001	340.23	510.14	0.5494	493.05	588.75	0.8503	248.59	280.40
0.2499	395.04	554.37	0.6007	475.93	560.74	0.9000	175.36	196.61
0.2997	432.69	581.44	0.6503	448.69	522.97	0.9500	92.42	103.04
0.3498	465.91	604.01						

^a Ternary term for representing $H_{m,1+23}^E$ by Eqs. (3) and (4): $H_{m,T}^E$ (J mol⁻¹) = $x_1x_2x_3(-145.83 - 10623.46x_1 + 605.86x_2 + 36045.75x_1^2 + 6582.74x_1x_2 - 4276.90x_2^2 - 35570.98x_1^3 - 30255.85x_1^2x_2)$; s (J mol⁻¹) = 3.85.

which consists of a sum of binary contributions [11], and an added ternary term $H_{m,T}^E$. The form

$$H_{m,T}^E = x_1x_2x_3(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + \dots) \quad (4)$$

which was adopted for the latter is similar to the form used by Morris et al. [12]. The values of the coefficients c_j were adjusted by least-squares analyses in which Eqs. (3) and (4) were fitted to the values of $H_{m,1+23}^E$ in Tables 3 and 4. In doing this, the values of $H_{m,ij}^E$ for the binary contributions were calculated from Eq. (2) using the appropriate coefficients from Table 2. The resulting forms for $H_{m,T}^E$ are given in the footnotes of Tables 3 and 4, along with the standard deviation s for the representation of the values of $H_{m,1+23}^E$.

The solid curves in Figs. 1 and 2 were calculated from Eq. (3) using values of $H_{m,T}^E$ given by the formulae in the footnotes of Tables 3 and 4. It is evident from these, that the representation of the experimental results is quite good.

Some constant $H_{m,123}^E$ contours, calculated from Eqs. (1)–(4), are plotted on the Roozeboom diagrams in Figs. 3a and 4a. In both the figures, there is an internal maximum, which amounts to 361.1 and 637.5 J mol⁻¹ for the DIPE and MTHF systems, respectively.

In our earlier work [1] on the enthalpies of the analogous systems containing nC6 and nC16 in place of cC6 and nC7, it was found that the Liebermann–Fried model [13,14] could provide useful estimates of the ternary enthalpies using only the properties of the pure components and interaction parameters derived

