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Excess enthalpies of the system containing pentyl ethanoate, 1,2-dimethylbenzene and *n*-nonane at 298.15 and 318.15 K

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Abstract

Calorimetric measurements of excess enthalpies are reported for the ternary system pentyl ethanoate + 1,2-dimethylbenzene + *n*-nonane and for binaries pentyl ethanoate + 1,2-dimethylbenzene at 298.15 and 318.15 K and pentyl ethanoate + *n*-nonane at 318.15 K. The results, together with those previously published for constituent binaries, were well correlated with a modified Redlich–Kister equation. The ternary excess enthalpies at 318.15 K were considered together with the excess Gibbs energies calculated by the Wilson equation with temperature dependence parameters. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The excess thermodynamic properties of multicomponent systems constitute a key element for the prediction ability of theoretical models. The excess molar enthalpies, H^E, are useful for fitting model parameters and for determination of the temperature dependence of interaction parameters in predictive models. In this paper, excess molar enthalpies of the ternary mixture pentyl ethanoate + 1,2-dimethylbenzene + *n*-nonane at temperatures 298.15 and 318.15 K are reported. The measurements are a part of a long-term study of ternary systems containing different families of organic compounds.

There appears to be no H^E data in the literature at 298.15 and 318.15 K for this ternary system as well as for the binary pentyl ethanoate + 1,2-dimethylbenzene and at 318.15 K for the binary pentyl ethanoate + *n*-nonane. The excess molar enthalpies for pentyl ethanoate + *n*-nonane at 298.15 K and for 1, 2-dimethylbenzene + *n*-nonane obtained by us earlier [1,2] were used in this work.

The new experimental H^E data are intended to complement the data available in the literature and they are compared with values correlated using the modified Redlich–Kister equation [2]. To connect the ternary H^E data with those of vapor–liquid equilibrium for this ternary system reported recently [3], the Wilson excess Gibbs energy model [4] was used.

The interaction parameters of this model considered to vary linearly with temperature [5].

2. Experimental

A Calvet-type differential microcalorimeter DAK-1-1 [6] was used for measurements of excess enthalpies at 298.15 and 318.15 K. The details of

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calorimetric procedure and reproducibility have been described elsewhere [7]. 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 [8] and 1-propanol + n-heptane at 318.15 K [9].

Experiments were carried out at atmospheric pressure. All mixtures were prepared by mass. The mole fractions, x_i, were determined with an accuracy of ±0.0002.

Pentyl ethanoate and 1,2-dimethylbenzene "purum" grade materials were twice distilled. n-Nonane "puriss" grade material was used without further purification.

Pentyl ethanoate (GLC purity >99.8%), 1,2-dimethylbenzene (GLC purity >99.5%) and n-nonane (GLC purity >99.8%) densities were found to be 875.4, 880.1 and 717.6 kg m^{-3} at 293.15 K, respectively. Densities were measured using a capillary pycnometer with a calibrated accuracy of ±0.2 kg m^{-3}.

3. Results

The experimental molar excess enthalpies of two binary systems containing pentyl ethanoate are given in Table 1. Table 2 lists ternary experimental results. Binary H^E data were fitted with Eq. (1)

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

by the method of least squares, all points were weighed equally. The H^E data for pentyl ethanoate + n-nonane at 298.15 K and for 1,2-dimethylbenzene + n-nonane at 298.15 and 318.15 K of interest investigated earlier, for convenience, are given in Table 3 as correlation results with Eq. (1).

The ternary H^E concentration dependence was represented as sum of binary terms with an added ternary contribution, Eq. (2):

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

where the values of H^E_{jk} were calculated from Eq. (1), and H^E_{123} is the ternary term expressed as

