EXCESS MOLAR ENTHALPIES OF THE TERNARY SYSTEM *o*-XYLENE + HEXAN-2-ONE + NONANE AT 298.15 K

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Abstract. Microcalorimetric measurements of excess molar enthalpies are reported for *o*-xylene + hexan-2-one + nonane and *o*-xylene + hexan-2-one at 298.15 K. The results for the ternary system are compared with those calculated by a modified Redlich–Kister equation. The temperature effect on the excess enthalpy is discussed.

INTRODUCTION

Excess enthalpy data for the mixtures composed of organic compounds are important both in theory and practice. Researches on these thermodynamic properties not only provide reliable data and empirical rules for science and technology, but also enhance the understanding of the behaviour of liquid mixtures. It is helpful to have available a variety of experimental data. Therefore we report here experimental data on excess molar enthalpy at 298.15 K for ternary mixtures containing *o*-xylene, hexan-2-one, and nonane and for the constituent binary system *o*-xylene + hexan-2-one.

In a previous study we determined the excess molar enthalpies (H^E) for the same ternary system and of all its constituent binaries at 318.15 K [1]. In order to examine the temperature effect on the H^E, these earlier studies are here extended with enthalpies at 298.15 K. There appears to be no H^E data in the literature at 298.15 K for this ternary system and for the binary system *o*-xylene + hexan-2-one.

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Excess molar enthalpy of binary hexan-2-one + nonane has been studied at temperatures 298.15 K [2], 308.15 K [3], and 318.15 K [1] and that of o-xylene + nonane at 298.15 K and 318.15 K [4]. The results obtained at 298.15 K for both systems have been used in this work. The experimental excess molar enthalpies of the ternary system were compared with those calculated by a modified Redlich–Kister equation reported earlier [4].

EXPERIMENTAL

All the substances used in the present study were the same as in our earlier work [1]. o-Xylene (1,2-dimethylbenzene) and hexan-2-one (butyl methyl ketone), Reakhim (Ukraine) "purum" grade materials, were twice fractionally distilled in a Teflon rotor column until trace impurities were not detectable by GLC. Nonane, Reakhim (Ukraine) "puriss" grade material (GLC purity > 99.8%), was used without further purification. Densities measured at 293.15 K in a capillary pycnometer were 880.1, 811.2, and 717.6 kg m^{-3} for o-xylene, hexan-2-one, and nonane, respectively.

A Calvet-type differential microcalorimeter DAK-1-1 (USSR) maintained at 298.15 ± 0.05 K was used to determine the excess molar enthalpies. Details of the equipment and operating procedure were described previously [5, 6]. The control measurements at 298.15 K on benzene-cyclohexane were in agreement within 2% (over entire range of composition) with the data reported in [7].

In studying ternary mixtures, excess molar enthalpies of mixing, H_{i+jk}^{M}, were determined for several pseudobinary mixtures (prepared by weighing) in which the component i was added to binary mixtures of components j and k having a fixed molar ratio x_j / x_k = 0.5, 1.0, or 2.0.

The excess molar enthalpy of the ternary mixture was determined by the expression

$$H_{ijk}^{\mathrm{E}} = H_{i+jk}^{\mathrm{M}} + (1 - x_i) H_{jk}^{\mathrm{E}}, \tag{1}$$

where x_i is the mole fraction of the component i in the ternary mixture, and H_{jk}^{E} is the excess molar enthalpy of the binary system $j + k$ at molar ratio x_j / x_k. The errors of H_{ijk}^{E} were estimated to be less than 2%. Errors in the mole fraction of the final ternary mixture were estimated to be less than 0.0005.

RESULTS AND DISCUSSION

Excess molar enthalpies of the system o-xylene + hexan-2-one determined experimentally are listed in Table 1.

Table 1. Experimental excess molar enthalpies, H^E, for binary mixtures o-xylene (1) + hexan-2-one (2) at 298.15 K

x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}
0.111	–50.8	0.670	–89.1
0.202	–81.8	0.707	–83.9
0.325	–106.1	0.750	–71.1
0.362	–111.9	0.790	–58.2
0.421	–112.5	0.836	–43.4
0.477	–113.9	0.862	–35.3
0.557	–106.5	0.899	–27.3
0.619	–99.0		

The binary data were fitted to Eq. 2:

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

where x_1 is the mole fraction of o-xylene. To find values of coefficients A_i, the experimental data were fitted by the least squares regression with all points weighed equally. The values of coefficients A_i are given in Table 2 together with standard deviation $\sigma(H^E)$, defined by Eq. 3:

$$\sigma(H^E) = \left[\sum_i (H^E_{\text{exp}} - H^E_{\text{calc}})^2_i \big/ (n-k) \right]^{1/2}, \qquad (3)$$

where k stands for a number of coefficients needed to represent results adequately ($k = 5$) and the sum is taken over the set of n results ($n = 15$). For convenience, the H^E data for o-xylene + nonane and hexan-2-one + nonane at 298.15 K of present interest investigated earlier are also given in Table 2 as correlation results with Eq. 2.

