Excess Enthalpies of Binary and Ternary Mixtures Containing Dibutyl Ether, Cyclohexane, and 1-Butanol at 298.15 K[†]

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Experimental excess enthalpies of the ternary system dibutyl ether (DBE) + cyclohexane + 1-butanol and the corresponding binary systems at 298.15 K are reported. A quasi-isothermal flow calorimeter has been built and tested to make the measurements. All the binary and the ternary systems show endothermic character. The experimental data have been fitted using a polynomial equation for the binary and ternary systems. The values of the standard deviation indicate good agreement between the experimental results and those calculated from the equation.

Introduction

The use of oxygenated compounds as gasoline-blending agents has been proposed to reduce emissions of new reformulated gasoline. Ether + alkane + alcohol mixtures are of interest as model mixtures for gasoline in which the alcohol and the ether act as nonpolluting, high octane number blending agents. From this point of view, the study of the ternary mixture dibutyl ether + cyclohexane + 1-butanol is very interesting. Cyclohexane is a usual compound of gasoline. Dibutyl ether (DBE) is used as a blending agent in reformulated gasoline, and 1-butanol is a basic component in the synthesis of the ether and therefore is always contained as an impurity. Experimental excess enthalpies of the ternary system DBE + cyclohexane + 1-butanol and the corresponding binary systems at 298.15 K are reported in this work. Excess enthalpies have been measured with a new quasi-isothermal flow calorimeter recently built at the University of Burgos. The experimental data have been fitted using a Redlich−Kister[1] equation and NRTL[2] and UNIQUAC[3] models. The values of the standard deviation indicate the agreement between the experimental results and those calculated from the equations.

Experimental Section

Materials. All the chemicals used here were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (of the series puriss p.a.) with a stated purity > 99.5 %. All reagents were checked by gas chromatography, and the values of purity obtained were > 99.6 % for DBE, > 99.9 % for cyclohexane, and > 99.8 % for 1-butanol. The water content for 1-butanol was checked to be less than 0.009 %.

Apparatus and Procedure. Excess enthalpies have been measured with a new quasi-isothermal flow calorimeter recently built at the University of Burgos, based on the previous experience of the research group.[4,5] Figure 1 shows schematically the quasi-isothermal calorimeter. Two precision positive displacement pumps (Agilent, model 1100) deliver the liquids through stainless-steel tubing at programmable constant flow rates into the mixing coil sitting in the flow cell, which is included in the measure unit, following the scheme shown in Figure 2. The flow cell has been built in the TERMOCAL laboratory at the University of Valladolid. In the case of binary systems, the two liquids are the pure components, and in the case of ternary systems, one of them is a pure component and the other the corresponding binary mixture. The flow cell is immersed in a water bath (Hart Scientific, model 6020E) thermostatted at the temperature the mixing process is taking place. The stability of the temperature is better than ± 0.01 K. The bath temperature is measured by its calibrated standard PRT-100, resolving 10 mK in the reading of temperature and estimating an overall uncertainty of ± 30 mK.

Isothermal calorimetry is based on measuring the energy required to maintain the mixing vessel at a constant temperature. To achieve this condition, a Peltier cooler removes at a constant rate energy from the flow cell and a control heater compensates this energy and additionally the energy liberated (exothermic) or absorbed (endothermic) by the mixing process and maintains the temperature of the flow cell constant. The variation of temperature is detected by a control sensor, a NTC thermistor. The resistance is measured by a 4-wire resistance bridge with a micro-ohm meter from Hewlett-Packard, model HP-34420A. The Peltier cooler, the control heater, and the calibration heater are connected, each one to its respective DC power supply. The control of these devices is made by a computer through a GPIB connection and specific software that has been developed. The change of heating power of the control heater before, during, and after measurements is a direct measure for the excess enthalpy H^E. The calibration of the measurement system is made by simulating an exothermic mixing process by a calibration resistor.

Knowing the volumetric flow rates delivered, the molar masses, and the densities of the pure compounds, the mole

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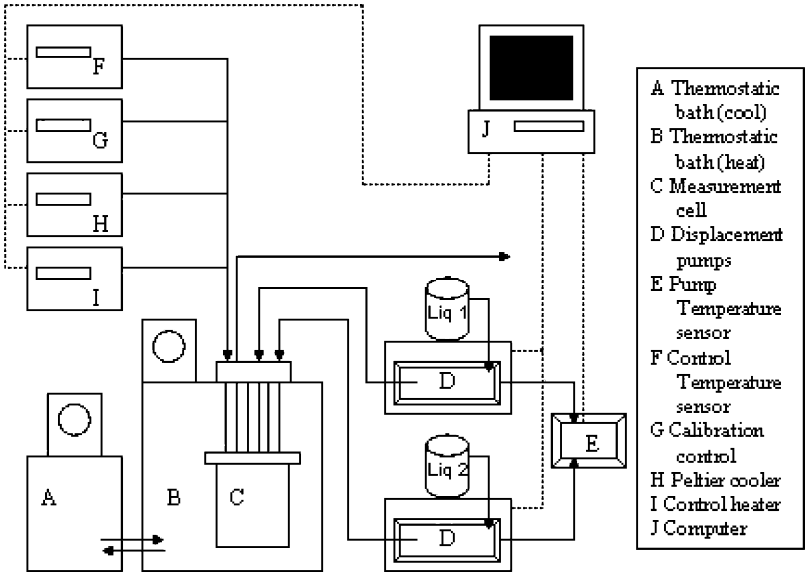

Figure 1. Quasi-isothermal flow calorimeter. Schematic diagram.

