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Excess Molar Enthalpies of Dipropyl Ether + Dibutyl Ether + (1-Hexene or Tetrahydrofuran) at 298.15 K

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ABSTRACT: Excess molar enthalpies, measured at the temperature 298.15 K and atmospheric pressure conditions by means of a flow microcalorimeter, are reported for the ternary mixtures $\{x_1$ dipropyl ether $+ x_2$ dibutyl ether $+ (1 - x_1 - x_2)$ (1-hexene or tetrahydrofuran)$\}$. A smooth representation of the results is described and used to construct constant-enthalpy contours on a Roozeboom diagram. It is shown that good estimates of the excess molar enthalpies of the ternary systems can be obtained from the Liebermann−Fried model by using the physical properties of the pure components and the parameters determined from their binary mixtures.

INTRODUCTION

Addition of oxygenated compounds to gasoline as additives instead of lead has been proposed to reduce the emissions of hazardous compounds, such as carbon monoxide and unburned hydrocarbons. In this connection, ethers are used as oxygenating agents in gasoline blending technology to enhance the octane rating of automotive fuels. In the present study, excess molar enthalpy values for two ternary mixtures at (T = 298.15 K) comprised of dipropyl ether (DNPE), dibutyl ether (DNBE), and {1-hexene (1HX), or tetrahydrofuran (THF)} have been measured.

EXPERIMENTAL SECTION

The DNPE and 1HX were obtained from Alfa Aesar. The mole fraction purities of these chemicals, as specified by the manufacturer and verified by means of gas chromatography in this laboratory, exceeded 0.990. The DNBE and THF were obtained from Sigma-Aldrich and had a purity of at least 0.999 mol fraction. Apart from degassing, all of the components were used without further purification. Densities, $\rho(T = 298.15\ \text{K})/(\text{kg}\cdot\text{m}^{-3})$, measured by means of a densimeter (Anton-Paar DMA-5000M), which has a temperature stability of ± 0.001 K and a precision in density measurement of ± 0.001 $\text{kg}\cdot\text{m}^{-3}$, were (742.00, 763.81, 668.76, and 882.08) $\text{kg}\cdot\text{m}^{-3}$ for DNPE, DNBE, 1HX, and THF, respectively. These results are in good agreement with the values of (742.59, 763.94, 668.73, and 882.08) $\text{kg}\cdot\text{m}^{-3}$ for DNPE,[1] DNBE,[2] 1HX[2], and THF,[3] respectively.

A flow microcalorimeter (LKB model-10700-1), thermostatted at 298.150 K, was used to measure the excess molar enthalpies. The temperature of the bath was controlled within ± 0.005 K of the specified temperature. The calorimeter system was essentially the same one that was used in the previous work[1−7] except for a modified flow measuring system. The modification involved replacing the old direct current motors and controllers with two new stepper motors and digital speed controllers. Each of the transparent disks with 120 equally spaced radial photo-masked sectors for optical sensor was also replaced by a similar disk with 180 sectors. This replacement has increased the counts per revolution of the motor from 120 to 180; the precision of the flow rate readings has thus been improved by about 50 %. Details of the equipment and the operating procedure have been described previously.[6,7] In studying the ternary systems $\{x_1$ DNPE $+ x_2$ DNBE $+ (1 - x_1 - x_2)$ (1HX or THF)$\}$, the excess molar enthalpies $H^{\text{E}}_{\text{m},1+23}$ were determined for several pseudobinary mixtures. The ternary mixtures were formed by adding component 1 (DNPE) to binary mixtures of fixed composition of component 2 (DNBE) and component 3 (1HX or THF). The fixed-composition binary mixtures with selected values of $x_2/(1 - x_1 - x_2)$ were prepared by weighing. The excess molar enthalpy $H^{\text{E}}_{\text{m},123}$ for the ternary mixture was then obtained from the relation

$$H^{\text{E}}_{\text{m},123} = H^{\text{E}}_{\text{m},1+23} + (1 - x_1)H^{\text{E}}_{\text{m},23} \qquad (1)$$

where $H^{\text{E}}_{\text{m},23}$ is the excess molar enthalpy of the particular binary mixture. Over most of the composition range, the errors of the excess molar enthalpies and those of the mole fractions of the final ternary mixtures are estimated to be less than $0.005\cdot|H^{\text{E}}_{\text{m}}|$ and less than $5\cdot10^{-4}$, respectively.

