Excess Molar Enthalpies of Propyl Propanoate + Hexane + Benzene at 298.15 K and 308.15 K

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Excess molar enthalpies of the ternary system {x_1 propyl propanoate + x_2 hexane + (1 − x_1 − x_2) benzene} and of their binary mixtures {x_1 propyl propanoate + x_2 hexane}, {x_1 propyl propanoate + x_2 benzene}, and {x_1 hexane + x_2 benzene} have been determined at 298.15 K and 308.15 K and atmospheric pressure, over the whole composition range. The excess molar enthalpies were measured using a Calvet microcalorimeter. The experimental values were compared with the results obtained with empirical expressions for estimating ternary properties from binary data.

Introduction

Forming part of our work with six carbon atom compounds (Souza et al., 1992; Franjo et al., 1994, 1995a; Casas et al., 1998; García-Garabal et al., 1998), we present here the excess molar enthalpies (H^E_m) at 298.15 K and 308.15 K and atmospheric pressure of {x_1 propyl propanoate + x_2 hexane + (1 − x_1 − x_2) benzene} and of their corresponding binary mixtures {x_1 propyl propanoate + x_2 hexane}, {x_1 propyl propanoate + x_2 benzene}, and {x_1 hexane + x_2 benzene}. Excess molar enthalpies complete our study of different physical properties as densities, excess molar volumes, viscosity deviations, and changes of refractive index on mixing for this ternary mixture (Casas et al., 1998).

The results obtained for the ternary mixture were used to test the empirical methods of Kohler (1960), Jacob and Fitzner (1977), Colinet (Colinet, 1967; Souza et al., 1992), Tsao and Smith (1953), Toop (1965), Scatchard et al. (1952), and Hillert (1980). These methods predict excess properties of the ternary mixtures from those of the involved binary mixtures.

Experimental Section

The substances employed were supplied by Fluka and Sigma. The mass fraction purities were propyl propanoate (Fluka, >0.99), hexane (Sigma, >0.99), and benzene (Fluka, >0.995). The liquids 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 agree with published values, as Table 1 shows.

The excess molar enthalpies were measured using a Calvet microcalorimeter connected to a Philips PM 2535 voltmeter. The inaccuracy of excess molar enthalpies is better than 1%. Details of calibration and procedures were described by Paz Andrade et al. (1967, 1970). The mixtures were prepared using a Mettler AT201 balance with a precision of 1 × 10^{-8} kg. Several experimental runs were carried out for the ternary mixture formed by adding benzene to a binary mixture of {x'_1 propyl propanoate + (1 − x'_1 hexane} where x'_1 is the mole fraction of propyl propanoate in the binary mixture. The ternary excess molar enthalpies at x_1, x_2, and x_3 can be expressed as

$$H^E_{m,123} = H^E_{m,\phi} + (x_1 + x_2)H^E_{m,12} \quad (1)$$

where $H^E_{m,\phi}$ 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.

Table 1. Data for Pure Liquids at 298.15 K

	ρ/(g·cm^{-3})	
substance	exp	lit.
propyl propanoate	0.875 53	0.875 52[a]
		0.875 54[b]
hexane	0.655 28	0.655 2[c]
benzene	0.873 45	0.873 5[c]

[a] Franjo et al. (1995b). [b] Souza et al. (1996). [c] Eduljee and Boyes (1980).

Results and Discussion

The experimental excess molar enthalpies for the binary mixtures were fitted to a variable-degree polynomial of the form

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

using a least-squares method. The number of parameters was determined using a F test (Bevington and Robinson, 1994). The experimental results for the binary mixtures are listed in Table 2.

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Table 2. Excess Molar Enthalpies for the Binary Mixtures at 298.15 K and 308.15 K

