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THE TERNARY SYSTEM PROPYL PROPANOATE+ HEXANE+CHLOROBENZENE AT 298.15 K

Excess molar enthalpies

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Abstract

Excess molar enthalpies for the ternary mixture {propyl propanoate + hexane + chlorobenzene} and the binary mixtures {propyl propanoate + chlorobenzene} and {hexane + chlorobenzene} were determined at the temperature 298.15 K and normal atmospheric pressure. The experimental values were measured using a Calvet microcalorimeter. Excess molar enthalpies obtained were also used to test empirical expressions for estimating ternary properties from binary results.

Keywords: Calvet microcalorimeter, excess molar enthalpies, ternary mixture

Introduction

The present communication continues our calorimetric studies of ternary systems containing propyl propanoate and aromatic hydrocarbon as components [1, 2]. We report here the excess molar enthalpies at 298.15 K and normal atmospheric pressure of {propyl propanoate+hexane+chlorobenzene} and the binary mixtures {propyl propanoate+chlorobenzene}, and {hexane+chlorobenzene}. The excess molar enthalpies of {propyl propanoate+hexane} have been published previously [1].

The results obtained for the ternary mixture were used to test the symmetric empirical methods of Kohler [3], Jacob–Fitzner [4], Colinet [5], Knobeloch–Schwartz [6] and the asymmetric ones due to Tsao–Smith [7], Toop [8], Scatchard *et al*. [9], Hillert [10] and Mathieson–Tynne [11]. These methods predict excess molar enthalpies of the ternary mixtures from those of the involved binary mixtures.

Experimental

The chemical substances employed, propyl propanoate (purity>99%, supplied by Aldrich), hexane (purity>99.5%, supplied by Fluka), and chlorobenzene (pu-

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rity>99.9%, supplied by Aldrich) were degassed by ultrasound and dried over molecular sieves (Sigma Union Carbide, type 0.4 nm) and otherwise used as supplied. The densities of the pure liquids presents a good agreement with literature values as shown in Table 1.

Table 1 Densities of the pure liquids at 298.15 K

Compound	ρ/g cm^{-3}	
	exp.	lit.
Propyl propanoate	0.87549	0.87549[a]
Hexane	0.65468	0.65477[b]
Chlorobenzene	1.10093	1.1008[c]

[a] Tanaka *et al*. [12], [b] Jiménez *et al*. [13], [c] Orge *et al*. [14]

All the experimental excess measurements were determined using a Calvet microcalorimeter connected to a Philips PM 2535 voltameter. The accuracy of excess molar enthalpies is better than 1%. Calibration was performed electrically using a Setaram EJP 30 stabilised current source and tested further with hexane and cyclohexane mixture [15]. Details of procedure were described by Paz Andrade *et al*. [16, 17]. The mixtures were prepared using a Mettler AT201 balance with a precision of $1\cdot10^{-8}$ Kg. Six experimental runs were carried out for the ternary mixture formed by adding chlorobenzene to a binary mixture of {propyl propanoate (x_1')+hexane (x_2')} where $x_2'=1-x_1'$. A ternary mixture may be considered as a pseudobinary mixture composed of that binary mixture (x_1) and chlorobenzene (x_2).

The ternary excess molar enthalpies at composition x_1, x_2 and x_3 can be expressed as:

$$H^{E}_{m,123}=H^{E}_{m,\varphi}+(x_1+x_2)H^{E}_{m,12} \tag{1}$$

where $H^{E}_{m,\varphi}$ is the measured excess molar enthalpy and $H^{E}_{m,12}$ is the excess molar enthalpy of the initial binary {propyl propanoate+hexane}. Values of $H^{E}_{m,12}$ at different mole fractions were interpolated by using a spline-fit method.

Results

The experimental excess molar enthalpies of the binary mixtures at 298.15 K are presented in Table 2. The excess volume and excess molar enthalpy for the hexane+chlorobenzene binary mixture have been published before [18]. A variable-degree Redlich–Kister [19] polynomial of the form:

$$H^{E}_{m,ij}\,(\mathrm{J\ mol^{-1}})=x_i x_j \sum_{p=0}^{n} A_p (x_i-x_j)^{p} \tag{2}$$

was employed to fit the results using a least-squares method, and the number of parameters was determined using a F-test [20]. Excess molar enthalpies for ternary mixtures are shown in Table 3. The experimental values were correlated by the Cibulka equation [21]:

$$H^{E}_{m,123}\,(\mathrm{J\ mol^{-1}}) = H^{E}_{m,12} + H^{E}_{m,13} + H^{E}_{m,23} + x_1 x_2 (1 - x_1 - x_2)\Delta_{123} \tag{3}$$