RESULTS AND DISCUSSION

Excess molar enthalpies, $H^{\text{E}}_{\text{m},ij}$ ($i < j$), for one of the five constituent binary mixtures of the present interest, have been reported previously: {DNBE (2) + 1HX (3)}.[3] In the course of the present investigation, the experimental excess molar enthalpy values for the other four binary mixtures {DNPE (1) + DNBE (2) or 1HX (2) or THF (2)} and {DNBE (2) + THF (3)} at T = 298.15 K have been measured and are summarized in Table 1.

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Table 1. Experimental Mole Fraction x_i and Excess Molar Enthalpies $H^{E}_{m,ij}$ at 298.15 K, for $\{x_1 + (1 - x_1)\ \text{DNBE}\}$, $\{x_1\ \text{DNPE} + (1 - x_1)\ \text{1HX}\}$, $\{x_1\ \text{DNPE} + (1 - x_1)\ \text{THF}\}$, and $\{x_1\ \text{DNBE} + (1 - x_1)\ \text{THF}\}$[a]

	$H^{E}_{m,ij}$		$H^{E}_{m,ij}$		$H^{E}_{m,ij}$		$H^{E}_{m,ij}$
x_i	J·mol^{-1}	x_i	J·mol^{-1}	x_i	J·mol^{-1}	x_i	J·mol^{-1}
			DNPE (i) + DNBE (j)				
0.0500	2.23	0.3000	9.57	0.5004	11.85	0.7500	9.55
0.1000	4.27	0.3500	10.31	0.5500	11.88	0.8000	8.18
0.1500	5.86	0.3998	10.94	0.6001	11.76	0.8503	6.66
0.2001	7.32	0.4497	11.52	0.6500	11.32	0.9000	4.63
0.2500	8.56	0.4998	11.85	0.6999	10.57	0.9500	2.56
			DNPE (i) + 1HX (j)				
0.0529	6.60	0.3002	24.91	0.5001	28.00	0.7500	21.54
0.1001	12.08	0.3499	26.45	0.5500	27.65	0.8003	18.83
0.1500	16.49	0.4001	27.35	0.5998	26.83	0.8500	15.38
0.2001	20.10	0.4501	28.09	0.6499	25.48	0.9000	11.33
0.2500	22.82	0.5001	28.00	0.6996	23.85	0.9500	6.10
			DNPE (i) + THF(j)				
0.0500	52.28	0.2998	216.9	0.4998	248.6	0.7499	184.5
0.1000	96.88	0.3503	232.8	0.5499	244.6	0.7999	159.4
0.1501	136.1	0.3998	242.6	0.5999	236.3	0.8500	127.7
0.2000	168.2	0.4500	247.3	0.6502	223.7	0.9000	90.47
0.2498	195.9	0.4998	248.3	0.7003	206.2	0.9500	48.08
			DNBE (i) + THF(j)				
0.0500	78.75	0.3000	305.8	0.4998	339.3	0.7501	240.4
0.0998	143.6	0.3499	324.9	0.5498	331.9	0.8000	204.1
0.1502	198.4	0.4000	336.8	0.6002	318.2	0.8500	162.2
0.2000	243.4	0.4502	341.5	0.6499	297.9	0.9000	112.1
0.2500	278.7	0.4998	339.0	0.7000	272.7	0.9500	59.48

[a] Where $i < j$.

Table 2. Coefficients h_k and Standard Deviations s for the Representations of the Excess Molar Enthalpies $H^{E}_{m,ij}$ of the Constituent Binary Mixtures at 298.15 K by Equation 2

component							s
i	j	h_1	h_2	h_3	h_4	h_5	J·mol^{-1}
DNPE	DNBE	47.28	−7.34	3.61	6.59		0.06
DNPE	1HX	111.98	7.48	26.22	−3.83		0.10
1HX	DNBE	−96.39	−4.16	−8.74			0.20[a]
DNPE	THF	993.78	66.65	91.65	−36.23	−23.01	0.43
DNBE	THF	1358.73	192.51	108.67	34.27		0.49

[a] Wang et al.[2]

The smoothing function

$$H^{E}_{m,ij}/(\text{J}\cdot\text{mol}^{-1}) = x_i(1 - x_i)\sum_{k=1}^{n} h_k(1 - 2x_i)^{k-1} \qquad (2)$$

was fitted to these experimental values by the method of unweighted least-squares. The results of the data correlation for the binary systems are summarized in Table 2, along with the standard deviations of the representations. For convenience, the coefficients for the {DNBE (2) + 1HX (3)}[3] binary mixture are also included in Table 2. The experimental results and their representations by eq 2 for the four binary mixtures investigated in this study are plotted in Figure 1. It is seen that for all four binary mixtures the maximum values of $H^{E}_{m,ij}$ occur near $x_1 \approx 0.50$, and the curves are nearly symmetric about that point.