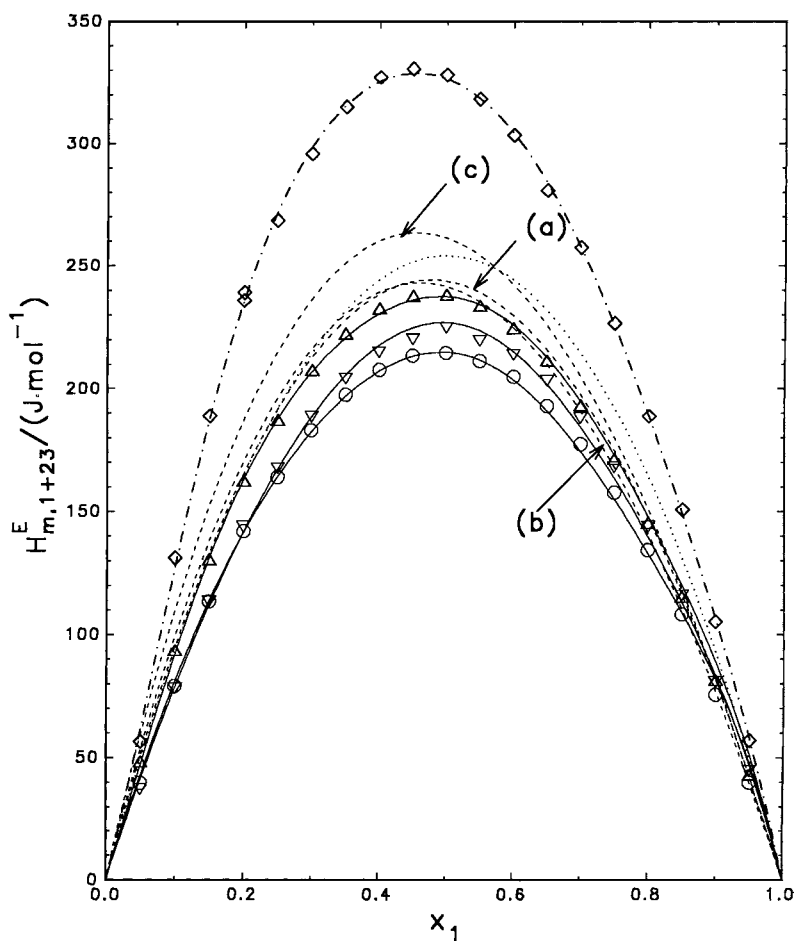


Fig. 1. Excess molar enthalpies, $H_{m,1+23}^E$, for $x_1C_6H_{14}O + x_2C_6H_{12} + x_3C_7H_{16}$ mixtures at 298.15 K. Experimental results: (∇) $x_2/x_3 = 0.3332$; (\circ) $x_2/x_3 = 0.9996$; (\triangle) $x_2/x_3 = 2.9989$; (\diamond) $x_3 = 0$. Curves: (—) calculated from Eq. (3) with $H_{m,T}^E$ from the footnote of Table 3; (\cdots) $x_2 = 0$ and ($-\cdot-$) $x_3 = 0$ calculated with Eq. (2) using the coefficients in Table 2; ($---$) estimated by the Liebermann–Fried model. (a) $x_2/x_3 = 0.3332$, (b) $x_2/x_3 = 0.9996$, (c) $x_2/x_3 = 2.9989$.

from analyses of the excess enthalpies of their constituent binaries. This approach was investigated for the present systems. Reference can be made to the work of Wang et al. [15] for the equations used in this application.

The values of the Liebermann–Fried interaction parameters A_{ij} and A_{ji} for the constituent binaries are given in Table 5. These were obtained by fitting the Liebermann–Fried formula for $H_{m,ij}^E$ to the primary experimental data for the excess molar enthalpies, as given in Table 1 and [7–9]. Also included in the table are values of the standard deviation s achieved in the fitting process, and values of the isobaric expansivity

α_p [2,3,16,17], used in evaluating the contributions due to different sizes of the molecules.

Estimates of $H_{m,1+23}^E$, derived from the Liebermann–Fried model, are shown as dashed curves in Figs. 1 and 2. It can be seen that, although the fits of the constituent binaries are reasonable, as indicated by the standard deviations in Table 5, the model over-estimates $H_{m,1+23}^E$ for the ternary mixtures. For the 57 points in each of Tables 3 and 4, the root mean square deviations are 19.4 and 33.9 J mol⁻¹, respectively.

Constant $H_{m,123}^E$ contours, estimated on the basis of the model, are shown on the Roozeboom diagrams in