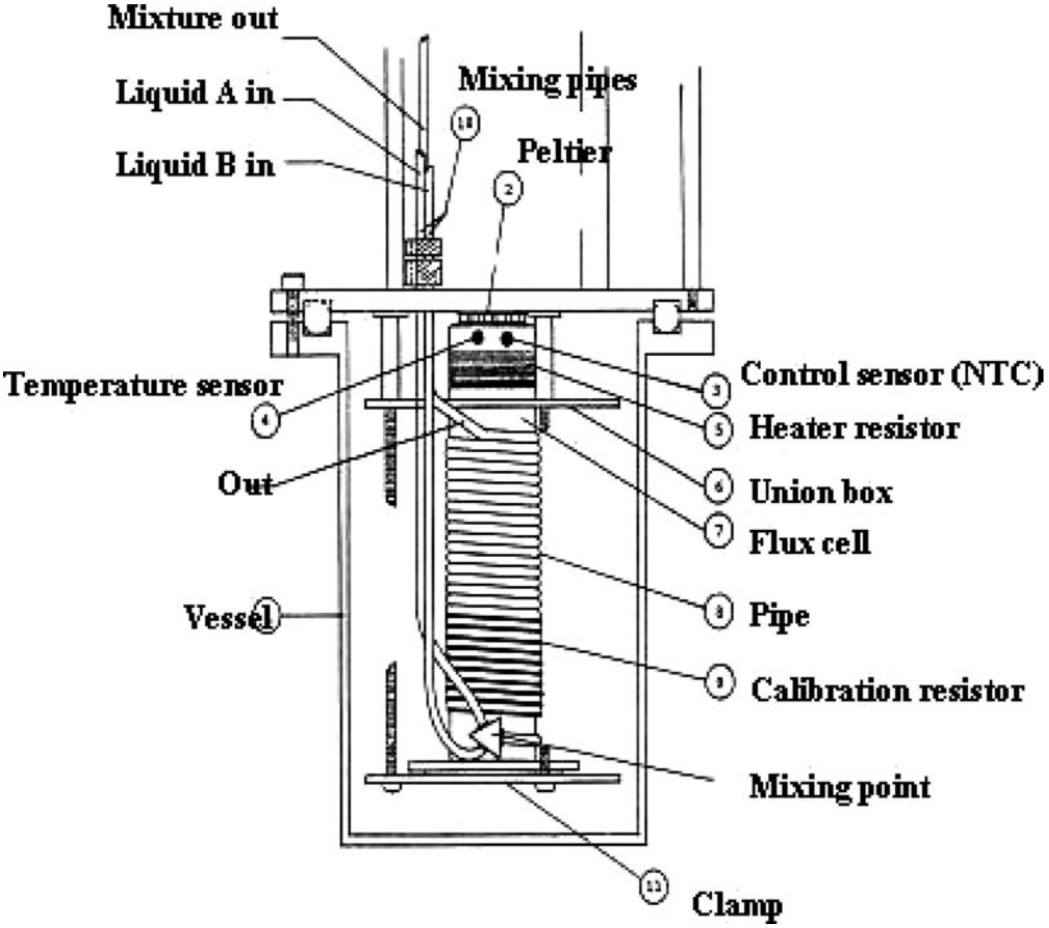

Figure 2. Mixing flow cell. Schematic diagram.

fractions of the mixtures obtained in the mixing coil can be calculated. The maximum absolute uncertainty of mole fraction at equimolar composition is ± 0.0008. Densities of pure liquids are determined interpolating density data obtained from Riddick et al.[6] at the measured temperature of delivery. Table 1 shows agreement between our estimated density data and literature data. The temperature of pure liquids is measured by a calibrated standard PRT-100 inserted in the pump body, using as an indicator an a/c resistance bridge (ASL model F250) resolving 1 mK in the reading of temperature and estimating an overall uncertainty of ± 10 mK. Mixtures of different compositions are studied by changing the ratio of flow rates, and in this way the dependence of H^E on mole fraction can be determined. The estimated relative uncertainty of the determined $H^E/\mathrm{J \cdot mol^{-1}}$ is $\pm\, 0.01 \cdot H^E$.

To check the above apparatus, we have used two systems traditionally considered as test systems for calorimetric techniques: cyclohexane + hexane and benzene + cyclohexane at

Table 1. Comparison of Density Data of Pure Compounds, Cyclohexane, Hexane, Benzene, DBE, and 1-Butanol at 298.15 K

	cyclohexane		hexane		benzene		DBE		1-butanol	
	this work	lit.	this work	lit.	this work	lit.	this work	lit.	this work	lit.
ρ/g·cm^{-3}	0.77389[a]	0.7738[b]	0.65484[a]	0.6551[c]	0.87360[a]	0.8736[d]	0.76410[a]	0.76411[e]	0.80575[a]	0.80561[f]

[a] Riddick et al.[6] [b] Rodríguez et al.[7] [c] Iglesias et al.[8] [d] Iglesias et al.[9] [e] Jiménez et al.[10] [f] Rezanova et al.[11]

