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Excess enthalpies of 1-nonene–*n*-nonane, 1-hexanol–2-hexyn-1-ol, 1-nonene–2-hexyn-1-ol–*n*-nonane, and 1-hexanol–2-hexyn-1-ol–*n*-nonane at 298.15 K

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Abstract

Excess enthalpies for the two binary systems, 1-nonene–*n*-nonane and 1-hexanol–2-hexyn-1-ol, and the two ternary systems, *n*-nonane–1-hexanol–*n*-nonane and 1-hexanol–2-hexyn-1-ol–*n*-nonane, at 298.15 K have been determined with a Calvet-type microcalorimeter. The experimental results of the binary systems have been fitted to Redlich–Kister equations. Some modified Redlich–Kister equations and the UNIFAC group contribution model have been applied in predicting ternary excess enthalpies.

INTRODUCTION

Continuing our studies of mixtures containing unsaturated organic compounds, we report here the experimental excess molar enthalpies H^E of the two ternary systems 1-nonene–2-hexyn-1-ol–*n*-nonane and 1-hexanol–2-hexyn-1-ol–*n*-nonane, at 298.15 K. The aim of this work was to test the ability of some methods to predict H^E data of ternary systems using excess enthalpies of binary mixtures. Two binary systems, 1-nonene–*n*-nonane and 1-hexanol–2-hexyn-1-ol, were also investigated in this work: the H^E data for the other binary mixtures related to the ternary systems studied have already been reported [1–3].

EXPERIMENTAL

A Calvet-type differential microcalorimeter was used for the measurements; the operational procedure has been described in detail [4]. The precision of H^E determined on the basis of the system benzene–cyclohexane [5], and the mole fraction x were estimated to be better than 2.0% and 1×10^{-3}, respectively.

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2-Hexyn-1-ol was prepared in our laboratory [1]. It was fractionally distilled in the Teflon bristle-rotor 50-plate column, as were the 1-nonene and 1-hexanol. Both the alcohols were stored in a dry box and were distilled before use. The *n*-nonane (puriss grade) obtained from Reakhim (Kharkov, Ukraine) was used without further purification. Analysis by capillary GLC showed that the purity of the hydrocarbons and alcohols was higher than 99.8 and 99.5 mol%, respectively. The densities of the final products, measured with an Ostwald pyknometer at 293.15 K, were (in kg m^{-3}) 725.3 for 1-nonene, 713.8 for *n*-nonane, 815.5 for 1-hexanol and 889.9 for 2-hexyn-1-ol.

RESULTS

The measured excess enthalpies of the binary systems are given in Table 1 together with the deviations Δ between the experimental H^E values and those calculated from the Redlich–Kister equation

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

fitted to each set of values by the method of unweighted least squares. Values of the coefficients A_i are presented in Table 2. The number of coefficients *m* was varied, and in each case the minimum number needed to

TABLE 1

Excess enthalpies H^E for 1-nonene(1)–*n*-nonane(2) and 1-hexanol(1)–2-hexyn-1-ol(2) at 298.15 K and deviations Δ between experimental H^E values and those calculated from eqn. (1)

x_1	H^E/J mol^{-1}	Δ/J mol^{-1}	x_1	H^E/J mol^{-1}	Δ/J mol^{-1}
1-Nonene(1)–*n*-nonane(2)					
0.198	25.4	0.2	0.526	39.3	−0.8
0.287	32.0	−0.8	0.564	40.0	0.5
0.318	34.8	0.0	0.605	36.9	−1.3
0.425	39.1	−0.2	0.687	34.2	0.0
0.439	40.3	0.7	0.805	23.8	0.7
0.478	39.6	−0.5	0.824	23.3	0.7
0.495	40.5	0.3			
1-Hexanol(1)–2-hexyn-1-ol(2)					
0.126	81	1	0.556	186	2
0.344	161	−3	0.656	168	−3
0.346	166	1	0.783	135	3
0.464	183	0	0.796	130	3
0.499	184	0	0.863	92	−2