where

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \tag{4}$$

Table 2 Experimental excess molar enthalpies for the binary mixtures at 298.15 K

x	H^{E}_{m}/J mol^{-1}	x	H^{E}_{m}/J mol^{-1}	x	H^{E}_{m}/J mol^{-1}
		x propyl propanoate + (1–x) chlorobenzene			
0.0347	–73	0.3577	–460	0.7014	–383
0.1058	–189	0.4190	–487	0.7604	–335
0.1452	–247	0.4885	–496	0.8122	–282
0.2041	–323	0.5554	–479	0.8617	–209
0.2536	–377	0.6036	–459	0.9291	–128
0.3048	–428	0.6529	–427	0.9665	–61
		x hexane + (1–x) chlorobenzene			
0.0466	117	0.3808	632	0.6883	580
0.1057	254	0.4112	659	0.7285	531
0.1531	347	0.4803	664	0.8127	417
0.2219	460	0.5376	661	0.8489	354
0.2622	528	0.5932	640	0.9101	226
0.3050	565	0.6437	614	0.9708	77

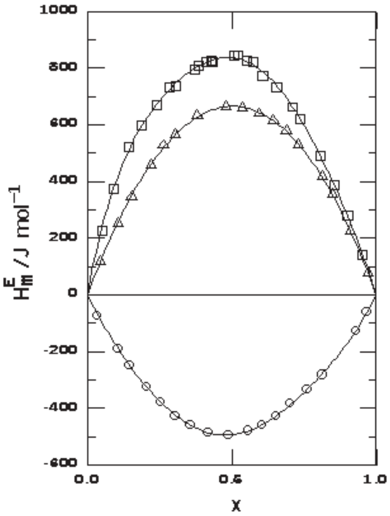

Fig. 1 $H^{E}_{m,ij}$ for the binary mixture at 298.15 K: a, □ – x propyl propanoate+(1–x) hexane; b, △ – x hexane+(1–x) chlorobenzene; c, o – x propyl propanoate+(1–x) chlorobenzene

Table 3 Experimental excess molar enthalpies for the ternary system at 298.15 K

x_1	x_2	$H^{E}_{m,\varphi}$/J mol^{-1}	$H^{E}_{m,123}$/J mol^{-1}
x_1=0.1503		$H^{E}_{m,12}$=525	
0.0071	0.0402	66	91
0.0212	0.1200	204	279
0.0385	0.2177	275	409
0.0538	0.3043	315	503
0.0707	0.4000	316	563
0.0882	0.4988	300	608
0.1042	0.5895	254	618
0.1197	0.6769	190	608
0.1367	0.7729	66	91
x_1=0.3015		$H^{E}_{m,12}$=743	
0.0111	0.0257	34	61
0.0446	0.1033	65	175
0.0783	0.1815	86	279
0.1092	0.2531	92	361
0.1440	0.3338	69	424
0.1754	0.4066	53	486
0.2072	0.4800	39	550
0.2398	0.5556	30	621
0.2730	0.6325	8	681
x_1=0.4552		$H^{E}_{m,12}$=836	
0.0219	0.0262	–12	28
0.0649	0.0777	–37	83
0.1158	0.1386	–67	146
0.1630	0.1950	–87	213
0.2119	0.2536	–110	279
0.2664	0.3164	–136	350
0.3163	0.3786	–119	462
0.3602	0.4311	–103	559
0.4104	0.4911	–64	690
x_1=0.6001		$H^{E}_{m,12}$=793	
0.0296	0.0197	0.0296	0.0197
0.0874	0.0583	0.0874	0.0583
0.1479	0.0985	0.1479	0.0985
0.2174	0.1449	0.2174	0.1449

Table 3 Continued

x_1	x_2	$H^E_{m,\varphi}$/J mol^{-1}	$H^E_{m,123}$/J mol^{-1}
0.2791	0.1860	0.2791	0.1860
0.3157	0.2104	0.3157	0.2104
0.3477	0.2317	0.3477	0.2317
0.4108	0.2738	0.4108	0.2738
0.4709	0.3138	0.4709	0.3138
0.5426	0.3616	0.5426	0.3616
x_1=0.7503		$H^E_{m,12}$=597	
0.0246	0.0082	–17	2
0.1073	0.0357	–168	–83
0.1882	0.0626	–271	–121
0.2640	0.0879	–343	–133
0.3532	0.1175	–388	–107
0.4039	0.1344	–395	–73
0.4389	0.1460	–386	–36
0.5178	0.1723	–327	85
0.5926	0.1972	–261	211
0.6817	0.2268	–131	412
x_1=0.8998		$H^E_{m,12}$=280	
0.0439	0.0049	–82	–68
0.1257	0.0140	–209	–170
0.2264	0.0252	–347	–277
0.3239	0.0361	–422	–321
0.4208	0.0468	–458	–327
0.5292	0.0589	–438	–274
0.6190	0.0689	–391	–198
0.7120	0.0793	–299	–77
0.8028	0.0894	–193	56

The B_i parameters were calculated by the unweighted least-squares method using a non-linear optimisation algorithm due to Marquardt [22].

Table 4 shows the values of the parameters A_p, B_i of the Eqs (2) and (4) respectively, and the corresponding standard deviations. The A_p parameters for the binary mixture {propyl propanoate+hexane} were taken from Casas *et al*. [1].