Table 2. Comparison of H^E Data for the Binary Systems Cyclohexane + Hexane and Benzene + Cyclohexane, at 298.15 K[a]

calorimeter technique	A_1	A_2	A_3	A_4	rms ΔH^E J·mol^{-1}	max $\lvert\Delta H^E\rvert$ J·mol^{-1}
			Cyclohexane (1) + Hexane (2)			
isothermal displacement calorimeter[b]	864.7	249.5	99.1	33.2	0.1	0.2
continuous dilution calorimeter[c]	863.5	248.8	104.5	31.1	0.2	0.4
isothermal flow calorimeter[e]	861.6	264.4	103.8		0.8	1.6
isothermal flow calorimeter[d]	867.2	245.3	63.8	23.7	0.8	1.4
			Benzene (1) + Cyclohexane (2)			
isothermal displacement calorimeter[f]	3197.1	175.4	121.5	28.5	0.2	0.5
continuous dilution calorimeter[g]	3196.7	153.9	123.0		2.0	2.7
continuous dilution calorimeter[h]	3190.4	163.5	112.5	36.7	0.3	0.6
isothermal flow calorimeter[d]	3201.3	171.8	151.5		0.9	2.3

[a] Parameters A_i of the Redlich−Kister equation, standard deviation rms ΔH^E, and maximum excess enthalpy deviation max $\lvert\Delta H^E\rvert$. [b] Marsh and Stokes.[12] [c] Murakami and Benson.[13] [d] This work. [e] Gmehling and Meents.[14] [f] Ewing et al.[15] [g] Lundberg.[16] [h] Savini et al.[17]

298.15 K. The first system, cyclohexane (1) + hexane (2), was measured by Marsh and Stokes[12] with an isothermal displacement microcalorimeter. This work presents the most complete amount of data and is taken as a reference system. However, we have considered also the comparison with data from Murakami et al.,[13] which used a continuous dilution calorimeter, and from Gmehling et al.,[14] whose data were taken with an isothermal flow calorimeter of the same characteristics as ours. Table 2 presents the results found in the references for this system and the results obtained in this work, as well as the maximum deviation of the excess enthalpy with respect to the calculated value, max ΔH^E, and the standard deviation, rms ΔH^E. The Redlich−Kister equation is used for the adjustment of each data set, with the number of parameters employed by each author

$$H^E = x\cdot(1-x)\cdot\sum_{i=1}^{n} A_i\cdot(2x-1)^{i-1} \tag{1}$$

The comparison of the calculated values of the Redlich−Kister coefficients and scattering parameters in this work with those from the literature shows that our values are similar with regard to the same type of isothermal flow calorimeter and more scattered in relation with the isothermal displacement microcalorimeter and the continuous dilution calorimeter.

A comparison between experimental data of this work and those from the literature is presented in Figure 3. For each data set, the calculated enthalpy H^E_{calc} has been determined using the Redlich−Kister coefficients of the correlation determined by Marsh and Stokes.[12] The scattering of experimental data obtained in this work is within ± 1 % of the calculated enthalpy corresponding to each mole fraction in the central range of composition.

The second test system is the binary mixture benzene (1) + cyclohexane (2) at 298.15 K. In a way similar to the former system, comparison between the data of Ewing et al.,[15] Lundberg,[16] Savini et al.,[17] and this work is reported in Table 2 and Figure 3, with the coefficients of Ewing et al.[15] being used to obtain the calculated enthalpy H^E_{calc} for each data set. In this case, also the agreement between this work and literature data is within ± 1 % of the calculated enthalpy.

Results and Discussion

The experimental excess molar enthalpies obtained in this work for the binary mixtures DBE (1) + cyclohexane (2), DBE (1) + 1-butanol (3), and cyclohexane (2) + 1-butanol (3) at 298.15 K are listed in Table 3.

For binary systems, there are several models and empirical equations proposed to fit the H^E measurements. One of them, the Redlich−Kister equation, is given by eq 1, in which the A_i coefficients are determined by the unweighted least-squares method. Another equation employed often is the modified Margules equation (eq 2), proposed by Abbot and van Ness[18]

$$H^E = x_1x_2RT \times \left[a_{21}x_1 + a_{12}x_2 - \frac{x_1x_2b_{12}b_{21}}{b_{21}x_1 + b_{12}x_2 + x_1x_2(c_{21}x_1 + c_{12}x_2)}\right] \tag{2}$$

Binary systems have also been correlated using the NRTL model, for which the expression for the molar excess enthalpy is indicated by eq 3

$$H^E = -RT\sum_{i=1}^{n} x_i\eta_i \tag{3}$$

where x_i is the mole fraction of the component i and η_ι is given by

$$\eta_i = \frac{\sum_{k=1}^{p} x_k\tau_{ki}G_{ki}[\alpha(\tau_{ki} - (\sum_{n=1}^{p} x_n\tau_{ni}G_{ni}/\sum_{l=1}^{n} x_lG_{li})) - 1]}{\sum_{l=1}^{p} x_lG_{li}}$$

$$G_{ji} = \exp(-\alpha\tau_{ij})$$

The NRTL theory assumes that the excess molar enthalpy of a multicomponent mixture depends only on the binary parameters. In this work, the nonrandomness parameter α was assigned