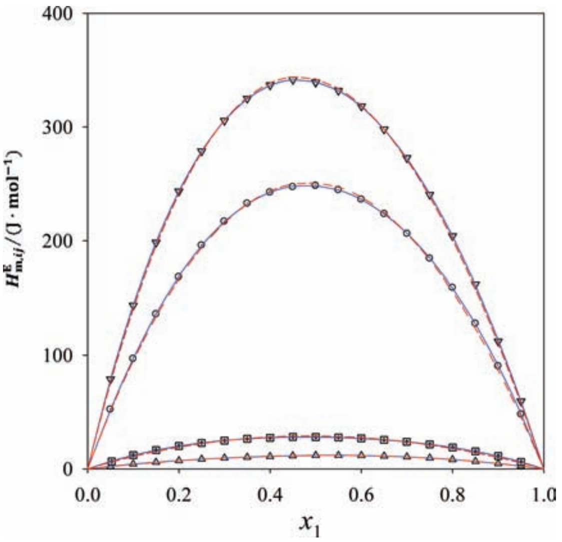

Figure 1. Excess molar enthalpies, $H^{E}_{m,ij}/(\text{J}\cdot\text{mol}^{-1})$, for binary systems presented in Table 1 at the temperature 298.15 K. Experimental results: Δ, $\{x_1\ \text{DNPE} + (1 - x_1)\ \text{DNBE}\}$; ⊞, $\{x_1\ \text{DNPE} + (1 - x_1)\ \text{1HX}\}$; ⊙, $\{x_1\ \text{DNPE} + (1 - x_1)\ \text{THF}\}$; ∇, $\{x_1\ \text{DNBE} + (1 - x_1)\ \text{THF}\}$. Curves: blue —, calculated from the representations of the results by eq 2 with values of the coefficient given in Table 2; red - - -, fit of results by the Liebermann−Fried model.

The experimental results for the ternary mixtures are reported in Tables 3 and 4, where values of $H^{E}_{m,1+23}$ are listed against the mole fraction x_1 of DNPE. Also included in the table are the corresponding values of $H^{E}_{m,123}$ calculated from eq 1. The values of $H^{E}_{m,1+23}$ are plotted in Figures 2 and 3, along with curves for the constituent binary mixtures having $x_3 = 0.0$ and $x_2 = 0.0$. In all cases, the maximum values of $H^{E}_{m,1+23}$ and $H^{E}_{m,123}$ occur near $x_1 \approx 0.50$.

Representation of the values of $H^{E}_{m,1+23}$ is based on the relation[8]

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

which consists of the sum of the binary contributions and an added ternary term $H^{E}_{m,T}$. The ternary term is given by

$$H^{E}_{m,T}/(\text{J}\cdot\text{mol}^{-1}) = x_1x_2\left(\frac{1 - x_1 - x_2}{1 - x_1 + x_2}\right)(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + ...) \qquad (4)$$

and is similar to that used by Morris et al.[9] with an extra skewing factor $(1 - x_1 + x_2)^{-1}$ inserted.[1,2,4,5] Values of the coefficients c_i were obtained from least-squares analyses in which eqs 3 and 4 were fitted to the experimental values in Tables 3 and 4. In doing this, the values of $H^{E}_{m,ij}$ for the binary contributions were calculated from eq 2 using appropriate coefficients from Table 2. The resulting representations of $H^{E}_{m,T}$ are given in the footnote of Tables 3 and 4, along with the standard deviations s of

Table 3. Experimental Excess Molar Enthalpies $H^{E}_{m,1+23}$ at the Temperature 298.15 K for the Addition of DNPE to DNBE and 1HX to Form $\{x_1$ DNPE $+ x_2$ DNBE $+ (1 - x_1 - x_2)$ 1HX$\}$ and Values of $H^{E}_{m,123}$ Calculated from Equation 1 Using $H^{E}_{m,23}$ Obtained from Equation 2 with Coefficients from Table 2[a]

