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Excess molar enthalpies of the ternary system toluene + p-xylene + 1,2-dichloroethane at 298.15 K

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Abstract

Excess molar enthalpies (H^E) were measured for the ternary system toluene + p-xylene + 1,2-dichloroethane and for the binary system toluene + 1,2-dichloroethane at 298.15 K, using a Calvet-type microcalorimeter. The ternary H^E data obtained were correlated by a modified Redlich–Kister equation.

Keywords: Liquid mixtures; Excess enthalpy; Ternary system; Hydrocarbons; 1,2-Dichloroethane

1. Introduction

The present work forms a part of our investigation on ternary systems containing two hydrocarbons and one component of different families of organic compounds. We have reported excess enthalpies (H^E) of o-xylene+nonane with cyclohexanol [1], hexan-2-one [2,3] at 298.15 and 318.15 K and with pentyl ethanoate at 298.15 K [4]. The current study on H^E in toluene + p-xylene + 1,2-dichloroethane at 298.15 K and atmospheric pressure is undertaken. No H^E information has been found for this ternary system in the literature, but there are H^E data sets at different temperatures for the constituent binaries [5–9]. Among them the data of interest at temperature 298.15 K for toluene + p-xylene were obtained by Murakami et al. [5] and Hsu and Clever [6], for toluene + 1,2-dichloroethane reported by Mahl and Khurma [7] (in a correlated form) as well as by Ortega and Plácido [8]. The H^E data for p-xylene+1,2-dichloroethane are reported by Rao and Viswanath [9] and given as correlation results in [7].

The purpose of this work was to measure excess enthalpies for the title ternary system and to carry out test measurements for constituent binaries in order to use the literature data in the correlation and prediction of ternary H^E by a modified Redlich–Kister equation [1].

2. Experimental

As described in our previous works [4,10], we used a Calvet-type differential microcalorimeter DAK-1-1 to measure heats of mixing. The apparatus and procedure have been described in detail elsewhere [11]. The uncertainty of H^E was estimated to be less than ±2% as a result of electrical calibration confirmed by check measurements on cyclohexane + benzene at 298.15 K [12]. The mole fractions, x_i, were determined with

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Table 1
Density d in kg m^{-3} and refractive indices n_D at 298.15 K

Substance	d		n_D	
	Experimental	Literature	Experimental	Literature
Toluene	862.2	862.19[a]	1.4940	1.49413[a]
p-Xylene	856.7	856.6[b]	1.4930	1.4931[b]
1,2-Dichloroethane	1246.3	1246.37[a]	1.4419	1.4421[a]

[a] From [13].
[b] From [14].

accuracy of ±0.0002. H^E measurements were carried out at atmospheric pressure.

Chemicals were supplied by Reakhim (Kharkov, Ukraine). Toluene and *p*-xylene "purum" grade materials were twice distilled. 1,2-Dichloroethane "puriss" grade material, was used without further purification. Densities and refractive indices at 298.15 K of pure liquids agree with the literature values, as seen from Table 1.

3. Results and discussion

Figs. 1–3 show a comparison of our measurement results with binary H^E data given in the literature, indicating a good agreement between our control measurements for toluene+*p*-xylene [5,6] (Fig. 1), and for *p*-xylene+1,2-dichloroethane [9] (Fig. 3). In toluene+1,2-dichloroethane, there is a significant discrepancy in H^E data (Fig. 2) for which we do not have ready explanation.

Our experimental H^E data for the binary system toluene+1,2-dichloroethane are given in Table 2. They were fitted with the following equation:

$$H^E\ (\mathrm{J\,mol^{-1}}) = x_1(1-x_1)\sum_{i=0}^{k-1} A_i(2x_1-1)^i \qquad (1)$$

by the method of least-squares, all points were weighed equally. Correlation results are given in Table 3 together with those of toluene + *p*-xylene and *p*-xylene + 1,2-dichloroethane investigated by Murakami et al. [5] and Rao and Viswanath [9], respectively. They were used for the correlation of ternary H^E data.

Table 4 lists ternary experimental results in comparison with correlation results obtained by the following equation:

$$H^E_{\mathrm{calc}} = H^E_{12} + H^E_{31} + H^E_{23} + H^E_{123} \qquad (2)$$

where the values H^E_{ij} were calculated using Eq. (1), and H^E_{123} is the ternary term [1] expressed as

$$H^E_{123} = x_1x_2x_3[C_0 + C_1x_1^m + C_2x_2^m + C_3x_3^m] \qquad (3)$$

The parameters C_i, calculated by the least-squares method using the ternary H^E data and the value $m = 4$ as an optimum value, are given in Table 5 together with the standard deviation $\sigma(H^E)$.