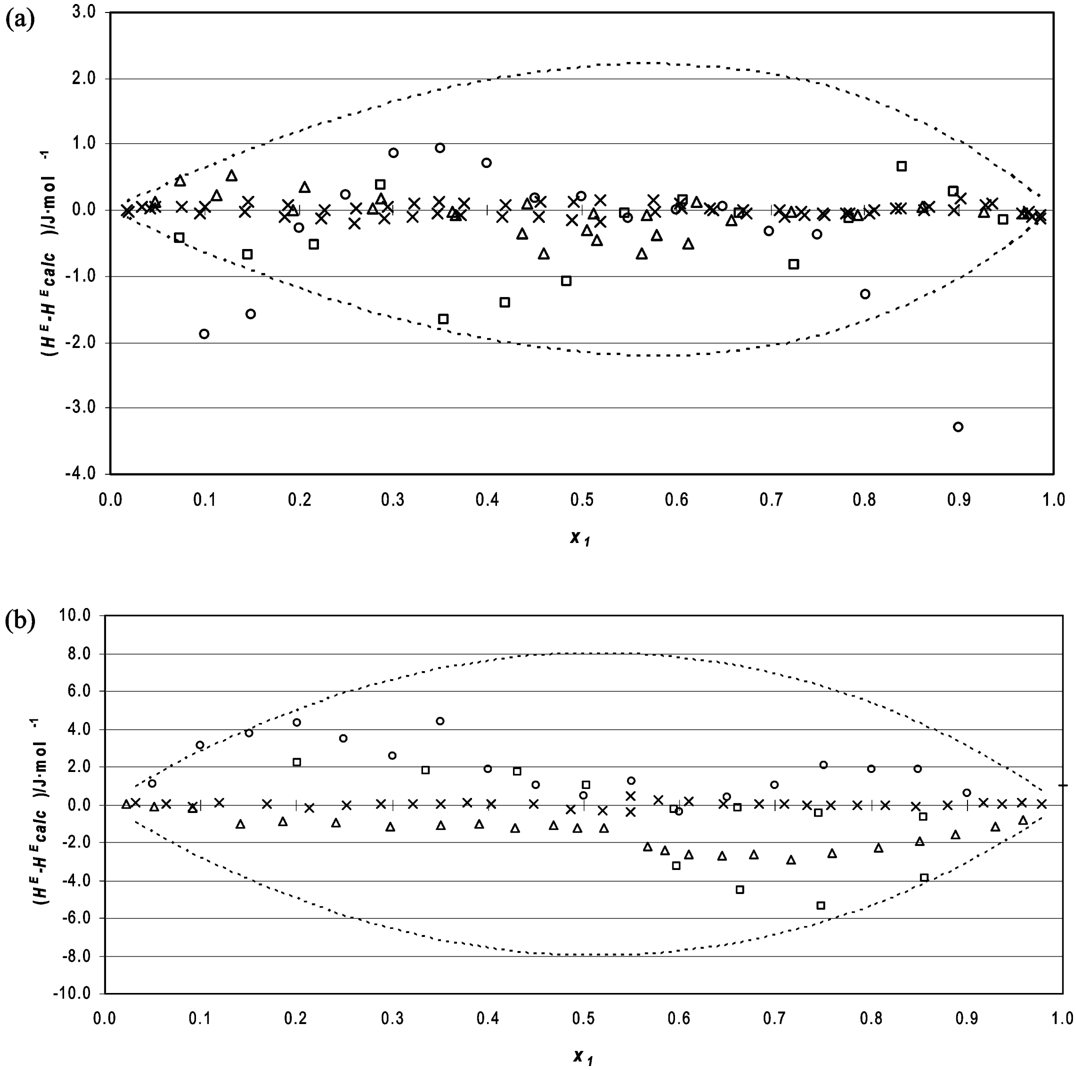

Figure 3. Comparison of residuals between the measured excess enthalpy, H^E, and the calculated excess enthalpy, H^E_{calc}, at the temperature of 298.15 K, for the following systems: (a) cyclohexane (1) + hexane (2), ○, this work; ×, Marsh and Stokes;[12] Δ, Murakami and Benson;[13] □, Gmehling and Meents.[14] (b) Benzene (1) + cyclohexane (2), ○, this work; ×, Ewing et al.;[15] □, Lundberg;[16] Δ, Savini et al.[17] In Figure 3a, the calculated enthalpy H^E_{calc} has been determined using the Redlich−Kister coefficients of the correlation determined by Marsh and Stokes[7] for each data set, while those from Ewing et al.[15] have been used in Figure 3b. The dotted line shows the ± 1 % deviation from the calculated enthalpy corresponding to each mole fraction.

Table 3. Experimental Excess Molar Enthalpies of Binary Systems DBE (1) + Cyclohexane (2), DBE (1) + 1-Butanol (3), and Cyclohexane (2) + 1-Butanol (3) at 298.15 K

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
x DBE + (1 − x) Cyclohexane							
0.0499	75.2	0.2999	255.4	0.5495	248.1	0.7990	136.7
0.0997	134.1	0.3500	264.9	0.6000	232.6	0.8500	104.1
0.1502	180.4	0.3996	268.6	0.6491	213.9	0.9001	69.3
0.2002	214.5	0.4497	266.4	0.6992	191.1	0.9507	32.8
0.2497	238.5	0.4990	259.6	0.7501	164.1		
x DBE + (1 − x) 1-Butanol							
0.0501	119.4	0.3004	624.6	0.5506	879.8	0.8000	772.8
0.1002	236.0	0.3498	698.4	0.5998	892.4	0.8501	679.1
0.1497	344.5	0.4006	762.1	0.6505	890.6	0.8994	543.1
0.2003	447.6	0.4507	814.0	0.7000	872.6	0.9493	330.1
0.2503	540.2	0.4997	853.2	0.7509	833.2		
x Cyclohexane + (1 − x) 1-Butanol							
0.0503	68.3	0.2997	407.6	0.5501	613.4	0.7996	567.1
0.0998	144.8	0.3500	461.6	0.5997	629.5	0.8500	513.0
0.1502	217.4	0.4002	510.5	0.6501	634.6	0.9000	438.5
0.1998	286.8	0.4503	552.5	0.7002	626.7	0.9496	334.4
0.2502	349.6	0.5003	587.3	0.7501	604.7		

0.3 for the NRTL model of two parameters and as an adjustable parameter for the NRTL model of three parameters.