TABLE 2

Coefficients A_i of eqn. (1) and standard deviations $\sigma(H^E)$ (in J mol^{-1}) for the binary systems 1-nonene–*n*-nonane and 1-hexanol–2-hexyn-1-ol

System	A_0	A_1	A_2	$\sigma(H^E)$
1-Nonene–*n*-nonane	160.87	−1.94	−9.0	0.71
1-Hexanol–2-hexyn-1-ol	738.06	45.04	48.24	2.56

TABLE 3

Excess enthalpies H^E for the system 1-nonene(1)–2-hexyn-1-ol(2)–*n*-nonane(3) at 298.15 K

x_1	x_2	x_3	H^E/J mol^{-1}
$x_{12} = 1.020$ [a]			
0.173	0.169	0.658	805
0.255	0.250	0.495	945
0.309	0.303	0.388	987
0.420	0.411	0.169	986
$x_{12} = 0.616$ [a]			
0.107	0.174	0.719	744
0.151	0.245	0.604	908
0.274	0.445	0.281	1047
0.300	0.486	0.214	1007
0.349	0.567	0.084	930
$x_{12} = 2.021$ [a]			
0.154	0.076	0.770	561
0.178	0.088	0.735	632
0.541	0.268	0.191	927
0.572	0.283	0.145	938
$x_{13} = 0.729$ [a]			
0.253	0.400	0.347	1038
0.285	0.325	0.390	1010
0.333	0.210	0.457	892
0.349	0.170	0.480	829
$x_{13} = 2.509$ [a]			
0.156	0.782	0.062	688
0.191	0.733	0.076	743
0.228	0.681	0.091	835
0.376	0.474	0.150	1009
0.564	0.211	0.225	935
0.625	0.126	0.249	798
$x_{13} = 1.004$ [a]			
0.064	0.872	0.064	496
0.129	0.743	0.128	759
0.198	0.605	0.197	960
0.357	0.288	0.355	997
0.367	0.267	0.366	967
0.403	0.196	0.401	881
0.451	0.100	0.449	555
$x_{23} = 0.992$ [a]			
0.167	0.415	0.419	1018
0.482	0.258	0.260	957
0.631	0.184	0.185	875
0.779	0.110	0.111	689
$x_{23} = 0.965$ [a]			
0.441	0.275	0.284	970
0.739	0.128	0.133	797
$x_{23} = 0.667$ [a]			
0.200	0.320	0.480	1001
0.210	0.316	0.474	1002
0.429	0.228	0.343	922
0.797	0.081	0.122	670

[a] Obtained by mixing the pure component *j* with the binary mixture $i + k$ in which the mole fraction ratio is $x_{ik} = x_i/x_k$.

represent the results (consisting of n experimental points) was found in order to obtain a minimum standard deviation according to

$$\sigma(H^{\mathrm{E}}) = \sum_{n} \{(H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{calc}})^2/(n - m)\}^{1/2} \tag{2}$$

Values of $\sigma(H^{\mathrm{E}})$ for the best fit (for both the systems, m was equal to 3) are given in Table 2.

Tables 3 and 4 list the ternary experimental results for 1-nonene–2-hexyn-1-ol–*n*-nonane and 1-hexanol–2-hexyn-1-ol–*n*-nonane, respectively.

The results are compared with those obtained using some of the modified Redlich–Kister equations recommended by Prchal et al. [6] for predicting

TABLE 4

Excess enthalpies H^{E} for the system 1-hexanol(1)–2-hexyn-1-ol(2)–*n*-nonane(3) at 298.15 K

x_1	x_2	x_3	H^{E}/J mol^{-1}	x_1	x_2	x_3	H^{E}/J mol^{-1}
$x_{12} = 0.976$ [a]				$x_{23} = 1.053$ [a]			
0.081	0.083	0.836	639	0.599	0.206	0.195	498
0.258	0.264	0.477	825	0.748	0.129	0.123	327
0.309	0.317	0.374	784	$x_{23} = 0.992$ [a]			
0.341	0.349	0.310	725	0.095	0.450	0.454	955
0.388	0.397	0.215	598	0.231	0.383	0.386	852
0.444	0.455	0.101	400	0.344	0.327	0.329	766
$x_{13} = 0.996$ [a]				0.385	0.307	0.309	724
0.135	0.729	0.136	483				
0.190	0.619	0.191	606				
0.359	0.281	0.360	756				
0.419	0.160	0.421	720				
0.430	0.138	0.432	712				
0.447	0.104	0.449	702				