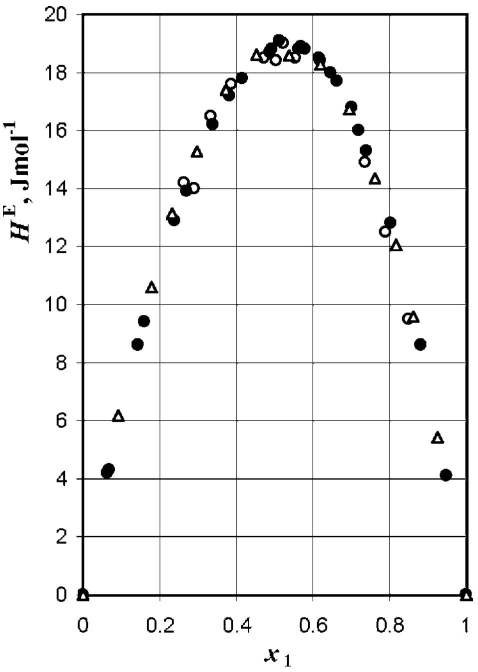

Fig. 1. Excess molar enthalpies at 298.15 K of toluene (1) + *p*-xylene (2): (●) Murakami et al. [5]; (▲) Hsu and Clever [6]; (○) this work.

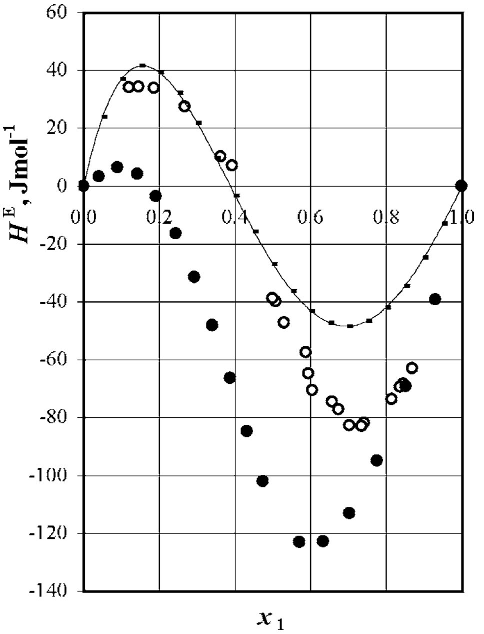

Fig. 2. Excess molar enthalpies at 298.15 K of toluene (1) + 1,2-dichloroethane (2): (●) Ortega and Plácido [8]; (—) Mahl and Khurma [7]; (○) this work.

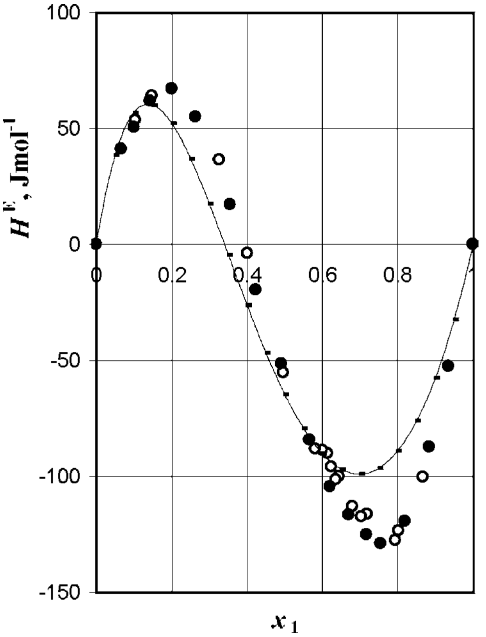

Fig. 3. Excess molar enthalpies at 298.15 K of p-xylene (1) + 1,2-dichloroethane (2): (●) Rao and Viswanath [9]; (—) Mahl and Khurma [7]; (○) this work.

Table 2
The experimental molar excess enthalpies H^E in J mol^{-1} for the binary system toluene (1) + 1,2-dichloroethane (2) at 298.15 K

x_1	H^E
0.120	34.0
0.145	34.2
0.187	33.8
0.268	27.3
0.362	10.1
0.393	7.1
0.500	−39.0
0.508	−40.0
0.531	−47.3
0.588	−57.6
0.595	−64.9
0.605	−70.5
0.657	−74.6
0.674	−77.2
0.704	−82.8
0.736	−83.0
0.743	−82.0
0.815	−73.8
0.837	−69.4
0.846	−68.4
0.870	−63.1

The standard deviation is defined by the following equation:

$$\sigma(H^E)\,(\mathrm{J\,mol^{-1}}) = \left[\frac{\sum(H^E_{\mathrm{calc}} - H^E_{\mathrm{exp}})^2}{N-k}\right]^{1/2} \qquad (4)$$

where N is the number of experimental points and k the number of parameters.

The fit to the H^E data is satisfactory (standard deviation is 3.74 J mol^{-1}) as it was also the case with other ternary systems studied by us.

The values of H^E may be interpreted as the result of the contributions of two types of interactions, operating between the aromatic hydrocarbon and 1,2-dichloroethane molecules. The negative values of H^E may be attributed to the H^E predominance of the interactions between π-electrons of aromatic hydrocarbons and polar Cl groups of 1,2-dichloroethane. The positive H^E attribute to the predominance of the contribution due to the breaking dipole–dipole bonds in 1,2-dichloroethane.