x_1	H^E_m/(J·mol^{-1})	x_1	H^E_m/(J·mol^{-1})	x_1	H^E_m/(J·mol^{-1})
		x_1 Propyl Propanoate + x_2 Hexane			
		T = 298.15 K			
0.0504	227	0.3841	807	0.6069	774
0.0912	375	0.4117	824	0.6549	732
0.1420	521	0.4304	827	0.7092	663
0.1880	597	0.4317	823	0.7358	620
0.2385	668	0.5095	846	0.8067	491
0.2854	731	0.5199	847	0.8550	386
0.3058	739	0.5538	826	0.9013	279
0.3717	796	0.5751	821	0.9522	142
		T = 308.15 K			
0.0988	375	0.3627	764	0.6520	735
0.1504	516	0.4095	800	0.7177	637
0.1950	585	0.4667	798	0.7756	540
0.2403	649	0.4770	797	0.8581	384
0.2491	670	0.5646	788	0.9115	257
0.2576	674	0.6066	758		
		x_1 Propyl Propanoate + x_2 Benzene			
		T = 298.15 K			
0.0334	−10	0.2874	−94	0.7433	−73
0.0681	−24	0.4198	−99	0.7848	−67
0.1078	−40	0.5213	−99	0.8794	−31
0.1857	−68	0.5908	−97	0.9331	−19
0.2280	−81	0.6298	−93		
		T = 308.15 K			
0.0341	−15	0.3099	−118	0.6559	−96
0.0730	−33	0.3433	−121	0.7357	−79
0.1061	−48	0.4116	−131	0.8036	−63
0.1385	−61	0.4591	−132	0.8501	−44
0.1829	−81	0.5119	−129	0.9263	−27
0.2109	−95	0.6167	−108	0.9358	−23
0.2696	−106				
		x_1 Hexane + x_2 Benzene			
		T = 298.15 K			
0.0342	153	0.3672	901	0.6146	839
0.0639	277	0.3978	928	0.6562	785
0.1031	402	0.4328	933	0.7166	689
0.1405	532	0.4420	939	0.7333	657
0.1738	614	0.4426	938	0.7850	562
0.2367	752	0.4632	939	0.8546	399
0.2660	793	0.5378	899	0.9314	200
0.3089	848	0.5960	857		
		T = 308.15 K			
0.0371	153	0.3399	855	0.5850	825
0.0759	290	0.3927	888	0.6615	740
0.1002	370	0.4639	889	0.7286	625
0.1304	487	0.4918	872	0.8055	496
0.1607	559	0.5003	872	0.8603	380
0.2442	736	0.5492	861	0.9333	210
0.3126	828				

Table 3 lists the excess molar enthalpies for ternary mixtures that were adequately correlated by the Cibulka (1982) equation:

$$H^E_{m,123}\,(\text{J·mol}^{-1}) = H^E_{m,12} + H^E_{m,13} + H^E_{m,23} + x_1x_2(1 - x_1 - x_2)\Delta_{123} \quad (3)$$

where

$$\Delta_{123} = B_0 + B_1x_1 + B_2x_2 \quad (4)$$

The B_i parameters were calculated by the unweighted least-squares method using a nonlinear optimization algorithm due to Marquardt (1963).

Table 4 shows the values of the parameters A_p and B_i of eqs 2 and 4, respectively, and the corresponding standard deviations.

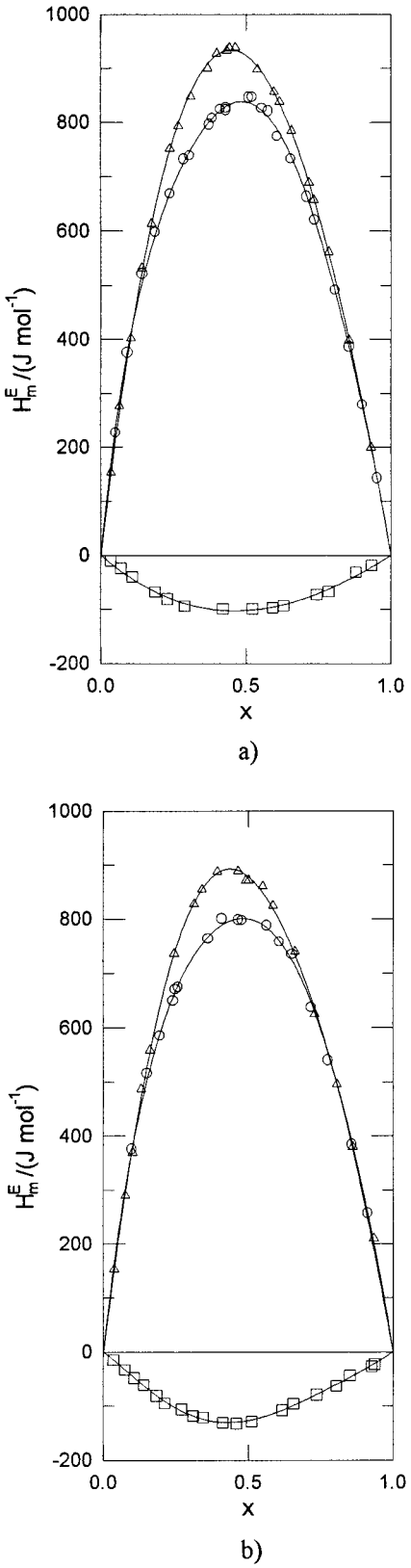

Figure 1. Excess molar enthalpies at (a) 298.15 K and (b) 308.15 K of (○) {x propyl propanoate + (1 − x) hexane}, (—) {x propyl propanoate + (1 − x) benzene}, and (△) {x hexane + (1 − x) benzene}.

