Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 85–88

ENTHALPIES OF MIXING OF BINARY AND TERNARY MIXTURES CONTAINING DIISOPROPYLETHER, BENZENE AND CYCLOHEXANE AT 303.15 K

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Enthalpies of mixing *H* have been measured for liquid binary mixtures of diisopropylether (DIPE)+benzene or cyclohexane and for liquid ternary mixtures diisopropylether+benzene+cyclohexane at 303.15 K and constant pressure using a C80 calorimeter. A Redlich–Kister type equation was used to correlate experimental results.

Keywords: *diisopropylether, excess enthalpy, Redlich–Kister equation, ternary mixtures*

Introduction

From a practical point of view diisopropylether (DIPE) is one of the new oxygenated additives which has potential use as blending agent in the formulation of unleaded gasoline because of its antiknocking effect and its environment-friendly nature.

From a theoretical point of view, data of mixtures involving branched monoethers, such as diisopropylether with cyclohexane or benzene are of high interest because they make possible to study a number of effects (e.g. steric or proximity effects) on the interactions present in the mixtures considered.

This paper will be contributed with an experimental investigation of thermodynamics properties of binary and ternary mixtures containing DIPE with cyclohexane and benzene.

Experimental

A C80 Setaram calorimeter was used to measure enthalpies of mixing *H* for binary and ternary mixtures at 303.15±0.01 K and constant pressure. Details of the equipment and its operation have been described previously [1, 2].

In studying the ternary system, the enthalpies of mixing H_{12+3} for several pseudo-binary mixtures, in which component (3) DIPE was added to binary mixtures of component (1) cyclohexane and (2) benzene having a fixed mole ratio x_1/x_2. For this purpose, binary mixtures with selected values of x_1/x_2 were prepared by weighing. Over most of the mole fraction range, the errors in the mole fractions of the binary and ternary mixtures are estimated to be less than 0.001.

Diisopropylether (DIPE) and benzene were obtained from Fluka. The cyclohexane was obtained from Merck. In all cases, their stated purities exceeded 99 mol%. All of the components were used as received.

The performance of the apparatus was checked by determining *H* of cyclohexane (1)+benzene (2) at 303.15 K. Our results given in Table 1, were in agree-

Table 1 Experimental values for enthalpies of mixing at 303.15 K for cyclohexane (1)+benzene (2)

x_1	H/J mol^{-1}
0.112	313.9
0.199	511.4
0.299	677.8
0.411	778.5
0.448	777.0
0.521	772.1
0.544	761.8
0.581	736.1
0.631	698.9
0.643	684.7
0.676	643.0
0.786	491.1
0.842	377.0
0.860	347.1
0.877	303.0
0.900	266.8

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1388–6150/$20.00

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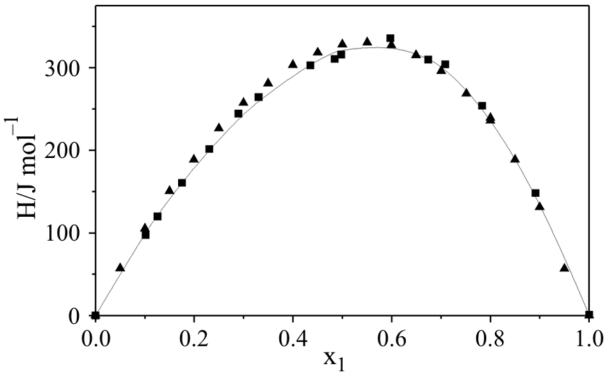

Fig. 1 Enthalpies of mixing of binary system cyclohexane (1)+diisopropylether (3); ■ – experimental values of 303.15 K; —– curve calculated from Eq. (1) at 303.15 K; ▲ – experimental values at 298.15 K (Wang *et al.*)

ment to within 1% (over central range of concentration) with the data reported in [2, 3].

Results and discussion

Experimental values of enthalpies of mixing at 303.15 K for the two binary mixtures are listed in Tables 2 to 3 and plotted in Figs 2 to 3. These values have been fitted with the following smoothing function,which are frequently used in calculation [4–6].

$$H = x_i x_j \sum_{k=0} a_k (x_i - x_j)^k \qquad (1)$$

and standard deviation σ for each representation is defined as:

$$\sigma = \left[\sum \frac{(H_{\exp} - H_{\mathrm{cal}})^2}{N - n} \right]^{1/2} \qquad (2)$$

Table 2 Experimental values for enthalpies of mixing at 303.15 K for cyclohexane (1)+diisopropylether (3)

x_1	H/J mol^{-1}
0.101	97.4
0.125	119.8
0.175	160.6
0.230	201.4
0.289	244.3
0.330	264.3
0.435	302.8
0.484	310.5
0.497	315.9
0.597	335.5
0.673	309.8
0.708	304.0
0.783	253.9
0.891	148.2

