Excess enthalpies of pentyl ethanoate–1-hexanol, pentyl ethanoate–n-nonane and pentyl ethanoate–1-hexanol–n-nonane at 298.15 K

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Abstract

Excess enthalpies for pentyl ethanoate–1-hexanol, pentyl ethanoate–n-nonane and pentyl ethanoate–1-hexanol–n-nonane mixtures at 298.15 K have been determined with a Calvet-type microcalorimeter. The UNIFAC group contribution model fitted to binary H^E data and several modified Redlich–Kister equations have been applied to predicting ternary excess enthalpies. The predicted results agree satisfactorily with the experimental values.

INTRODUCTION

The purpose of the present work was to measure molar excess enthalpies (H^E) for the ternary system pentyl ethanoate–1-hexanol–n-nonane at 298.15 K with the aim of making a comparison between the predicted and experimental H^E data. We present here also, the excess enthalpies of two binary systems, pentyl ethanoate +1-hexanol and +n-nonane, involved in the ternary system investigated. The H^E data for the third binary system, 1-hexanol–n-nonane, have been reported by Ortega [1].

EXPERIMENTAL

A Calvet-type differential microcalorimeter was used in these experiments. The operational procedure has been described in detail [2]. The precision of H^E determined on the basis of the standard system benzene–cyclohexane [3], and the mole fraction x were estimated to be better than 2.0% and 1×10^{-3}, respectively.

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Pentyl ethanoate and 1-hexanol (special commercial grade reagents) were distilled before use in vacuum in a teflon rotor column at a reflux ratio of 0.1. Nonane (puriss grade) was obtained from Reakhim (Kharkov, Ukraine) and used without further purification. Analysis by GLC showed purity levels to be higher than 99.8% for pentyl ethanoate and n-nonane and higher than 99.5% for 1-hexanol. Densities of the purified materials at 298.15 K measured with an Ostwald pyknometer were in close agreement with the literature values: pentyl ethanoate ($870.8\,\mathrm{kg\,m^{-3}}$), 1-hexanol ($815.5\,\mathrm{kg\,m^{-3}}$), n-nonane ($713.7\,\mathrm{kg\,m^{-3}}$).

RESULTS

The measured molar enthalpies H^E of two binary systems containing pentyl ethanoate are given in Table 1 together with the values of H^E calculated from the least-squares fit to the equation

$$H^E_{\mathrm{calc}}/\mathrm{J\,mol^{-1}} = x_1(1 - x_1)\sum_{i=0}^{4} A_i(2x_1 - 1)^i \tag{1}$$

where x_1 is the mole fraction of pentyl ethanoate.

TABLE 1

Excess enthalpies H^E for pentyl ethanoate(1)–1-hexanol(2) and pentyl ethanoate(1)–n-nonane(2) at 298.15 K

x_1	$H^E/\mathrm{J\,mol^{-1}}$		x_1	$H^E/\mathrm{J\,mol^{-1}}$	
	Exp	Calc		Exp	Calc
Pentyl ethanoate(1) + 1-hexanol(2)					
0.081	408	409	0.501	1550	1546
0.217	1014	1001	0.606	1567	1553
0.359	1369	1379	0.773	1271	1279
0.381	1397	1417	0.845	996	1002
0.459	1516	1515	0.868	896	889
0.492	1549	1541			
Pentyl ethanoate(1) + n-nonane(2)					
0.104	400	400	0.598	889	880
0.192	634	633	0.611	858	868
0.306	832	831	0.658	816	816
0.344	876	874	0.724	727	721
0.381	898	906	0.767	641	646
0.480	936	937	0.858	453	452
0.499	941	935			

TABLE 2

Coefficients A_i of eqn. (1) and standard deviations $\sigma(H^E)$ in J mol^{-1} for binary systems

Pentyl ethanoate +	A_0	A_1	A_2	A_3	A_4	$\sigma(H^E)$
1-hexanol	6182.94	1126.26	1838.26	478.58	−1506.4	13.4
n-nonane	3738.70	−409.26	60.84	149.74	686.55	6.6

The coefficients of eqn. (1) for mixtures are listed in Table 2 together with the estimated standard deviation, $\sigma(H^E)$, calculated from

$$\sigma(H^E) = \left[\sum (H^E_{obs} - H^E_{calc})^2/(n - m) \right]^{1/2} \tag{2}$$

where the sum was taken over the set of n results and m is the number of coefficients.

Table 3 lists ternary experimental results.

In our predictions for the concentration dependence of ternary H^E values the correlation eqns. (1) for constituent binary systems were used. One of the prediction relations was that of the binary contributions method

$$H^E_{ijk} = \sum_{i<j} \sum_j H^E_{ij}(x_i, x_j) \tag{3}$$

TABLE 3

Excess enthalpies H^E at 298.15 K for the system pentyl ethanoate(1)–1-hexanol(2)-n-nonane(3)

x_1	x_2	x_3	H^E/J mol^{-1}	x_1	x_2	x_3	H^E/J mol^{-1}
$x_{12} = 0.441$ [a]				$x_{13} = 2.030$ [a]			
0.035	0.079	0.886	598	0.152	0.773	0.075	799
0.138	0.313	0.546	1226	0.337	0.497	0.166	1590
0.225	0.510	0.265	1284	0.345	0.485	0.170	1596
0.263	0.596	0.141	1289	0.566	0.155	0.279	1507
$x_{12} = 1.004$ [a]				$x_{23} = 0.996$ [a]			
0.102	0.102	0.796	940	0.271	0.364	0.365	1625
0.272	0.271	0.457	1565	0.301	0.349	0.350	1650
0.291	0.290	0.409	1587	0.351	0.324	0.325	1704
0.387	0.385	0.228	1663	0.609	0.195	0.196	1436
0.431	0.429	0.140	1674	0.830	0.085	0.085	725
$x_{13} = 0.488$ [a]				$x_{23} = 3.184$ [a]			
0.088	0.732	0.180	769	0.594	0.309	0.097	1708
0.264	0.194	0.542	1494	0.787	0.162	0.057	1207

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

where $H_{ij}^{E}(x_i, x_j)$ is the contribution obtained on inserting mole fractions of the ternary mixture into eqn. (1) for the binary system i–j.