The experimental excess molar enthalpies of binary mixtures plotted against mole fractions are shown in Figure 1. Those binary mixtures with hexane as the component show positive excess molar enthalpies. Figure 2 shows lines of constant ternary excess molar enthalpy,

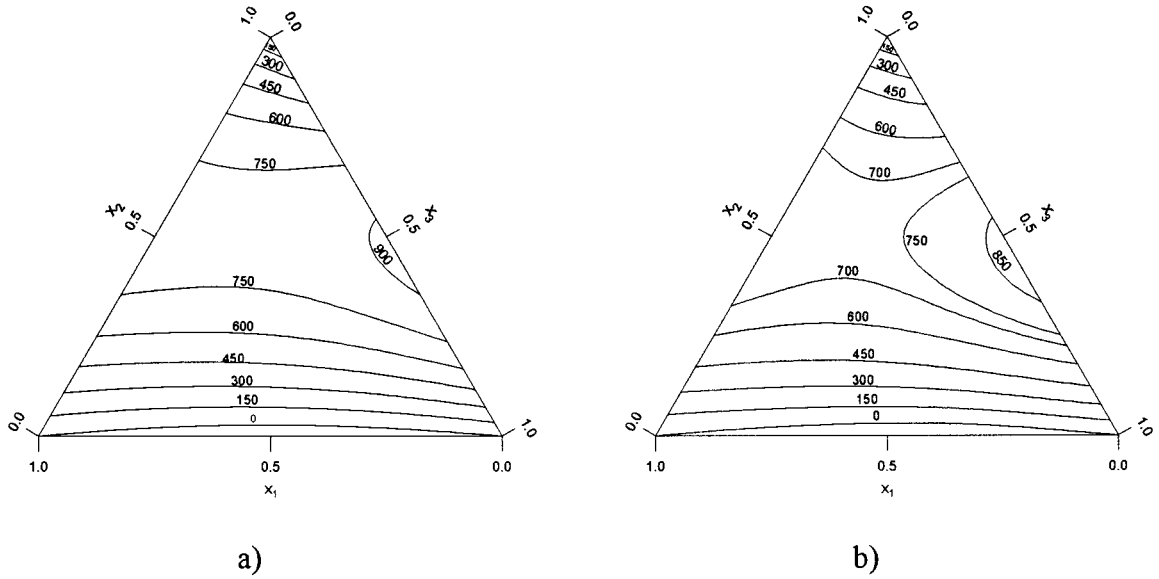

Figure 2. Curves of constant excess molar enthalpies in J·mol^{-1} at (a) 298.15 K and (b) 308.15 K of {x_1 propyl propanoate + x_2 hexane + (1 − x_1 − x_2) benzene}.

Table 3. Excess Molar Enthalpies of {x_1 Propyl Propanoate + x_2 Hexane + (1 − x_1 − x_2) Benzene} at 298.15 K and 308.15 K