x_1	$H^{E}_{m,1+23}/\mathrm{J\cdot mol^{-1}}$	$H^{E}_{m,123}/\mathrm{J\cdot mol^{-1}}$	x_1	$H^{E}_{m,1+23}/\mathrm{J\cdot mol^{-1}}$	$H^{E}_{m,123}/\mathrm{J\cdot mol^{-1}}$	x_1	$H^{E}_{m,1+23}/\mathrm{J\cdot mol^{-1}}$	$H^{E}_{m,123}/\mathrm{J\cdot mol^{-1}}$
$x_2/x_3 = 0.3333$, $H^{E}_{m,23}/(\mathrm{J\cdot mol^{-1}}) = -18.87$								
0.0500	5.17	−12.77	0.4001	25.56	14.24	0.7003	23.37	17.71
0.1000	9.58	−7.40	0.4496	26.42	16.03	0.7500	21.38	16.66
0.1500	13.58	−2.46	0.5002	26.74	17.30	0.7998	18.98	15.20
0.1998	17.00	1.89	0.5002	26.76	17.33	0.8500	15.79	12.96
0.2501	20.03	5.87	0.5503	26.63	18.14	0.9000	12.19	10.30
0.3001	22.34	9.13	0.5999	26.01	18.46	0.9500	7.12	6.18
0.3501	24.31	12.05	0.6501	24.91	18.31			
$x_2/x_3 = 0.9996$, $H^{E}_{m,23}/(\mathrm{J\cdot mol^{-1}}) = -24.10$								
0.0500	4.31	−18.59	0.4001	22.65	8.20	0.7001	21.29	14.06
0.1000	8.18	−13.51	0.4502	23.40	10.15	0.7499	19.61	13.58
0.1499	11.67	−8.82	0.5000	23.87	11.83	0.8001	17.29	12.48
0.2001	14.73	−4.54	0.5000	23.92	11.87	0.8500	14.71	11.09
0.2499	17.33	−0.75	0.5500	23.94	13.10	0.9000	11.65	9.24
0.2999	19.50	2.63	0.6003	23.52	13.89	0.9500	7.81	6.60
0.3502	21.17	5.51	0.6500	22.51	14.08			
$x_2/x_3 = 3.0000$, $H^{E}_{m,23}/(\mathrm{J\cdot mol^{-1}}) = -18.10$								
0.0500	3.03	−14.16	0.4000	16.89	6.04	0.6997	16.76	11.33
0.1000	5.83	−10.46	0.4501	17.62	7.67	0.7497	15.43	10.90
0.1500	8.45	−6.93	0.4996	18.12	9.06	0.7998	13.94	10.31
0.1999	10.66	−3.82	0.4997	18.16	9.11	0.8497	12.06	9.34
0.2501	12.75	−0.82	0.5497	18.28	10.13	0.9000	9.72	7.92
0.3001	14.43	1.77	0.6001	18.08	10.84	0.9500	6.39	5.48
0.3499	15.85	4.09	0.6497	17.51	11.17			

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by eqs 3 and 4: $H^{E}_{m,T}/(\mathrm{J\cdot mol^{-1}}) = [x_1x_2x_3/(1 - x_1 + x_2)]\,(-251.11 + 1270.01x_1 + 699.74x_2 - 2238.89x_1^2 - 428.01x_1x_2 - 798.02x_2^2 + 1557.48x_1^3)$; $s/(\mathrm{J\cdot mol^{-1}}) = 0.43$.

Table 4. Experimental Excess Molar Enthalpies $H^{E}_{m,1+23}$ at the Temperature 298.15 K for the Addition of DNPE to DNBE and THF to Form $\{x_1$ DNPE $+ x_2$ DNBE $+ (1 - x_1 - x_2)$ THF$\}$ and Values of $H^{E}_{m,123}$ Calculated from Equation 1 Using $H^{E}_{m,23}$ Obtained from Equation 2 with Coefficients from Table 2[a]