Table 2. Coefficients A_i of Eq. 2 for binary systems and C_i of Eq. 4 for the ternary system ($m = 4$), and standard deviation $\sigma(H^E)$ at 298.15 K

Binary system	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$, J mol^{-1}
o-Xylene (1) + hexan-2-one	–451.29	112.14	58.28	51.75	30.58	0	1.3
o-Xylene (1) + nonane(2) [4]	1727.90	420.51	29.90	–419.92	0	0	7.6
Hexan-2-one (1) + nonane [2]	4792.4	–699.75	743.73	795.47	–95.78	–1228.2	5.1

Ternary system	C_0	C_1	C_2	C_3	$\sigma(H^E)$, J mol^{-1}
o-Xylene + hexan-2-one + nonane	1425.61	7368.94	–5800.12	5911.99	18.5

Experimental results of H^E for the ternary system are listed in Table 3. Representation of ternary H^E was based on Eq. 4:

$$H_{calc}^E = H_{12}^E + H_{31}^E + H_{23}^E + (C_0 + C_1 x_1^m + C_2 x_2^m + C_3 x_3^m) x_1 x_2 x_3, \qquad (4)$$

where the values of H_{ij}^E were calculated from Eq. 2, x_i are the mole fractions in the ternary mixture, and m is equal to 4. The coefficients C_i calculated from ternary experimental data by the least squares method are given in Table 2.

Table 3. Experimental excess molar enthalpies, H^E, for the ternary system o-xylene (1) + hexan-2-one (2) + nonane (3) at 298.15 K

x_1	x_2	H^E, J mol^{-1}	x_1	x_2	H^E, J mol^{-1}
$x_1/x_2 = 1.0^*$			
0.083	0.083	532	0.084	0.747	576
0.142	0.142	745	0.164	0.507	877
0.180	0.180	810	0.230	0.310	864
0.243	0.243	889	0.303	0.091	612
0.267	0.267	839			
0.431	0.431	350		$x_1/x_3 = 2.0^*$	
			0.079	0.882	129
	$x_1/x_2 = 0.5^*$		0.110	0.835	162
0.065	0.130	691	0.213	0.680	306
0.074	0.150	745	0.291	0.564	401
0.099	0.198	865	0.455	0.318	524
0.129	0.257	954	0.577	0.135	505
0.138	0.277	966			
0.165	0.331	929		$x_2/x_3 = 1.0^*$	
0.176	0.351	923	0.138	0.431	1009
0.193	0.387	890	0.298	0.351	799
0.213	0.427	881	0.426	0.287	642
0.214	0.429	849	0.708	0.146	306
0.278	0.555	498			
				$x_2/x_3 = 0.5^*$	
	$x_1/x_2 = 2.0^*$		0.155	0.282	963
0.136	0.068	486	0.375	0.208	735
0.196	0.098	627	0.509	0.164	593
0.232	0.116	687	0.775	0.075	291
0.323	0.161	712			
0.338	0.169	730		$x_2/x_3 = 2.0^*$	
0.436	0.217	694	0.143	0.571	832
			0.299	0.467	624
	$x_1/x_3 = 1.0^*$		0.499	0.334	412
0.095	0.810	324	0.794	0.137	146
0.180	0.640	550			
0.285	0.430	690			
0.372	0.257	723			

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* Obtained by mixing the pure component i with a binary mixture $j + k$ in which the mole fraction ratio is x_j/x_k.

The modified Redlich–Kister equation, Eq. 4, represents the ternary excess molar enthalpies with the relative average deviation of 2.1%, providing useful estimation of H^E without a need of direct measurement of any additional ternary compositions.

Most of the ternary compositions exhibit endothermic mixing. A small exothermic mixing region adjoins the binary system o-xylene + hexan-2-one, whose mixing is exothermic. This suggests that in these binary mixtures specific interactions exist between the dissimilar molecules. Comparison with binary H^E data obtained at other temperatures [1–4] shows that H^E $vs.$ x of all constituent binaries have a small temperature effect, which is greatest for the o-xylene + hexan-2-one mixtures. Changing the temperature from 298.15 K to 318.15 K causes the H^E values to become less negative (from –113 J mol^{-1} to –71 J mol^{-1} at $x = 0.5$) due to the weakening of the intermolecular interactions between the polar ketone group (CO) and the π-electrons of o-xylene. The positive (endothermic) H^E values of binary mixtures containing nonane decrease with increasing temperature. This confirms the weakening of dipole–dipole (CO–CO) interactions in hexan-2-one, π–π interaction in o-xylene, and a decrease in short-range orientational order in liquid nonane [8].

The H^E temperature dependence can be expected to be the same in the ternary system. To serve as an example, some H^E values obtained at 298.15 K in this work and those for 318.15 K given in [1] for the same or close compositions are compared in Table 4.

Table 4. Comparison of excess molar enthalpy values in the ternary system o-xylene (1) + hexan-2-one (2) + nonane (3) at 298.15 K and 318.15 K

x_1	x_2	x_3	H^E, J mol^{-1}	
			298.15 K	318.15 K
0.372	0.258	0.372	723	709
0.285	0.430	0.285	690	677
0.180	0.640	0.180	550	531
0.180	0.180	0.640	810	786
0.095	0.810	0.095	324	344
0.142	0.142	0.716	745	695

Comparison reveals small and expected differences in ternary H^E values.

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KOLMIKSÜSTEEMI *o*-KSÜLEEN + HEKSAAN-2-OON + NONAAN MOLAARSED LIIGENTALPIAD TEMPERATUURIL 298,15 K

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On esitatud uued liigentalpia andmed kolmiksüsteemi *o*-ksüleen + heksaan-2-oon + nonaan ning selles sisalduva kaksiksüsteemi *o*-ksüleen + heksaan-2-oon kohta temperatuuril 298,15 K. Kolmiksüsteemi katseandmeid on korreleeritud Redlichi–Kisteri võrrandi modifikatsiooniga. Samale kolmiksüsteemile 318,15 K juures saadud liigentalpia võrdlusandmete abil on käsitletud molekulidevaheliste vastastikmõjude muutumist temperatuuri tõusuga.