For the UNIQUAC model, the molar excess enthalpy is given by

Table 4. Summary of Parameters for the Representation of H^{E} by the Redlich−Kister, Modified Margules Equation, NRTL (2 and 3 Parameters), and UNIQUAC Models, for Binary Systems DBE (1) + Cyclohexane (2), DBE (1) + 1-Butanol (3), and Cyclohexane (2) + 1-Butanol (3) at 298.15 K

binary systems[a]	correlation				
DBE (1) + cyclohexane (2)	Redlich−Kister	Modified Margules	NRTL	NRTL (3p)	UNIQUAC
A_0	1037.1	0.979	−0.2065	0.1153	−210.2
A_1	−362.2	0.277	0.8622	0.5691	467.4
A_2	166.2	0.328			
A_3	−139.2	117.8			
A_4	−29.0	2.6			
A_5		−106.4			
α_{12}			0.30	0.82	
rms $\Delta H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	0.5	0.6	2.9	1.5	1.4
max $\lvert\Delta H^{\mathrm{E}}\rvert/\mathrm{J\cdot mol^{-1}}$	1.2	1.5	5.0	3.8	3.5
max $(\lvert\Delta H^{\mathrm{E}}\rvert/H^{\mathrm{E}})$	3.6 %	4.5 %	5.7 %	11.5 %	10.5 %
DBE (1) + 1-butanol (3)	Redlich−Kister	Modified Margules	NRTL	NRTL (3p)	UNIQUAC
A_0	3414.8	1.011	2.3362	2.4081	2160.1
A_1	1259.1	1.037	0.6854	0.8333	−629.7
A_2	741.4	−256347			
A_3	1310.7	−0.5147			
A_4	1021.8	72852			
A_5		201903			
α_{13}			0.30	0.31	
rms $\Delta H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	2.9	2.4	14.3	11.9	43.2
max $\lvert\Delta H^{\mathrm{E}}\rvert/\mathrm{J\cdot mol^{-1}}$	4.9	4.0	29.0	21.8	84.5
max $(\lvert\Delta H^{\mathrm{E}}\rvert/H^{\mathrm{E}})$	3.5 %	2.6 %	8.8 %	9.7 %	23.1 %
cyclohexane (2) + 1-butanol (3)	Redlich−Kister	Modified Margules	NRTL	NRTL (3p)	UNIQUAC
A_0	2339.6	0.6024	1.9691	2.1696	1960.8
A_1	1371.5	8.2647	0.0910	0.6426	−588.4
A_2	1046.8	410.0			
A_3	−1202.8	7.181			
A_4	−2123.2	16.9			
A_5	3793.8	4.5			
A_6	4414.9				
α_{23}			0.30	0.42	
rms $\Delta H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	6.5	2.6	36.3	24.8	37.2
max $\lvert\Delta H^{\mathrm{E}}\rvert/\mathrm{J\cdot mol^{-1}}$	13.6	6.0	111.2	75.7	116.0
max $(\lvert\Delta H^{\mathrm{E}}\rvert/H^{\mathrm{E}})$	8.0 %	8.9 %	33.2 %	26.2 %	34.7 %

[a] Equivalence between parameters: NRTL, $A_0 = \tau_{12}$ and $A_1 = \tau_{21}$; UNIQUAC, $A_0 = \Delta u_{12}$; $A_1 = \Delta u_{21}$; Modified Margules, $A_0 = a_{12}$; $A_1 = a_{21}$; $A_2 = b_{12}$; $A_3 = b_{21}$; $A_4 = c_{12}$; $A_5 = c_{21}$.

Table 5. Experimental Excess Molar Enthalpies H^{E}_{2+13} at 298.15 K for the Addition of Cyclohexane to (DBE (1) + 1-Butanol (3)) to Form x_1 DBE + x_2 Cyclohexane + $(1 - x_1 - x_2)$ 1-Butanol, and Values of H^{E}_{123} Calculated from Equation 5, Using the Smooth Representation of H^{E}_{13} by the Redlich−Kister Equation with Parameters Given in Table 4

x_2	$\frac{H^{\mathrm{E}}_{2+13}}{\mathrm{J\cdot mol^{-1}}}$	$\frac{H^{\mathrm{E}}_{123}}{\mathrm{J\cdot mol^{-1}}}$	x_2	$\frac{H^{\mathrm{E}}_{2+13}}{\mathrm{J\cdot mol^{-1}}}$	$\frac{H^{\mathrm{E}}_{123}}{\mathrm{J\cdot mol^{-1}}}$
$x_1/x_3 = 0.2498$, $H^{\mathrm{E}}_{13}/\mathrm{J\cdot mol^{-1}} = 443.8$					
0.9000	394.4	395.0	0.40041	579.0	
0.8002	504.4	508.6	0.2998	387.6	549.7
0.6996	557.4	571.3	0.2003	277.7	514.2
0.6003	565.3	597.4	0.1001	144.2	474.2
0.5002	536.1	597.6			
$x_1/x_3 = 0.6669$, $H^{\mathrm{E}}_{13}/\mathrm{J\cdot mol^{-1}} = 764.2$					
0.8999	350.8	351.6	0.4006	422.9	592.1
0.7997	446.5	453.0	0.3007	348.0	614.8
0.6998	491.2	512.9	0.2003	250.1	646.2
0.6002	498.3	549.3	0.0997	130.0	691.4
0.5002	473.6	572.4			
$x_1/x_3 = 1.4988$, $H^{\mathrm{E}}_{13}/\mathrm{J\cdot mol^{-1}} = 890.0$					
0.9002	309.0	309.08	0.4001	369.5	554.9
0.8000	395.9	402.5	0.2998	303.5	600.9
0.6997	433.8	456.5	0.2005	216.8	663.4
0.5998	438.3	492.4	0.1001	112.8	755.5
0.4998	415.3	521.9			
$x_1/x_3 = 4.0531$, $H^{\mathrm{E}}_{13}/\mathrm{J\cdot mol^{-1}} = 773.3$					
0.8998	256.95	257.5	0.4005	322.0	460.4
0.8006	342.6	347.1	0.2999	263.1	492.5
0.7002	380.0	395.8	0.1997	186.6	544.6
0.6003	383.8	422.1	0.0995	97.1	632.5
0.5009	363.7	440.8			