x_1	x_2	$H^E_{m,\phi}$/(J·mol^{-1})	$H^E_{m,123}$/(J·mol^{-1})	x_1	x_2	$H^E_{m,\phi}$/(J·mol^{-1})	$H^E_{m,123}$/(J·mol^{-1})
		T = 298.15 K				T = 308.15 K	
x'_1 = 0.2994		$H^E_{m,12}$ = 741 J·mol^{-1}		x'_1 = 0.2503		$H^E_{m,12}$ = 670 J·mol^{-1}	
0.0210	0.0492	153	205	0.0087	0.0259	96	119
0.0422	0.0988	266	370	0.0152	0.0454	144	185
0.0690	0.1616	362	533	0.0202	0.0605	184	238
0.1486	0.3477	424	792	0.0296	0.0885	246	325
0.1233	0.2886	431	736	0.0433	0.1297	321	437
0.1888	0.4418	358	825	0.1139	0.3410	460	765
0.2251	0.5268	267	824	0.1293	0.3872	430	776
x'_1 = 0.4396		$H^E_{m,12}$ = 833 J·mol^{-1}		0.1433	0.4291	413	797
0.0284	0.0363	97	151	0.1956	0.5859	205	728
0.0669	0.0852	186	313	0.2185	0.6543	103	687
0.1836	0.2341	270	618	x'_1 = 0.4990		$H^E_{m,12}$ = 800 J·mol^{-1}	
0.2182	0.2781	264	677	0.0170	0.0171	40	67
0.2712	0.3457	227	741	0.2460	0.2470	200	595
0.3236	0.4126	170	783	0.2574	0.2584	195	608
0.3710	0.4730	107	810	0.2807	0.2819	185	635
x'_1 = 0.6075		$H^E_{m,12}$ = 787 J·mol^{-1}		0.3079	0.3092	170	664
0.0423	0.0273	52	107	0.3364	0.3377	147	686
0.0918	0.0593	91	210	0.3659	0.3674	111	698
0.1384	0.0894	110	290	0.4628	0.4647	27	769
0.1914	0.1237	120	368	x'_1 = 0.7552		$H^E_{m,12}$ = 588 J·mol^{-1}	
0.2492	0.1610	115	437	0.0254	0.0082	11	30
0.3140	0.2029	115	522	0.0581	0.0188	21	66
0.3931	0.2540	89	599	0.0837	0.0271	23	88
0.4460	0.2881	70	648	0.1141	0.0370	26	115
0.5355	0.3460	32	725	0.1365	0.0443	28	134
x'_1 = 0.7524		$H^E_{m,12}$ = 594 J·mol^{-1}		0.1653	0.0536	23	152
0.0523	0.0172	17	58	0.2818	0.0914	31	250
0.1072	0.0353	28	112	0.3037	0.0985	27	264
0.1599	0.0526	25	151	0.3438	0.1114	29	296
0.2329	0.0766	22	206	0.3826	0.1240	19	317
0.3056	0.1006	14	255	0.4221	0.1368	14	343
0.3959	0.1303	15	327	0.4604	0.1492	6	364
0.4559	0.1500	9	369	0.5015	0.1626	5	395
0.5705	0.1878	1	451	0.5479	0.1776	−14	412
0.6371	0.2096	0	503	0.6060	0.1964	−15	456
x'_1 = 0.8880		$H^E_{m,12}$ = 309 J·mol^{-1}		0.6452	0.2091	−15	487
0.0570	0.0072	−9	11	0.6937	0.2249	−6	534
0.1285	0.0162	−22	22				
0.1836	0.0232	−35	29				
0.2817	0.0355	−54	44				
0.4472	0.0564	−52	104				
0.5713	0.0721	−53	146				
0.6763	0.0853	−34	202				
0.7556	0.0953	−31	232				