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

Table 1
The experimental molar excess enthalpies H^E in J mol^{-1} for binary systems

x_1	H^E	x_1	H^E
Pentyl ethanoate (1) + 1,2-dimethylbenzene (2)			
At 298.15 K		At 318.15 K	
0.148	−90.6	0.075	−38.7
0.159	−95.6	0.108	−53.1
0.192	−106.3	0.164	−75.2
0.290	−131.5	0.219	−95.3
0.396	−148.7	0.295	−114.9
0.487	−149.7	0.323	−119.0
0.542	−147.5	0.340	−125.6
0.651	−128.0	0.354	−125.9
0.739	−104.9	0.386	−129.0
0.783	−93.7	0.490	−130.9
0.807	−84.8	0.597	−123.1
		0.693	−109.1
		0.727	−102.9
		0.823	−72.0
		0.835	−69.4
Pentyl ethanoate (1) + n-nonane (2) at 318.15 K			
0.125	373	0.530	934
0.192	550	0.601	911
0.200	566	0.630	904
0.301	747	0.660	839
0.398	873	0.707	809
0.419	911	0.802	666
0.471	941	0.843	558
0.493	940	0.874	435

The coefficients C_i were calculated by the least squares method using the ternary H^E data. The values of coefficients A_i of Eq. (1) and C_i of Eq. (3) are listed in Tables 3 and 4 along with the standard deviations $\sigma(H^E)$, defined by Eq. (4):

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

where N is a number of experimental values and k is a number of coefficients. The m value in Eq. (3) is equal to 4 as an optimum value in most cases found [2]. The ternary excess molar enthalpies calculated by Eq. (3) are compared with experimental values in Table 2.

The relative mean deviations between calculated and experimental results are equal to 1.92 and 2.83% at temperatures 298.15 and 318.15 K, respectively.

Table 2
The experimental molar excess enthalpies H^E in J mol^{-1} for ternary system pentyl ethanoate (1) + 1,2-dimethylbenzene (2) + *n*-nonane (3)

x_1	x_2	x_3	Experimental H^E at 298.15 K	(calculated)
$x_1/x_2 = 1.0$				
0.459	0.460	0.081	90	90
0.416	0.416	0.168	305	301
0.176	0.176	0.648	654	629
0.121	0.121	0.758	509	520
$x_1/x_2 = 0.5$				
0.272	0.543	0.185	311	302
0.209	0.418	0.373	553	540
0.150	0.301	0.549	595	583
0.100	0.199	0.701	491	503
$x_1/x_2 = 2.0$				
0.560	0.280	0.160	343	333
0.463	0.232	0.305	614	602
0.336	0.168	0.496	758	756
0.151	0.075	0.774	541	570
$x_1/x_3 = 1.0$				
0.437	0.126	0.437	793	790
0.278	0.444	0.278	660	683
0.242	0.516	0.242	399	393
0.152	0.696	0.152	235	229
$x_1/x_3 = 0.5$				
0.072	0.785	0.143	226	217
0.153	0.542	0.305	443	445
0.229	0.313	0.458	623	623
0.284	0.148	0.568	747	750
$x_2/x_3 = 1.0$				
0.148	0.426	0.426	547	538
0.292	0.354	0.354	570	571
0.628	0.186	0.186	445	434
0.784	0.108	0.108	287	292
$x_2/x_3 = 0.5$				
0.696	0.101	0.203	510	517
0.482	0.172	0.346	699	688
0.337	0.221	0.442	702	705
0.114	0.295	0.591	549	543
$x_2/x_3 = 2.0$				
0.196	0.536	0.268	424	416
0.340	0.440	0.220	395	386
0.504	0.331	0.165	337	323
0.711	0.193	0.096	211	216
$x_1/x_2 = 1.0$				
0.427	0.427	0.146	295	288
0.375	0.376	0.249	497	495
0.263	0.263	0.474	700	682
0.199	0.199	0.602	701	638
$x_1/x_2 = 0.5$				
0.066	0.132	0.802	345	353
0.071	0.142	0.787	365	372
0.104	0.208	0.688	508	482
0.116	0.233	0.651	523	515
0.164	0.329	0.507	606	593
0.221	0.441	0.338	516	539
0.288	0.577	0.135	237	228
$x_1/x_2 = 2.0$				
0.296	0.148	0.556	761	754
0.323	0.162	0.515	744	765
0.492	0.246	0.262	532	574
0.570	0.285	0.145	315	326
$x_1/x_3 = 1.0$				
0.386	0.227	0.387	693	711
0.322	0.355	0.323	530	586
0.250	0.500	0.250	435	436
0.143	0.714	0.143	254	225
$x_1/x_3 = 0.5$				
0.288	0.138	0.574	*754*	*750*
0.255	0.235	0.510	687	690
0.118	0.647	0.235	357	361
0.037	0.888	0.075	124	126
$x_2/x_3 = 1.0$				
0.184	0.408	0.408	567	572
0.380	0.310	0.310	606	602
0.496	0.252	0.252	545	556
0.628	0.186	0.186	463	454
0.820	0.090	0.090	246	244
$x_2/x_3 = 2.0$				
0.108	0.595	0.297	423	422
0.140	0.574	0.286	428	432
0.379	0.414	0.207	419	412
0.439	0.374	0.187	389	391
0.528	0.315	0.157	340	346
0.588	0.275	0.137	299	309