Figure 1 shows the experimental excess molar enthalpies of binary mixtures *vs*. mole fraction. As observed, the H^E_m for the binary mixtures propyl propanoate + hexane and hexane+chlorobenzene are positive, which indicate that molecular interac-

Table 4 Coefficients A_p and B_i and standard deviations s

A_0	A_1	A_2	A_3	A_4	s/J mol^{-1}
		x propyl propanoate + (1–x) hexane[a]			
3353	–214	0	–1013	1085	7
		x propyl propanoate + (1–x) chlorobenzene			
–1973	225	353	–234	–495	3
		x hexane + (1–x) chlorobenzene			
2665		107			4
B_0	B_1	B_2			s/J mol^{-1}
		x_1 propyl propanoate + x_2 hexane + (1–x_1–x_2) chlorobenzene			
–1045	–895	–1012			8

[a] Casas *et al.* [1]

tions between the different molecules are weaker after the mixture than before for the pure liquids. Contrarily, for the binary mixture propyl propanoate+chlorobenzene the H_m^E is negative, which suggest that new interactions between both types of molecules appear. Figure 2 shows lines of constant ternary excess molar enthalpy, the maximum value is 823 J mol^{-1}, which corresponds to the coordinates x_1=0.47 and x_2=0.52. Figure 3 shows lines of ternary contribution $x_1\ x_2\ (1–x_1–x_2)\Delta_{123}$, the maximum value is 63 J mol^{-1}, which corresponds to the coordinates x_1=0.35 and x_2=0.36.

Several empirical methods have been proposed for estimating ternary excess enthalpy from experimental results of the constituent binary mixtures. The equations involved are asymmetric if the numerical predictions depend on the arbitrary desig-

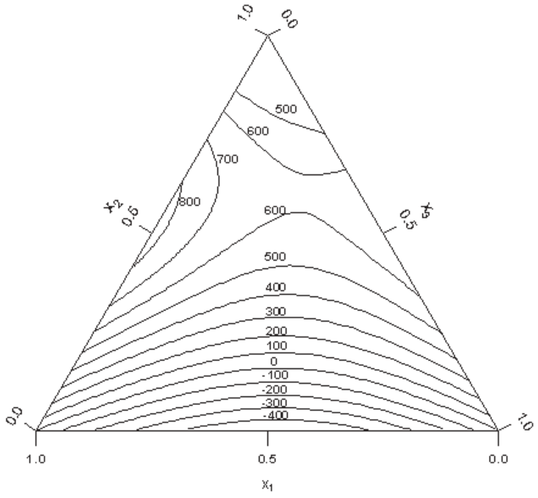

Fig. 2 Curves of constant excess molar enthalpies in J mol^{-1} of {x_1 propyl propanoate+x_2 hexane+(1–x_1–x_2) chlorobenzene}

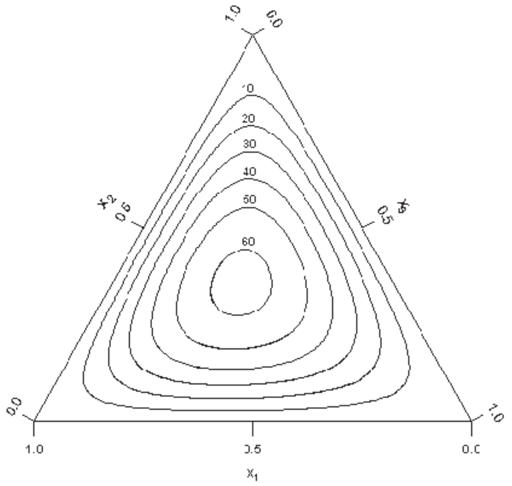

Fig. 3 Curves of ternary contribution in J mol^{-1} of {x_1 propyl propanoate+x_2 hexane+(1–x_1–x_2) chlorobenzene}

Table 5 Standard deviations s of empirical expressions for: a) x_1 propyl propanoate + x_2 hexane + (1–x_1–x_2) chlorobenzene; b) x_1 hexane + x_2 chlorobenzene + (1–x_1–x_2) propyl propanoate; c) x_1 chlorobenzene + x_2 propyl propanoate+(1–x_1–x_2) hexane

	s/J mol^{-1}
	a
Kohler	36
Jacob–Fitzner	33
Colinet	38
Knobeloch–Schwartz	127

	s/J mol^{-1}		
	a	b	c
Tsao–Smith	128	38	159
Toop	47	28	39
Scatchard	47	28	37
Hillert	47	29	41
Mathieson–Tynne	37	30	35

nation of component numbering, and symmetric otherwise. The standard deviations between experimental and predicted values are shown in Table 5. For the asymmetric equations we have found that the results agree with the rule given by Pando *et al.* [23]. This rule consists in designating as component 1 the common component of the two mixtures with the largest absolute values of excess molar enthalpies in their maxima or minima, hexane in our case.

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