x_1	$H^{E}_{m,1+23}/\mathrm{J\cdot mol^{-1}}$	$H^{E}_{m,123}/\mathrm{J\cdot mol^{-1}}$	x_1	$H^{E}_{m,1+23}/\mathrm{J\cdot mol^{-1}}$	$H^{E}_{m,123}/\mathrm{J\cdot mol^{-1}}$	x_1	$H^{E}_{m,1+23}/\mathrm{J\cdot mol^{-1}}$	$H^{E}_{m,123}/\mathrm{J\cdot mol^{-1}}$
$x_2/x_3 = 0.3333$, $H^{E}_{m,23}/(\mathrm{J\cdot mol^{-1}}) = 278.67$								
0.0500	21.23	285.9	0.4002	104.2	271.3	0.7016	91.32	174.5
0.1000	38.77	289.6	0.4497	106.8	260.2	0.7501	82.75	152.4
0.1500	55.28	292.2	0.5001	108.1	247.4	0.8000	70.77	126.5
0.2002	69.21	292.1	0.5001	108.1	247.4	0.8500	58.22	100.0
0.2502	80.89	289.9	0.5501	107.2	232.6	0.9001	42.52	70.37
0.3000	90.83	285.9	0.5999	104.6	216.1	0.9500	24.11	38.05
0.3499	98.35	279.5	0.6503	98.89	196.4			
$x_2/x_3 = 1.0004$, $H^{E}_{m,23}/(\mathrm{J\cdot mol^{-1}}) = 339.67$								
0.0500	6.53	329.2	0.4002	35.13	238.9	0.7000	33.19	135.1
0.1000	12.61	318.3	0.4502	36.49	223.2	0.7498	30.26	115.2
0.1500	17.85	306.6	0.5002	37.33	207.1	0.8001	26.65	94.56
0.2000	22.78	294.5	0.5001	37.29	207.1	0.8500	21.86	72.81
0.2503	27.02	281.7	0.5501	37.25	190.1	0.9000	15.93	49.89
0.3002	30.21	267.9	0.5998	36.64	172.6	0.9500	8.69	25.67
0.3499	32.90	253.7	0.6500	35.14	154.0			
$x_2/x_3 = 3.0000$, $H^{E}_{m,23}/(\mathrm{J\cdot mol^{-1}}) = 241.00$								
0.0500	1.93	230.9	0.4002	8.50	153.1	0.7001	7.80	80.09
0.1000	3.52	220.4	0.4503	8.80	141.3	0.7498	7.11	67.40
0.1555	5.01	208.5	0.5001	8.91	129.4	0.8000	6.25	54.45
0.2000	5.95	198.8	0.5001	8.91	129.4	0.8500	5.13	41.29
0.2498	6.89	187.7	0.5501	8.89	117.3	0.9000	3.75	27.86
0.2999	7.55	176.3	0.6000	8.68	105.1	0.9500	2.03	14.07
0.3502	8.16	164.8	0.6501	8.35	92.68			

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by eqs 3 and 4: $H^{E}_{m,T}/(\mathrm{J\cdot mol^{-1}}) = [x_1x_2x_3/(1 - x_1 + x_2)](-2979.96 + 2782.56x_1 + 675.29x_2 - 1947.11x_1^2 - 2677.41x_1x_2)$; $s/(\mathrm{J\cdot mol^{-1}}) = 0.69$.

the fit. The solid curves for $H^{E}_{m,1+23}$ in Figures 2 and 3 were calculated from eq 3.

Equations 1 to 4 were also used to calculate the constant $H^{E}_{m,123}$ contours plotted on the Roozeboom diagram in Figures 4(a) and 5(a). For the {DNPE (1) + DNBE (2) + 1HX (3)} ternary system, Figure 4(a) serves to show that there exists an internal saddle point. However, the point representing the maximum value of $H^{E}_{m,123}$ (28.4 $\mathrm{J\cdot mol^{-1}}$) is located on the DNPE-1HX edge. For the {DNPE (1) + DNBE (2) + THF (3)} ternary system, Figure 5(a) serves to show that there is no internal extremum; the point representing the maximum value (341.52 $\mathrm{J\cdot mol^{-1}}$) is located on the DNBE−THF edge.

Wang et al.[5] have shown that the Liebermann−Fried model[10,11] can be used to represent the excess molar enthalpies for both binary and multicomponent mixtures. For representing the excess molar enthalpy of a multicomponent mixture, only the properties of the pure components and interaction parameters derived from the analyses of the excess enthalpies of the constituent binaries are required. Details of the thermodynamic relations in connection with the derivation and application of the Liebermann−Fried model were described by Peng et al.[12] A brief discussion of the Liebermann−Fried model is presented below to facilitate our understanding of this model.

According to the Liebermann−Fried model, the excess molar enthalpy of an N-component mixture is represented by the equation

$$H^{E} = H(I) + H(V) \qquad (5)$$

where

$$H(I) = (RT^2/2)\sum_{j=1}^{N}\sum_{k=1}^{N} x_jx_k \times \left[\frac{\dfrac{(\partial A_{jk}/\partial T)}{A_{jk}} + \dfrac{(\partial A_{kj}/\partial T)}{A_{kj}} - \ln(A_{jk}A_{kj})\left\{\dfrac{\sum_{p=1}^{N} x_p(\partial A_{jp}/\partial T)}{\sum_{p=1}^{N} x_pA_{jp}} + \dfrac{\sum_{q=1}^{N} x_q(\partial A_{kq}/\partial T)}{\sum_{q=1}^{N} x_qA_{kq}}\right\}}{\left(\sum_{p=1}^{N} x_pA_{jp}\right)\left(\sum_{q=1}^{N} x_qA_{kq}\right)}\right] \qquad (6)$$