4. Discussion

H^E of pentyl ethanoate + 1,2-dimethylbenzene mixing is negative (exothermic) but relatively small and decreases with temperature increasing. Changing the temperature from 298.15 to 318.15 K causes the H^E values to become less negative (from −150 to −130.5 J mol^{-1} at $x = 0.5$) confirming the weak intermolecular interaction between the polar ester group (COO) and π-electrons of 1,2-dimethylbenzene. On

Table 3
Coefficients A_i of Eq. (1), and standard deviation $\sigma(H^E)$ for binary systems involved in pentyl ethanoate + 1,2-dimethylbenzene + n-nonane

Binary system	T (K)	A_1	A_2	A_3	A_4	A_5	A_6	σ (J mol^{-1})
Pentyl ethanoate (1) + 1,2-dimethylbenzene (2)	298.15	−600.45	102.26	86.13	24.33	−339.05		0.83
	318.15	−522.44	86.09	−122.21	−304.00	277.50	463.15	1.03
Pentyl ethanoate (1) + n-nonane (2)	298.15[a]	3738.40	−409.26	60.84	149.74	686.55		6.6
	318.15	3752.23	−363.07	54.17	−171.19			16.4
1,2-Dimethylbenzene (1) + n-nonane (2)	298.15[b]	1727.90	420.50	29.90	−419.92			7.6
	318.15[b]	1709.93	287.95	−74.09	−91.06	391.24		8.3

[a] [1].
[b] [2].

Table 4
Coefficients C_i of Eq. (3), and standard deviations $\sigma(H^E)$ for ternary systems pentyl ethanoate + 1,2-dimethylbenzene + n-nonane

Ternary system	T (K)	C_0	C_1	C_2	C_3	σ (J mol^{-1})
Pentyl ethanoate (1) + 1,2-dimethylbenzene (2)	298.15	1173.23	753.01	−2576.90	−5888.73	11.23
+ n-nonane (3)	318.15	1804.32	−3394.16	−765.75	−14275.75	20.67

the contrary, binary systems containing n-nonane investigated here and earlier [1,2] show endothermic mixing. H^E of those are relatively large and are in the temperature range from 298.15 to 318.15 K practically independent of temperature. All constituent binaries at both temperatures exhibit extremity at mole fraction close to 0.5. A small exothermic mixing region in ternary system adjoins the binary system pentyl ethanoate + 1,2-dimethylbenzene. The most of ternary compositions exhibit endothermic mixing due to destruction of packing in pure components and weakening of interaction between pentyl ethanoate and 1,2-dimethylbenzene.

The experimental H^E values of the ternary mixture at 318.15 K and molar ratio of two components x_j/x_k equal to 1 are shown in Fig. 1 together with excess molar Gibbs free energy, G^E, and excess entropy term TS^E. Assuming that Wilson parameters λ_{ij}–λ_{ii} and λ_{ji}–λ_{jj} vary linearly with temperature [5], the G^E values at 318.15 K were obtained from our vapor–liquid equilibrium data [3]. Table 5 shows the values of coefficients $m_{i(j)}$ and $n_{i(j)}$ of Eqs. (5) and (6) expressing the temperature dependence of Wilson interaction parameters.

$$\lambda_{ij} - \lambda_{ii} = m_i + n_i T \qquad (5)$$

$$\lambda_{ji} - \lambda_{jj} = m_j + n_j T \qquad (6)$$

TS^E versus x curves were calculated from well-known relation $TS^E = H^E - G^E$. In all three cases the positive excess molar enthalpy is larger than TS^E and G^E which are also positive and have close values. Only in the vicinity of the binary system pentyl ethanoate + 1,2-dimethylbenzene all three excess functions are negative, changing to positive with increasing mole fraction of n-nonane (Fig. 1a).