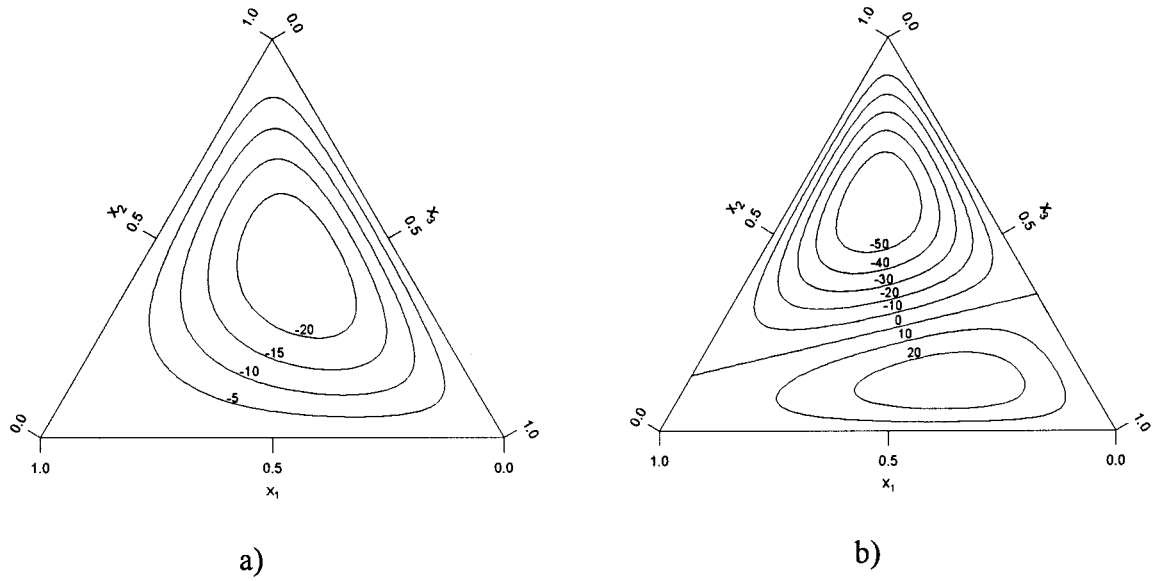

Figure 3. Curves of ternary contribution in J·mol^{-1} at (a) 298.15 K and (b) 308.15 K of {x_1 propyl propanoate + x_2 hexane + (1 − x_1 − x_2) benzene}.

Table 4. Coefficients A_p and B_i and Standard Deviations s

T/K	A_0	A_1	A_2	A_3	A_4	s/(J·mol^{-1})
			x_1 Propyl Propanoate + x_2 Hexane			
298.15	3352.7	−214.0	0	−1013.1	1084.5	7
308.15	3200.5	−189.6	695.3	−794.3		8
			x_1 Propyl Propanoate + x_2 Benzene			
298.15	−408.3	63.4				4
308.15	−507.4	195.8	118.2	−175.6		2
			x_1 Hexane + x_2 Benzene			
298.15	3696.4	−768.6	168.1			5
308.15	3513.5	−882.6	302.3	403.2		8

	B_0	B_1	B_2	s/(J·mol^{-1})
	x_1 Propyl Propanoate + x_2 Hexane + (1 − x_1 − x_2) Benzene			
298.15	−749.8	932.4	−472.7	5
308.15	2887.2	−1985.0	−8331.2	10

Table 5. Maxima and Minima for a Ternary Contribution

T/K	value/(J·mol^{-1})	coordinates	
298.15	minimum −25	$x_1 = 0.24$	$x_2 = 0.43$
308.15	minimum −61	$x_1 = 0.23$	$x_2 = 0.58$
	maximum 27	$x_1 = 0.30$	$x_2 = 0.12$

and in both cases the excess molar enthalpy decreases as the temperature increases. Figure 3 shows lines of ternary contribution ($H^E_{m,123} - H^E_{m,12} - H^E_{m,13} - H^E_{m,23}$). Table 5 shows maxima and minima for the ternary contribution.

Excess molar enthalpies of {x_1 hexane + x_2 benzene} have been measured previously, and the difference between our results and the values obtained by Harris and Dunlop (1970) at 298.15 K for $x_1 = 0.5$ is less than 3%. The {x_1 propyl propanoate + x_2 hexane} mixture was also studied previously (Lorenzana et al., 1989) at 298.15 K, and the difference for $x_1 = 0.5$ is less than 2%.

Several empirical methods have been proposed for estimating ternary excess enthalpies from experimental results of the constituent binary mixtures. The equations involved are asymmetric if the numerical predictions depend on the arbitrary designation of component numbering and are symmetric otherwise. The symmetric equations studied were those of Kohler (1960), Jacob and Fitzner (1977), and Colinet (Colinet, 1967; Souza et al., 1992). The asymmetric expressions were those of Tsao and Smith (1953), Toop (1965), Scatchard et al. (1952), and Hillert (1980). The standard deviations between experimental and predicted values are shown in Table 6. For the asymmetric equations we have found that the results at 308.15 K agree with the rule given by Pando et al. (1987). Nevertheless, Pando's rule does not agree with our results at 298.15 K. This rule consists of 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.

Table 6. Standard Deviations s of Empirical Expressions for (a) x_1 Propyl Propanoate + x_2 Hexane + (1 − x_1 − x_2) Benzene, (b) x_1 Hexane + x_2 Propyl Propanoate + (1 − x_1 − x_2) Benzene, and (c) x_1 Benzene + x_2 Hexane + (1 − x_1 − x_2) Propyl Propanoate

	s/(J·mol^{-1}) for a
T = 298.15 K	
Jacob and Fitzner	13
Kohler	17
Colinet	18
T = 308.15 K	
Jacob and Fitzner	22
Kohler	24
Colinet	27

	s/(J·mol^{-1}) a		
	a	b	c
T = 298.15 K			
Tsao and Smith	151	12	125
Toop	29	23	8
Scatchard	25	23	6
Hillert	26	23	8
T = 308.15 K			
Tsao and Smith	142	19	115
Toop	32	27	30
Scatchard	33	27	27
Hillert	34	28	28

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