Table 6. Summary of the Data Reduction and Prediction Results Obtained for the Ternary System DBE (1) + Cyclohexane (2) + 1-Butanol (3) at 298.15 K

correlation[a]	$\Delta H^{\mathrm{E}}_{123}$ (eq 7)	$\Delta H^{\mathrm{E}}_{123}$ (eq 8)	NRTL	UNIQUAC
B_0	2586.7		−0.3508	1294.6
B_1	−12380.7	−1936.1	0.4952	−711.7
B_2	−15976.6	−4187.3	1.7410	1416.8
B_3	17886.7	911.9	0.6327	−389.5
B_4	39625.0		3.7942	2869.9
B_5	7477.6		0.1853	−825.9
B_6	−12474.9			
B_7	−41723.8			
α_{12}			0.30	
α_{13}			0.30	
α_{23}			0.30	
rms $\Delta H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	5.0	11.9	49.9	55.2
max $\lvert\Delta H^{\mathrm{E}}\rvert/\mathrm{J\cdot mol^{-1}}$	13.4	27.5	94.1	178.5
max $(\lvert\Delta H^{\mathrm{E}}\rvert/H^{\mathrm{E}})$	5.2 %	8.9 %	20.0 %	44.9 %

prediction[a]	NRTL	UNIQUAC
B_0	−0.2065	−210.2
B_1	0.8622	467.4
B_2	2.3362	2160.1
B_3	0.6854	−629.7
B_4	1.9691	1960.8
B_5	0.0910	−588.4
α_{12}	0.30	
α_{13}	0.30	
α_{23}	0.30	
rms $\Delta H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	207.0	169.8
max $\lvert\Delta H^{\mathrm{E}}\rvert/\mathrm{J\cdot mol^{-1}}$	356.2	306.9
max $(\lvert\Delta H^{\mathrm{E}}\rvert/H^{\mathrm{E}})$	64.2 %	55.3 %

[a] Equivalence between parameters: NRTL, $B_0 = \tau_{12}$; $B_1 = \tau_{21}$; $B_2 = \tau_{13}$; $B_3 = \tau_{31}$; $B_4 = \tau_{23}$; $B_5 = \tau_{32}$; UNIQUAC, $B_0 = \Delta u_{12}$; $B_1 = \Delta u_{21}$; $B_2 = \Delta u_{13}$; $B_3 = \Delta u_{31}$; $B_4 = \Delta u_{23}$; $B_5 = \Delta u_{32}$.