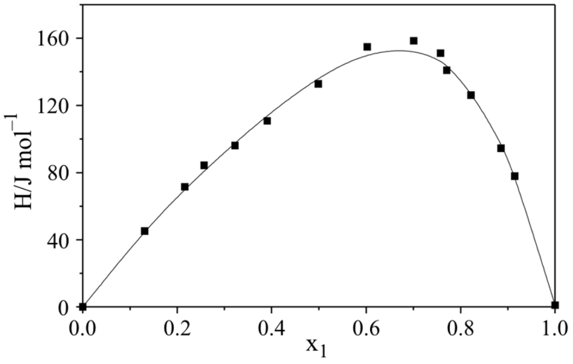

Fig. 2 Enthalpies of mixing of binary mixture benzene (2)+diisopropylether (3) at 303.15 K; ■ – experimental values; —– curve calculated by Eq. (1)

Table 3 Experimental values for enthalpies of mixing at 303.15 K for benzene (2)+diisopropylether (3)

x_1	H/J mol^{-1}
0.131	45.2
0.216	71.5
0.256	84.3
0.322	96.0
0.390	110.8
0.498	132.8
0.602	154.9
0.700	158.4
0.757	151.0
0.770	140.9
0.822	126.1
0.885	94.4
0.915	77.9

where N is the number of experimental points and n the number of parameters of smoothing function (1).

Values of coefficients a_k and standard deviation σ, are given in Table 4.

Since the completion of our measurements, we have become aware of recently reported enthalpies of mixing of DIPE+cyclohexane at 298.15 K, by Wang *et al*. [7].

Figure 1 shows a comparison of our measurement results at 303.15 K with binary H data given in the literature, indicating a slight difference (not exceeded 15 J mol^{-1}). Throughout the concentration ranges, experimental results for binary mixtures show a positive deviation from ideality.

As all the branched monoethers, any polar nature due to the lone pairs on the group is counterbalanced by steric effects of the alkyls groups adjacent to the oxygen atom. Experimental data of H show a small thermal effect, not exceeding 160 J mol^{-1} for ben-

Table 4 Coefficients a_k and standard deviations for the representations of the enthalpies of mixing of the constituent binary mixtures at 303.15 K by Eqs (1) and (2). The uncertainties on the coefficients are given in parentheses

Mixtures	a_0	a_1	a_2	a_3	σ
Cyclohexane (1)+DIPE (3)	1287.19 (9.36)	367.63 (37.94)	79.43 (46.25)	–118.52 (104.74)	5.14
Benzene (2)+DIPE (3)	549.31 (7.57)	367.30 (12.28)	223.03 (31.87)	–	3.40
Cyclohexane (1)+benzene (2)	3114.29 (7.24)	–458.74 (32.92)	–177.25 (36.15)	502.41 (83.44)	4.34

zene (2)+DIPE (3) comparing of the one for cyclohexane (1)+DIPE (3) (335 J mol^{-1}).

Enthalpies of mixing H_{123} of the ternary mixtures were obtained from the relation:

$$H_{123}=H_{12+3}+(1-x_3)H_{12} \qquad (3)$$

where H_{12} is the enthalpy of mixing for the binary mixture cyclohexane (1)+benzene (2) and H_{12+3} is the enthalpy of mixing of the pseudo-binary systems. H_{12+3} was calculated according to the method described previously in [8, 9].

The experimental values for H_{12+3} and the corresponding values of H_{12+3} determined for x_1/x_2=3.0268; x_1/x_2=0.7831 and x_1/x_2=0.3330 are listed in Table 5 and represented in Fig. 3.

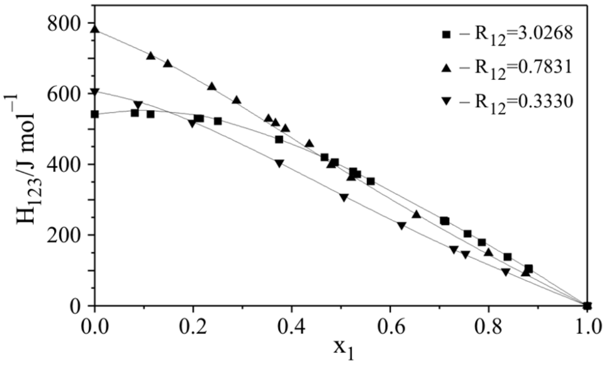

Fig. 3 Enthalpies of mixing of the ternary system cyclohexane (1)+benzene (2)+diisopropylether (3) at 303.15 K; ■ – experimental values; ▲ – experimental values; ▼ – experimental values; — – calculated from Eq. (4)

Representation of the values of H_{123} by solid curves in Fig. 3 was based on the relation

$$H_{123}=H_{12}+H_{13}+H_{23}+c_{123} \qquad (4)$$

which consists of a sum of binary contributions H_{12}, H_{13}, H_{23} calculated from Eq. (1) using the appropriate coefficients from Table 4 and an added ternary term c_{123} [10].