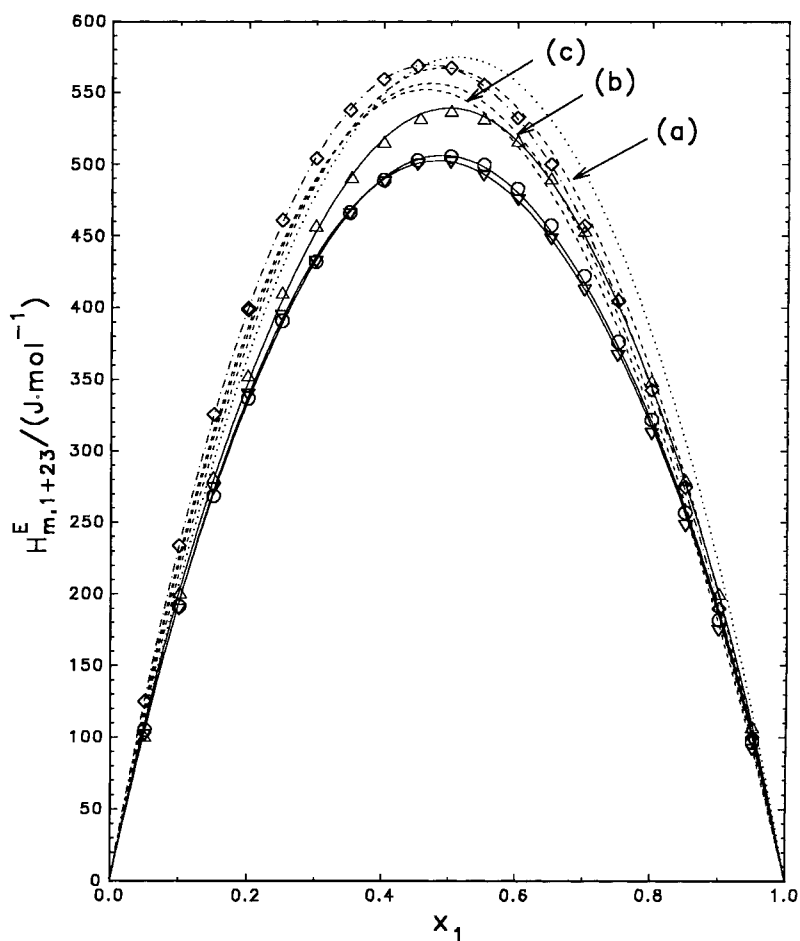


Fig. 2. Excess molar enthalpies, $H_{m,1+23}^E$, for $x_1C_5H_{10}O + x_2C_6H_{12} + x_3C_7H_{16}$ mixtures at 298.15 K. Experimental results: (Δ) $x_2/x_3 = 0.3332$; (\circ) $x_2/x_3 = 0.9996$; (∇) $x_2/x_3 = 2.9989$; (\diamond) $x_3 = 0$. Curves: (—) calculated from Eq. (3) with $H_{m,T}^E$ from the footnote of Table 4; (\cdots) $x_2 = 0$ and ($-\cdot-$) $x_3 = 0$ calculated with Eq. (2) using the coefficients in Table 2; ($---$) estimated by the Liebermann–Fried model. (a) $x_2/x_3 = 0.3332$, (b) $x_2/x_3 = 0.9996$, (c) $x_2/x_3 = 2.9989$.

Table 5

Values of the interaction parameters A_{ij} and A_{ji} , standard deviation s and the isobaric thermal expansivity α_p at 298.15 K, for Liebermann–Fried model calculations

Component		A_{ij}	A_{ji}	s (J mol $^{-1}$)	$\alpha_p/1000$ K	
i	j				i	j
DIPE	cC6	0.7510	1.0569	4.63	1.455 [2]	1.220 [16]
DIPE	nC7	0.9088	0.9106	1.07	1.455 [2]	1.256 [17]
cC6	nC7	1.2327	0.6762	2.66	1.220 [16]	1.256 [17]
MTHF	cC6	0.7230	0.9370	2.20	1.215 [3]	1.220 [16]
MTHF	nC7	0.8515	0.7946	2.62	1.215 [3]	1.256 [17]