The excess enthalpies of toluene + p-xylene were positive over the whole range of composi-

Table 3
Coefficients A_i of Eq. (1), and standard deviation $\sigma(H^E)$ in J mol^{-1} for binary systems involved in the ternary system toluene + p-xylene + 1,2-dichloroethane

Binary systems	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$
Toluene (1) + p-xylene (2) [5]	75.46	10.50	0.66	−3.54	0	0	0.08
Toluene (1) + 1,2-dichloroethane (3)	−142.77	−645.07	34.87	141.24	0	0	3.04
p-Xylene (2) + 1,2-dichloroethane (3) [9]	−215.52	−996.03	64.63	−154.75	87.97	370.33	2.01

tions, whereas H^E in binary systems containing 1,2-dichloroethane are wave-shaped, negative at lower mole fractions of 1,2-dichloroethane, and positive at higher mole fraction of that, with an inversion of H^E sign from negative to positive values occurring at mole fraction of 1,2-dichloroethane about 0.62 (see Figs. 2 and 3).

The ternary system toluene (1) + p-xylene (2) + 1,2-dichloroethane (3) exhibits two regions of endothermic mixing: a narrow region in the vicinity of

Table 4
The experimental and calculated (by Eq. (2)) molar excess enthalpies H^E in J mol^{-1} for the ternary system toluene (1) + p-xylene (2) + 1,2-dichloroethane (3) at 298.15 K

Mole fractions			H^E	
x_1	x_2	x_3	Experimental	Calculated
$x_1/x_2 = 1.0$				
0.064	0.063	0.873	49.5	46.5
0.078	0.078	0.844	47.5	50.6
0.142	0.141	0.717	32.0	41.7
0.212	0.211	0.577	−3.9	−1.1
0.216	0.216	0.568	−6.1	−4.4
0.277	0.276	0.447	−47.6	−48.0
0.317	0.316	0.367	−75.6	−69.9
0.324	0.323	0.353	−77.5	−73.3
0.379	0.379	0.242	−80.1	−82.6
0.398	0.398	0.204	−76.8	−78.8
0.449	0.449	0.102	−45.6	−47.2
$x_1/x_3 = 1.0$				
0.166	0.669	0.165	−77.6	−76.2
0.286	0.428	0.286	−76.8	−85.0
0.312	0.377	0.311	−77.0	−81.4
0.317	0.366	0.317	−76.0	−80.3
0.357	0.287	0.356	−67.1	−71.3
0.364	0.273	0.363	−68.4	−69.4
0.393	0.214	0.393	−62.3	−60.7
$x_2/x_3 = 1.0$				
0.802	0.099	0.099	−43.2	−42.3
0.747	0.127	0.126	−51.6	−51.6
0.678	0.161	0.161	−59.7	−62.1
0.582	0.209	0.209	−71.9	−72.9
0.517	0.242	0.241	−76.3	−77.4
0.475	0.263	0.262	−75.5	−79.0
0.413	0.294	0.293	−77.2	−79.4
0.339	0.331	0.330	−78.1	−77.3
0.312	0.344	0.344	−75.9	−75.8
0.245	0.378	0.377	−74.5	−71.2

Table 5
Coefficients C_i of Eq. (3), and standard deviations $\sigma(H^E)$ in $\mathrm{J\,mol^{-1}}$ for the ternary system toluene (1) + *p*-xylene (2) + 1,2-dichloroethane (3) at 298.15 K

C_0	C_1	C_2	C_3	$\sigma(H^E)$
−1308.54	1746.40	5832.63	−854.88	3.74

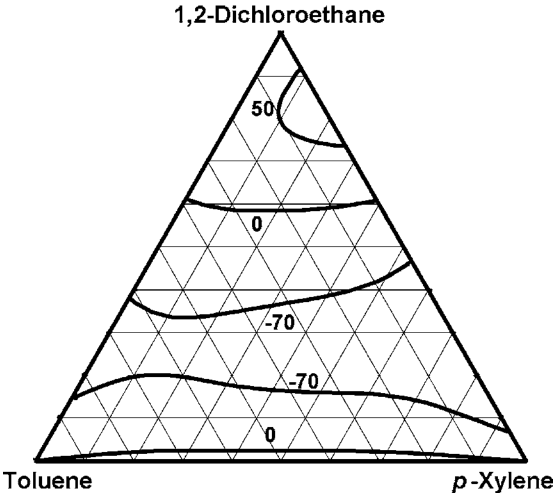

Fig. 4. Isoenthalpic lines for the ternary system toluene (1) + *p*-xylene (2) + 1,2-dichloroethane (3) at 298.15 K. Curves are calculated using the correlation equation (2) with coefficients of the ternary term (Eq. (3)) given in Table 5.

binary system toluene + *p*-xylene, and a bigger one at mole fractions of 1,2-dichloroethane higher than 0.58. A region of exothermic mixing exhibits between these two endothermic regions. The inversion points of H^E sign on the $\sec(x_1/x_2) = 1$ occur approximately at x_3 values 0.03 and 0.58. For illustration, the isoenthalpic curves for the ternary system, calculated using correlation equations (2) and (3), are presented on Gibbs triangle in Fig. 4.

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