$$\frac{1}{A_{jk}}\frac{\partial A_{jk}}{\partial T} = \left(\frac{\beta}{T}\right)\frac{\ln(A_{jk}A_{kj})}{\ln(A_{jk}A_{kj}) - 2} = \frac{1}{A_{kj}}\frac{\partial A_{kj}}{\partial T} \qquad (7)$$

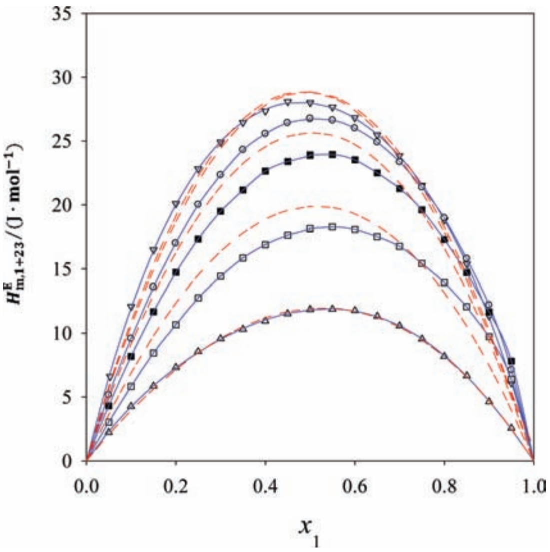

Figure 2. Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m},1+23}/(\mathrm{J\cdot mol^{-1}})$, for $\{x_1$ DNPE $+ x_2$ DNBE $+ (1 - x_1 - x_2)$ 1HX$\}$ mixtures at the temperature 298.15 K. Plotted against mole fraction x_1. Experimental results: Δ, $x_3 = 0.0$; ⊙, $x_2/x_3 = 0.3333$; ■, $x_2/x_3 = 0.9996$; ⊡, $x_2/x_3 = 3.0000$; ∇, $x_2 = 0.0$. Curves: blue —, calculated from the representation of the results by eqs 3 and 4 using the ternary term $H^{\mathrm{E}}_{\mathrm{m},T}$ given in the footnote of Table 3; red ---, estimated by means of the Liebermann−Fried model.

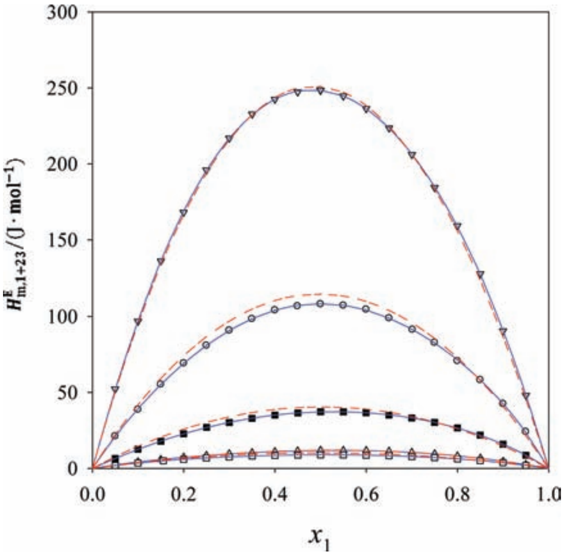

Figure 3. Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m},1+23}/(\mathrm{J\cdot mol^{-1}})$, for $\{x_1$ DNPE $+ x_2$ DNBE $+ (1 - x_1 - x_2)$ THF$\}$ mixtures at the temperature 298.15 K. Plotted against mole fraction x_1. Experimental results: Δ, $x_3 = 0.0$; ⊙, $x_2/x_3 = 0.3333$; ■, $x_2/x_3 = 1.0004$; ⊡, $x_2/x_3 = 3.0000$; ∇, $x_2 = 0.0$. Curves: blue —, calculated from the representation of the results by eqs 3 and 4 using the ternary term $H^{\mathrm{E}}_{\mathrm{m},T}$ given in the footnote of Table 4; red ---, estimated by means of the Liebermann−Fried model.