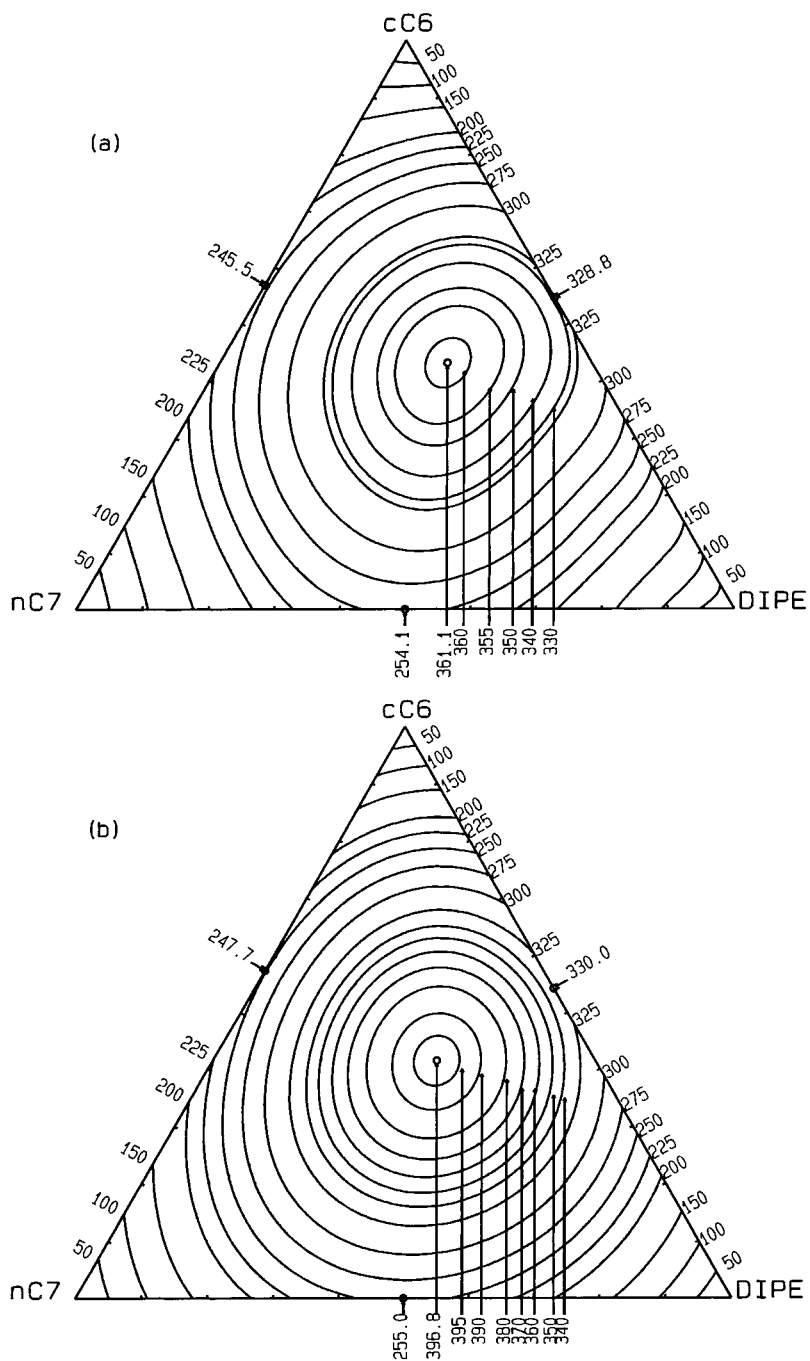


Fig. 3. Contours for constant values of $H_{m,123}^E$ (J mol⁻¹) for x_1 C₆H₁₄O + x_2 C₆H₁₂ + x_3 C₇H₁₆ mixtures at 298.15 K: (a) calculated from the representation of the experimental results by Eqs. (1)–(4) with $H_{m,T}^E$ from the footnote of Table 3; (b) estimated by the Liebermann–Fried model.