The three other relations covered by a common formula and described in detail by Prchal et al. [4] are those suggested and modified by Scatchard and that proposed by Tsao. With these equations we obtained the following mean percentage deviations $\delta(H^E)$ between the experimental and predicted results: 14.6% (eqn. (3)), the same result gives the Scatchard equation (is identical to eqn. (3)), 10.8% (the modified Scatchard equation for one polar component), and 10.3% (the Tsao equation). The mean deviation was calculated from

$$\delta(H^E)\% = \frac{1}{n}\sum_n \left[\frac{H_{exp}^E - H_{calc}^E}{H_{exp}^E}\right] \times 100 \tag{4}$$

where n is the number of experimental points.

Figure 1 depicts the location of the curves of the constant H^E (lines of isoenthalpies) in the Gibbs triangle calculated by means of the Tsao equation.

Table 4 shows the H^E predictions by the UNIFAC model obtained with two sets of group interaction parameters fitted to binary H^E data and based on the surface area parameters of the original UNIFAC (★) and the treble values of the latter (★★). The interaction parameters used have been published elsewhere [5–7] and for some groups they are given in Table 5. The H^E data of constituent binary systems have not been used for the determination of
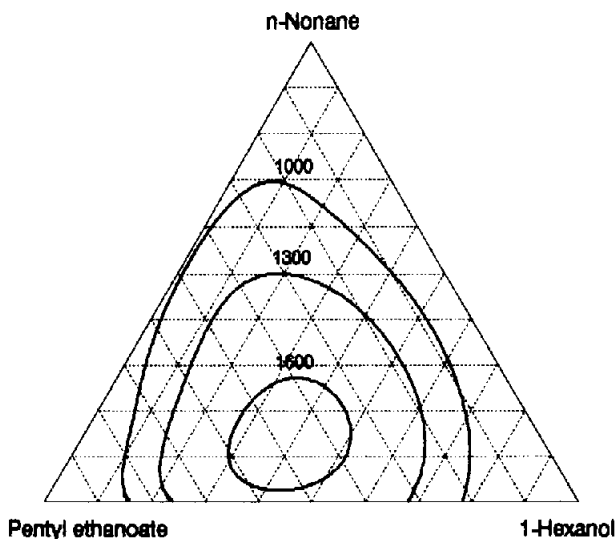

Fig. 1. The isoenthalpic curves of the excess enthalpy for the ternary system pentyl ethanoate–1-hexanol–n-nonane at 298.15 K calculated using the Tsao equation.

TABLE 4

Mean percentage deviation between experimental and predicted by the UNIFAC model ternary excess enthalpies $\delta(H^E)/\%$ for the system pentyl ethanoate–1-hexanol–n-nonane at 298.15 K

Groups of		$\delta(H^E)$ [a]	
Ester	Alcohol	★	★★
COO	OH	12.2	7.4
CH₃COO	OH	7.1	5.0
COO	CCOH	11.7	6.4
CH₃COO	CCOH	7.2	4.6

[a] Obtained with the group interaction parameters determined using the surface area parameters of the original UNIFAC (★) and the treble values of those (★★).

interaction parameters. Those given in Table 5 for the ester and alcohol groups have been determined by means of H^E data for the system ethyl propanoate–1-hexanol, propyl ethanoate–1-butanol, methyl butanoate–1-pentanol presented in [8] and for the system ethyl ethanoate–1-butanol obtained by Nagata et al. [9] at 298.15 K.

In order to obtain a better prediction, the ester and alcohol groups are characterized using different forms. As seen in Table 4, the mean deviations from the interaction parameters corresponding to the treble values of group surface area parameters are smaller and more uniform than those obtained with the interaction parameters based on the surface area ones originally normalized. Comparison of the mean deviations made in this work shows that the UNIFAC model fitted to H^E binary data gives a better prediction of H^E for the ternary system studied with respect to eqn. (3), and its modified forms mentioned above.

TABLE 5

The UNIFAC group interaction parameters (a_{st}) fitted to binary H^E data [a] and mean percentage deviation $\delta(H^E/\%)$

Groups		★			★★		
s	t	a_{st}	a_{ts}	$\delta(H^e)/\%$	a_{st}	a_{ts}	$\delta(H^E)/\%$
CH₃COO	OH	586.35	500.44	14.8	438.50	83.88	15.2
COO	CCOH	527.39	578.65	23.9	131.30	211.01	6.1
CH₃COO	CCOH	515.28	538.65	17.5	134.66	56.56	13.5
CH₂	CCOH		[b]		1855.78	56.02	15.5

[a] Determined using the surface area parameters of the original UNIFAC (★) and the treble values of those (★★). [b] Ref. 5.

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