[a] Obtained by mixing the pure component j with the binary mixture $i + k$ in which the mole fraction ratio is $x_{ik} = x_i/x_k$.

TABLE 5

The mean percentage deviations $\delta(H^{\mathrm{E}})$ between the experimental binary excess enthalpies and those predicted by the original UNIFAC model [7] and its modification [9]

Binary system	UNIFAC [a]	Mod. UNIFAC (Dortmund's version)
1-Nonene–2-hexyn-1-ol	10.7	13.5
1-Nonene–*n*-nonane	32.0	78.6
2-Hexyn-1-ol–*n*-nonane	11.2	43.2
1-Hexanol–2-hexyn-1-ol	108.8	111.5
1-Hexanol–*n*-nonane	8.8	18.5

[a] The group interaction parameters have been determined from binary H^{E} data [8].

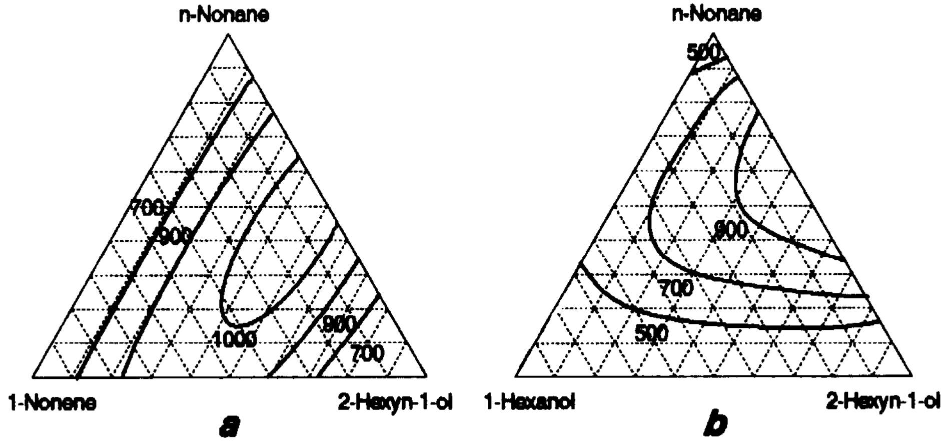

Fig. 1. The isoenthalpic curves of the excess enthalpy (in J mol^{-1}) at 298.15 K for the systems: (a) 1-nonene–2-hexyn-1-ol–*n*-nonane; and (b) 1-hexanol–2-hexyn-1-ol–*n*-nonane.

the excess enthalpy of ternary systems from binary data. The binary data correlations by eqn. (1) given here and those published earlier [1–3] were used. The best prediction results (with mean percentage deviation, $\delta H^E = 1.8\%$) for the system 1-nonene–*n*-nonane–2-hexyn-1-ol (system I) were obtained by the modified Scatchard equation, and for the system 1-hexanol–2-hexyn-1-ol–*n*-nonane (system II) by that of Tsao ($\delta H^E = 4.1\%$). The deviations using the UNIFAC model fitted to binary H^E data appeared much higher: 9.0% and 15.2% for the systems I and II, respectively. It can be seen from Table 5 that this model and its modification [9] also give considerable deviations between the experimental and predicted results for all the binary systems considered, particularly for the mixtures of two alcohols.

The influence of the replacement of 1-nonene by 1-hexanol in the ternary system on the H^E values is shown in Fig. 1 where the curves of constant H^E values (lines of isoenthalpy) have been calculated by means of the modified Redlich–Kister equations which gave the best H^E prediction.

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