Table 5
Coefficients of Eqs. (5) and (6)

i	j	m_i	n_i	m_i	n_i
1	2	3.4671	−0.00901	−5.0389	0.01355
1	3	−0.3361	0.00218	2.6048	−0.00528
2	3	2.7110	−0.00271	0.7052	−0.00154

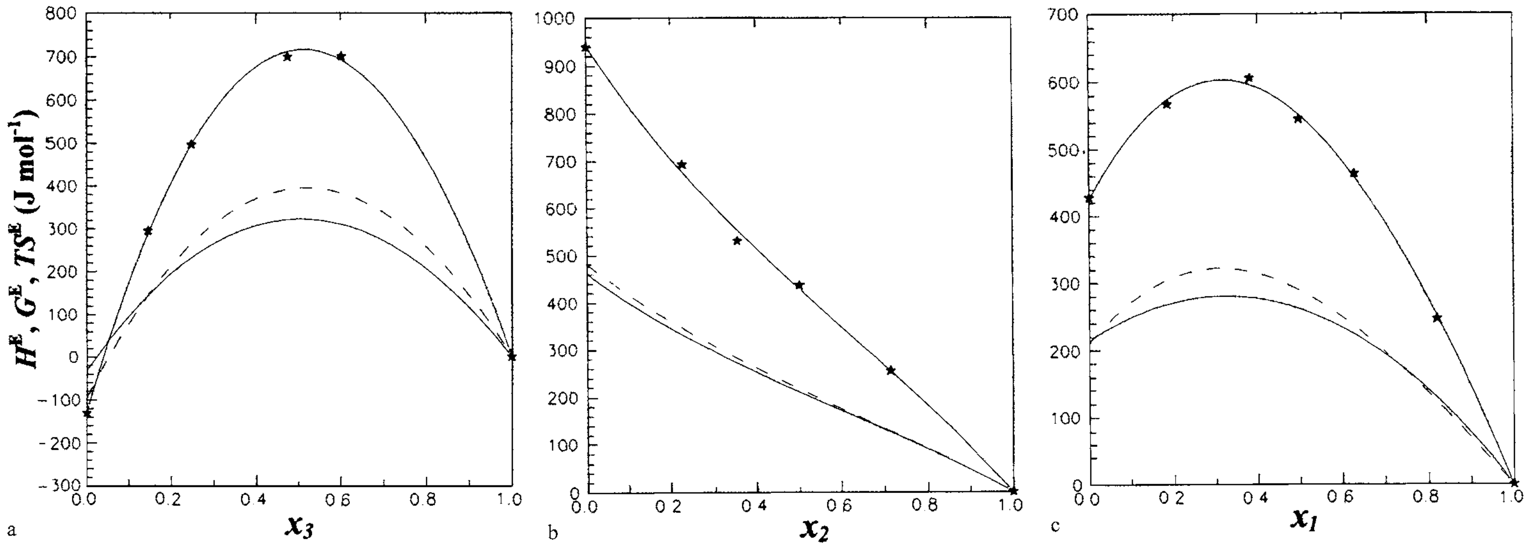

Fig. 1. Excess enthalpy H^E (–∗–), Gibbs energy G^E (—) and TS^E (- - -) values (J mol^{-1}) at different compositions of the ternary system pentyl ethanoate (1) + 1,2-dimethylbenzene (2) + *n*-nonane (3) at 318.15 K. For H^E, the experimental data (∗) and smoothed curves are given, G^E values are calculated using the modified Wilson equation, TS^E is calculated as $H^E - G^E$. Constant molar ratios used: a — $x_1/x_2 = 1$, b — $x_1/x_3 = 1$, c — $x_2/x_3 = 1$.

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