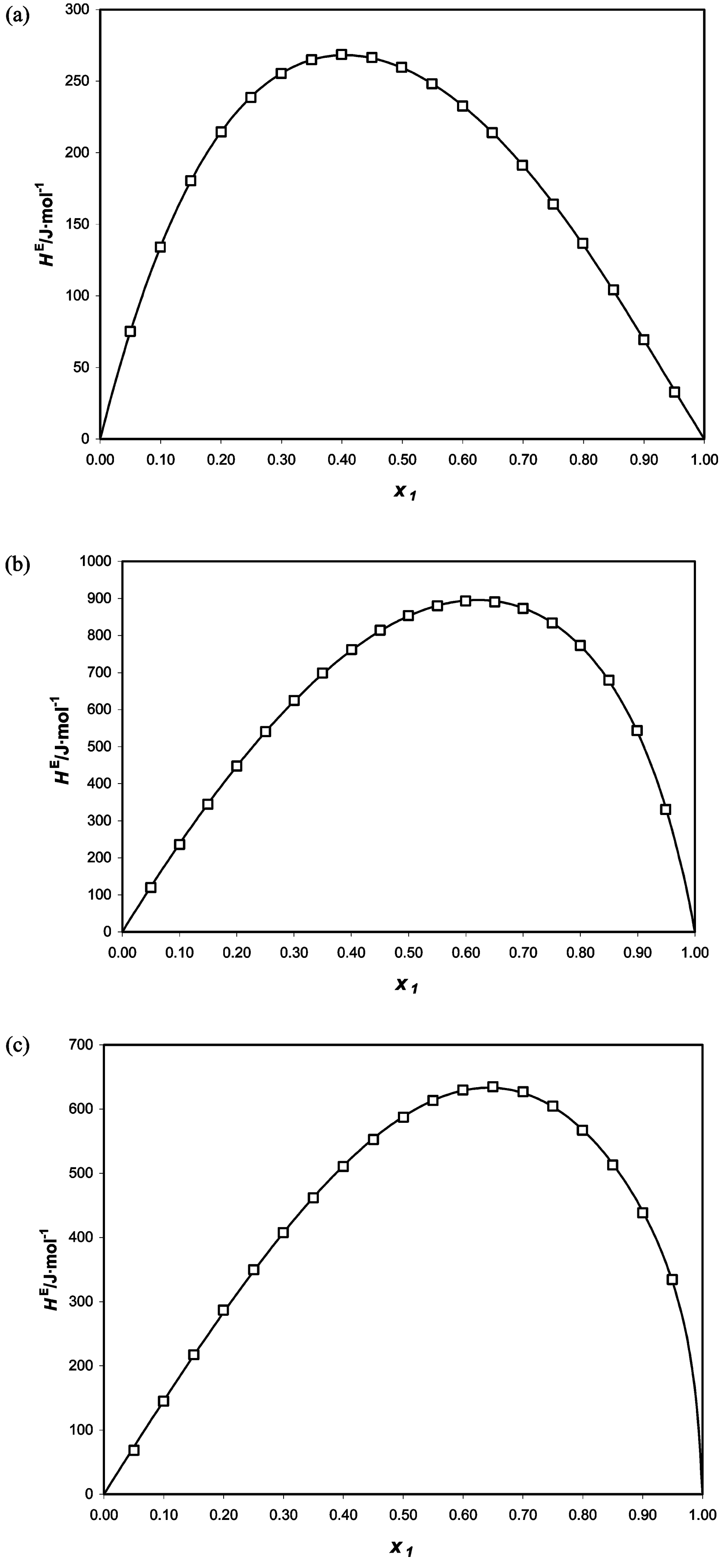

Figure 4. Excess molar enthalpy H^E at 298.15 K for (a) DBE (1) + cyclohexane (2); (b) DBE (1) + 1-butanol (3); and (c) cyclohexane (2) + 1-butanol (3). □, Experimental results; ___, calculated with eq 1 (Figure a) and eq 2 (Figures b and c) using parameters of Table 4.

$$H^{\mathrm{E}} = \sum_{i=1}^{n} q_i x_i \frac{\sum_{j=1}^{n} \vartheta_j \Delta u_{ji} \tau_{ji}}{\sum_{j=1}^{n} \vartheta_j \tau_{ij}} \tag{4}$$

where $\vartheta_i = (q_i x_i)/(\sum_j q_j x_j)$ and q_i is the molecular surface area, obtained as the sum of the contributions of the functional groups presents in the compound.

Results of data correlation for the binary systems are summarized in Table 4. A plot of the experimental and correlated data is shown in Figure 4.

The ternary mixtures DBE (1) + cyclohexane (2) + 1-butanol (3) at 298.15 K were formed by adding the cyclohexane (2) to binary mixtures of fixed composition of DBE (1) + 1-butanol (3). Four different starting binaries were used, with values of the ratio x_1/x_3 of 0.2498, 0.6669, 1.4988, and 4.0531, respectively. The experimental excess molar enthalpies listed in Table 5 are determined by eq 5, using the smooth representation of H_{13}^{E} by Redlich−Kister

$$H_{123}^{\mathrm{E}} = H_{2+13}^{\mathrm{E}} + (1 - x_2)H_{13}^{\mathrm{E}} \tag{5}$$

Experimental results for the excess molar enthalpy H_{123}^{E} are shown in Figure 5.

The following equation was used to fit the H^{E} measurements

$$H_{123}^{\mathrm{E}} = H_{12}^{\mathrm{E}} + H_{13}^{\mathrm{E}} + H_{23}^{\mathrm{E}} + x_1 x_2 x_3 \Delta H_{123}^{\mathrm{E}} \tag{6}$$

with

$$\Delta H_{123}^{\mathrm{E}} = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 + B_5 x_1 x_2 + B_6 x_1^3 + B_7 x_2^3 \tag{7}$$

where the parameters B_i were determined by the unweighted least-squares method. Another alternative for the calculation of $\Delta H_{123}^{\mathrm{E}}$ is eq 8