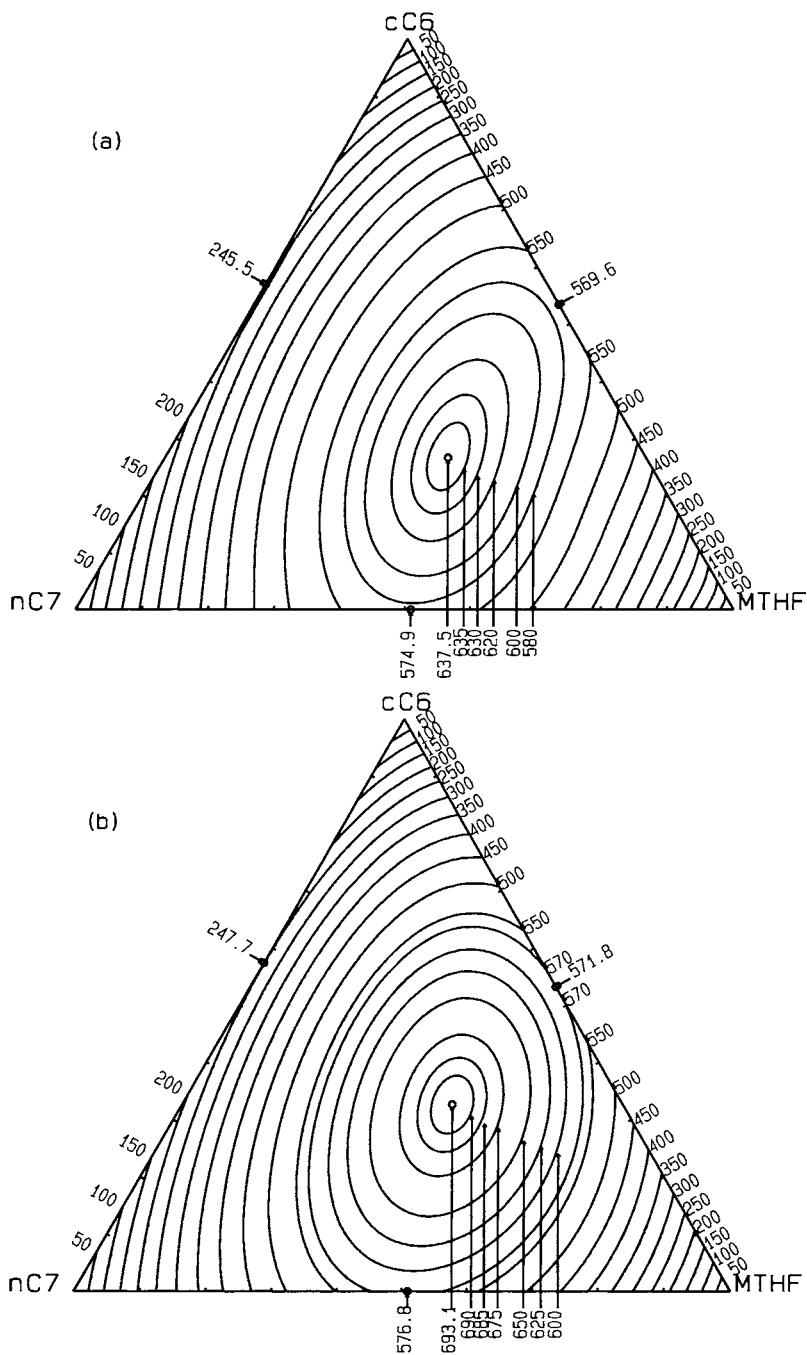


Fig. 4. Contours for constant values of $H_{m,123}^E$ (J mol^{-1}) for $x_1\text{C}_5\text{H}_{10}\text{O} + x_2\text{C}_6\text{H}_{12} + x_3\text{C}_7\text{H}_{16}$ mixtures at 298.15 K: (a) calculated from the representation of the experimental results by Eqs. (1)–(4) with $H_{m,T}^E$ from the footnote of Table 4; (b) estimated by the Liebermann–Fried model.

Figs. 3b and 4b. In both of these, the model predicts an internal maximum, which is considerably higher than that in part (a). However, despite the differences between parts (a) and (b) in these figures, it is clear that the Liebermann–Fried model provides useful predictions of the behavior of $H_{m,123}^E$ for both of the present systems, without requiring the study of any ternary mixtures.

Acknowledgements

The authors are indebted to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work. They also would like to thank Mr. Louis Tremblay for his continuing technical support of our investigations.

References

- [1] Z. Wang, G.C. Benson, B.C.-Y. Lu, J. Chem. Eng. Data 47 (2002) 1030.
- [2] M. Obama, Y. Oodera, N. Kohama, T. Yanase, Y. Saito, K. Kusano, J. Chem. Eng. Data 30 (1985) 1.
- [3] L. De Lorenzi, M. Fermeglia, G. Torriano, J. Chem. Eng. Data 41 (1996) 1121.
- [4] Loose-leaf data sheets 23-2-[1.10100]-a, page 1, 30 April 1995, and 23-2-[3.1110]-a, 30 April 1956, TRC Thermodynamic Tables—Hydrocarbons, Thermodynamic Research Center, The Texas A&M University System, College Station, TX 77843-311, 1996.
- [5] R. Tanaka, P.J. D'Arcy, G.C. Benson, Thermochem. Acta 11 (1975) 163.
- [6] F. Kimura, G.C. Benson, C.J. Halpin, Fluid Phase Equilib. 11 (1983) 245.
- [7] Z. Wang, Y. Horikawa, G.C. Benson, B.C.-Y. Lu, Fluid Phase Equilib. 181 (2001) 215.
- [8] G.W. Lundberg, J. Chem. Eng. Data 9 (1964) 193.
- [9] Z. Wang, G.C. Benson, B.C.-Y. Lu, J. Chem. Eng. Data 46 (2001) 1188.
- [10] C. Lafuente, P. Cea, M. Domínguez, F.M. Royo, J.S. Urieta, J. Solution Chem. 30 (2001) 795.
- [11] C.C. Tsao, J.M. Smith, Chem. Eng. Prog. Symp. Ser. 49 (7) (1953) 107.
- [12] J.W. Morris, P.J. Mulvey, M.M. Abbott, H.C. Van Ness, J. Chem. Eng. Data 20 (1975) 403.
- [13] E. Liebermann, V. Fried, Ind. Eng. Chem. Fundam. 11 (1972) 350.
- [14] E. Liebermann, V. Fried, Ind. Eng. Chem. Fundam. 11 (1972) 354.
- [15] Z. Wang, D.-Y. Peng, G.C. Benson, B.C.-Y. Lu, J. Chem. Thermodyn. 33 (2001) 1181.
- [16] J.A. Riddick, W.B. Bunger, T.K. Sakano, Techniques of Chemistry, vol. II, 4th ed., Organic Solvents, Wiley, New York, 1986, p. 90.
- [17] G.C. Benson, B. Luo, B.C.-Y. Lu, Can. J. Chem. 66 (1988) 531.