and

$$H(V) = (RT^2)\frac{\sum_{j=1}^{N}\sum_{k=1}^{N} x_j x_k \upsilon_k[(\alpha_P)_k - (\alpha_P)_j]}{\sum_{k=1}^{N} x_k \upsilon_k} \qquad (8)$$

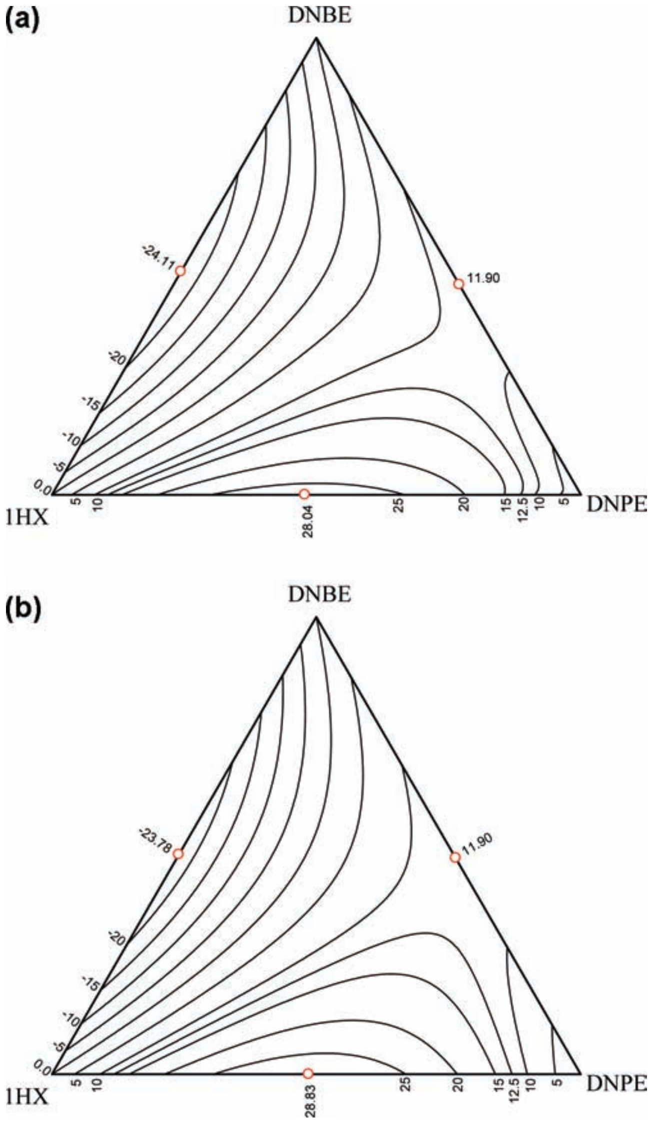

Figure 4. Contours for constant values of $H^{\mathrm{E}}_{\mathrm{m},123}/(\mathrm{J\cdot mol^{-1}})$ for $\{x_1$ DNPE $+ x_2$ DNBE $+ (1 - x_1 - x_2)$ 1HX$\}$ at 298.15 K. Part (a) calculated from the representation of the experimental results by eqs 3 and 4, with $H^{\mathrm{E}}_{\mathrm{m},T}$ from the footnote of Table 3. Part (b) estimated by means of the Liebermann−Fried model.

The term $H(I)$ accounts for the nonideal behavior arising from the interaction between molecules, whereas the term $H(V)$ accounts for the effect of the different sizes (i.e., molar volume) of the molecules in the mixture. The symbols υ_k and $(\alpha_P)_k$ in eq 8 represent, respectively, the molar volume and the isobaric thermal expansivity of pure component k.

The values of the interaction parameters A_{ij} and A_{ji} determined for the constituent binaries are given in Table 5. These parameters were obtained by fitting the Liebermann−Fried formula for $H^{\mathrm{E}}_{\mathrm{m},ij}$ to the experimental results for the excess molar enthalpies given in Table 1. Also included in that table are values of the standard deviations s and values of the isobaric thermal expansivities.[13] The Liebermann−Fried model has the potential to represent vapor−liquid equilibria of systems containing hydrocarbons and ethers using the pure component properties (i.e., isobaric thermal expansivities) and the binary parameters obtained by fitting the excess molar enthalpy data.[12,13]