$$\Delta H_{123}^{\mathrm{E}} = B_1 x_1 + B_2 x_2 + B_3 x_3 \tag{8}$$

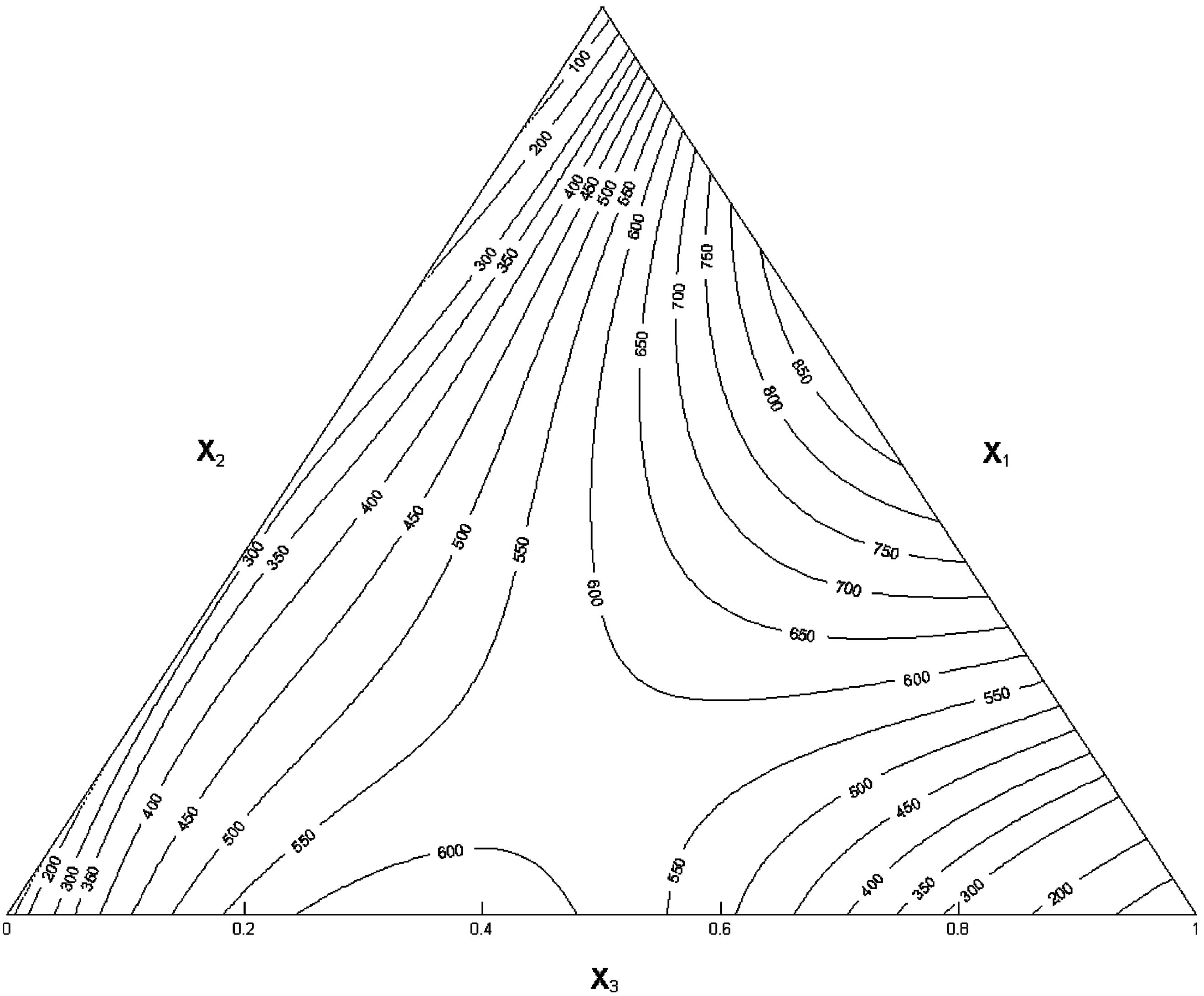

Figure 5. Contours for constant values of H_{123}^{E} for DBE (1) + cyclohexane (2) + 1-butanol (3) at 298.15 K.

Table 6 presents the summary of correlation results obtained for the ternary system with eqs 6, 7, and 8 and NRTL and UNIQUAC models. Table 6 also shows the prediction results obtained for the ternary system using the parameters of the binary systems.

The excess molar enthalpy of the system DBE (1) + cyclohexane (2) at 298.15 K shows endothermic behavior ($H^E > 0$) in the whole range of composition. The best fit of experimental data is obtained with the Redlich−Kister equation with a root-mean-square deviation, rms ΔH^E, of 0.5 $J \cdot mol^{-1}$ and a maximum value of the absolute deviation, max ΔH^E, of 1.2 $J \cdot mol^{-1}$. Deviations obtained with NRTL and UNIQUAC models are higher. The maximum value of the molar excess enthalpy is 267 $J \cdot mol^{-1}$, obtained at a mole fraction of DBE of about 0.40. Comparison with data for the same binary system and temperature reported by Marongiu et al.[19] shows that our H^E data are considerably higher, the difference being 15 % in the central range of composition, even when the calorimeter was recalibrated and the binary system measured three times.

The binary system DBE (1) + 1-butanol (3) measured at 298.15 K is also endothermic. The maximum value of H^E is 892 $J \cdot mol^{-1}$, at a mole fraction of DBE of about 0.60. The modified Margules equation gives the best fit with a root-mean-square deviation, rms ΔH^E, of 2.4 $J \cdot mol^{-1}$ at 298.15 K. The maximum values of the absolute deviation, max ΔH^E, are 4.0 $J \cdot mol^{-1}$. The remaining models give worse fits. Our H^E data agree to within 1.5 % in the central range of composition with the measurements for the same system and temperature obtained from Kammerer and Lichtenthaler.[20]

The third binary system which has been studied is the system cyclohexane (2) + 1-butanol (3) at 298.15 K, showing also an endothermic behavior. The maximum value of the molar excess enthalpy of the mixture is 635 $J \cdot mol^{-1}$. The mole fraction of cyclohexane at this maximum is approximately 0.65. The experimental data have been fitted by Redlich−Kister, modified Margules, NRTL, and UNIQUAC models, the modified Margules equation being the best fit with a root-mean-square deviation, rms ΔH^E, of 2.6 $J \cdot mol^{-1}$. The maximum value of the absolute deviation, max ΔH^E, is 6.0 $J \cdot mol^{-1}$. Comparison with data for the same binary system and temperature reported by Löwen and Schulz[21] shows that our H^E data agree to within 1.7 % in the central range of composition.

Concerning the measured ternary system, the best fit of experimental data is obtained with eqs 6 and 7. The root-mean-square deviation, rms ΔH^E, is 5.0 $J \cdot mol^{-1}$, and the maximum value of the absolute deviation, max ΔH^E, is 13.4 $J \cdot mol^{-1}$, which means about 5 % over the experimental molar excess enthalpy at this point. The results obtained with the other models are rather worse. This system shows an endothermic behavior in the whole range of composition. The maximum value of H^E is 890 $J \cdot mol^{-1}$. No data of the same system were found in the literature for comparison. Both NRTL and UNIQUAC models present high root-mean-square deviation values in the prediction of data.

Conclusions

Isothermal excess enthalpies at 298.15 K for the ternary system dibutyl ether (DBE) + cyclohexane + 1-butanol and its constituent binary systems were determined by using an isothermal flow calorimeter. All the binary systems show positive values and strongly asymmetric H^E behavior in the measured temperature. The measured excess enthalpy data were correlated well with various common H^E models.

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