$$c_{123}=(c_0+c_1x_1+c_2x+..........)x_1x_2x_3 \qquad (5)$$

Table 5 Experimental values of enthalpies of mixing at 303.15 K of ternary mixtures cyclohexane (1)+benzene (2)+diisopropylether (3)

x_1	x_2	H_{12+3}/J mol^{-1}	H_{123}/J mol^{-1}
x_1/x_2=3.0268; H_{12}=541.9/J mol^{-1}			
0.690	0.228	47.8	545.6
0.666	0.220	61.1	541.6
0.594	0.196	101.7	530.2
0.591	0.195	103.9	530.0
0.563	0.186	115.8	522.2
0.469	0.155	131.6	470.4
0.401	0.132	130.8	420.0
0.385	0.127	128.3	406.1
0.357	0.118	122.5	380.0
0.350	0.116	118.9	372.0
0.330	0.109	113.5	351.8
0.218	0.072	83.8	241.5
0.216	0.071	83.3	239.7
0.216	0.071	83.1	239.0
0.182	0.060	72.2	203.9
0.160	0.053	63.4	179.4
0.121	0.040	50.5	138.3
0.088	0.029	41.9	106.4
0.089	0.029	39.7	103.9
x_1/x_2=0.7831; H_{12}=779.9/J mol^{-1}			
0.389	0.496	13.3	704.3
0.374	0.477	18.1	682.3
0.334	0.427	23.5	618.0
0.312	0.399	24.4	579.7
0.284	0.362	23.7	528.3
0.277	0.354	22.6	516.1
0.269	0.343	21.3	499.5
0.247	0.316	16.7	456.7
0.228	0.291	–7.6	397.9
0.210	0.268	–12.4	361.5
0.152	0.194	–14.8	255.7
0.081	0.112	–7.8	148.7
0.054	0.071	–6.1	91.4

Table 5 Continued

x_1	x_2	H_{12+3}/J mol^{-1}	H_{123}/J mol^{-1}
x_1/x_2=0.3330; H_{12}=606.5/J mol^{-1}			
0.227	0.684	16.9	569.9
0.200	0.601	31.4	517.7
0.156	0.468	25.8	404.9
0.123	0.370	8.4	308.0
0.094	0.282	–0.2	228.4
0.067	0.203	–3.2	161.1
0.061	0.185	–3.5	146.5
0.041	0.124	–2.7	97.8

The values of the coefficients c_j were adjusted by least-squares analyses in which Eqs (4) and (5) were fitted to the values of H_{123} in Table 5.

The best correlation was obtained at $c_{123}=c_0x_1x_2x_3$. Values of c_0 and standard deviation δ for the representation are given in Table 6. It is evident from these, that the representation of experimental results (Fig. 3) is quite good.

Table 6 Coefficient c_0 and standard deviation σ for the ternary system using Eq. (4)

Cyclohexane (1)+benzene (2)+diisopropylether (3)	
c_0	–155.6
σ/J mol^{-1}	6.1

Experimental H_{123} data of the ternary mixtures are positive, at constant mole ratio x_1/x_2, excess molar enthalpy decreases as x_3 mole fraction of DIPE increases.

The maximum value of H_{12+3} located for the pseudobinary system which corresponds to x_1/x_2=3.0268, is shifted to the weak concentration of DIPE in the other pseudobinary mixture when x_1 of the mole ratio increases.

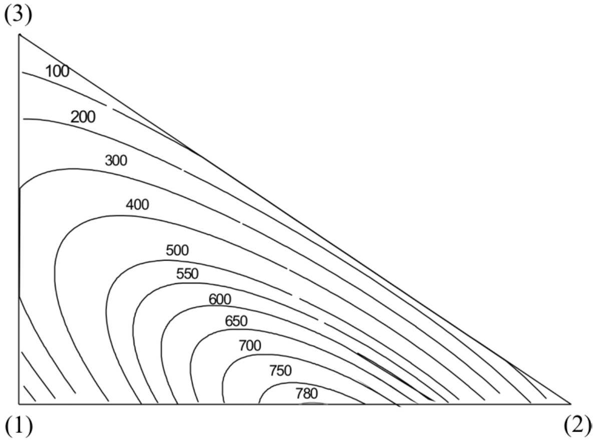

Fig. 4 Contours for constant values of H_{123}/J mol^{-1} for cyclohexane (1) + benzene (2) + diisopropylether (3)

The constant H_{123} contours were estimated using Eqs (4) and (5) and represented in Fig. 4. All of the contours extend to the edges of the triangle. The results for the ternary system under study show a positive deviation from ideal behavior, which is always increasing in the direction of the less ideal binary (benzene+cyclohexane) with a maximum value of enthalpy of mixing 780 J mol^{-1}.

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Received: January 29, 2004
In revised form: April 20, 2004