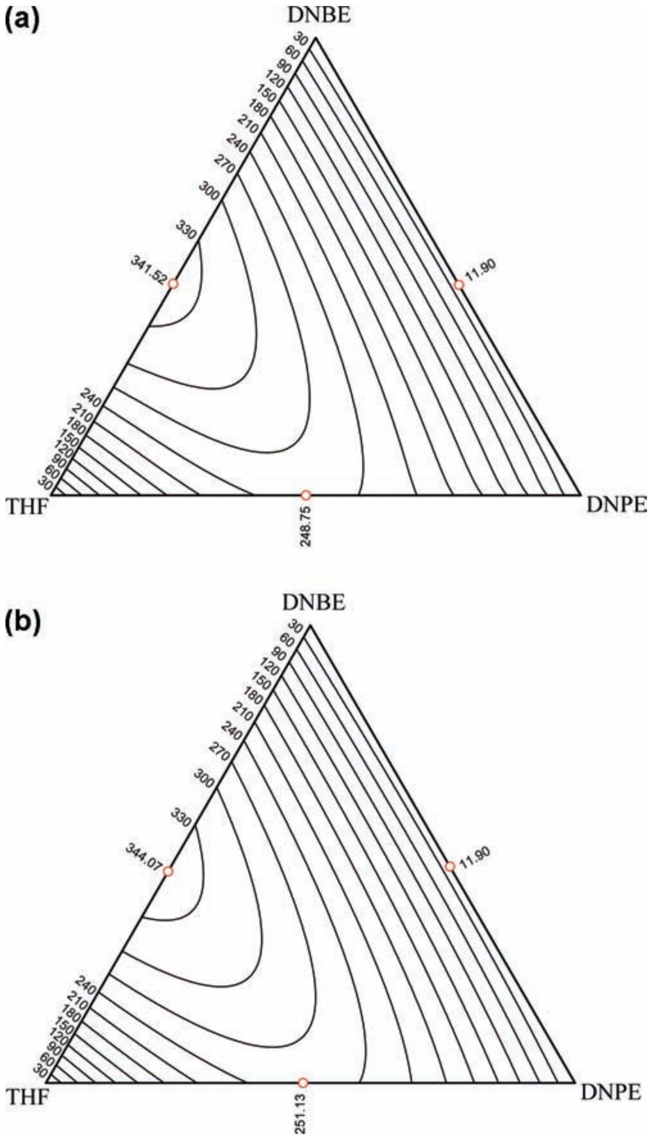

Figure 5. Contours for constant values of $H^{\mathrm{E}}_{\mathrm{m},123}/(\mathrm{J\cdot mol^{-1}})$ for $\{x_1\ \mathrm{DNPE} + x_2\ \mathrm{DNBE} + (1 - x_1 - x_2)\ \mathrm{THF}\}$ at 298.15 K. Part (a) calculated from the representation of the experimental results by eqs 3 and 4, with $H^{\mathrm{E}}_{\mathrm{m},T}$ from the footnote of Table 4. Part (b) estimated by means of the Liebermann−Fried model.

Table 5. Values of the Interaction Parameters A_{ij} and A_{ji}, Standard Deviation s, and Isobaric Thermal Expansivities α_p at 298.15 K Used in the Liebermann−Fried Model Calculation

component				s	$\alpha_p/\mathrm{kK^{-1}}$	
i	j	A_{ij}	A_{ji}	$\mathrm{J\cdot mol^{-1}}$	i	j
DNPE	DNBE	1.1072	0.8908	0.15	1.261[b]	1.126[b]
DNPE	1HX	0.9329	1.0455	0.86	1.261	1.411[b]
1HX	DNBE	0.9354[a]	1.0759[a]	0.59	1.411	1.126
DNPE	THF	0.8743	0.9575	2.38	1.261	1.138[b]
DNBE	THF	0.7579	1.0287	2.41	1.126	1.138

[a] Wang et al.[2] [b] Wang et al.[13]

Estimates of $H^{\mathrm{E}}_{\mathrm{m},1+23}$, derived from the Liebermann−Fried model, are shown as dashed curves in Figures 2 and 3. In both cases, it can be seen that the theory predicts correctly the order of the three experimental curves and their positions relative to the curves for the two constituent binaries. The root-mean-square deviations of the values presented in Tables 3 and 4, each with 60 data points, are 1.59 J·mol^{-1} and 6.0 J·mol^{-1}.

Constant $H^{\mathrm{E}}_{\mathrm{m},123}$ contours, estimated on the basis of the Liebermann−Fried model, are shown on the Roozeboom diagram in Figures 4(b) and 5(b). It is clear from a comparison of the two parts in each figure that the Liebermann−Fried model provides useful estimation of $H^{\mathrm{E}}_{\mathrm{m},123}$ for both the present mixtures, including predictions of the locations and magnitudes of the external maxima.

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