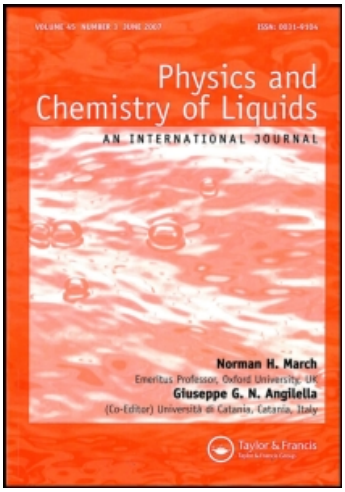

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Molar Enthalpies for the (Ethyl Propanoate *n*-Hexane *n*-Tetradecane) System at the Temperature 298.15 K

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To cite this Article López, M. , Andrade, M. I. Paz , Legido, J. L. , Romaní, L. , Peleteiro, J. and Jiménez, E.(1993) 'Excess Molar Enthalpies for the (Ethyl Propanoate *n*-Hexane *n*-Tetradecane) System at the Temperature 298.15 K', Physics and Chemistry of Liquids, 25: 3, 145 — 152
To link to this Article: DOI: 10.1080/00319109308030356
URL: http://dx.doi.org/10.1080/00319109308030356

Phys. Chem. Liq., 1993, Vol. 25, pp. 145–152
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EXCESS MOLAR ENTHALPIES FOR THE (ETHYL PROPANOATE + *n*-HEXANE + *n*-TETRADECANE) SYSTEM AT THE TEMPERATURE 298.15 K

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(Received 15 May 1992)

Excess molar enthalpies at 298.15 K were measured for (ethyl propanoate + *n*-hexane + *n*-tetradecane), (ethyl propanoate + *n*-hexane), (ethyl propanoate + *n*-tetradecane) and (*n*-hexane + *n*-tetradecane, using a Calvet microcalorimeter. The experimental results were compared with those calculated by using the Nitta–Chao model; good agreement was obtained.

KEY WORDS: Excess molar enthalpies, ternary mixture, ester, alkane, Nitta–Chao model.

INTRODUCTION

The present article continues our studies on the excess enthalpies of ternary systems[1]. We report here the excess molar enthalpies at 298.15 K and normal atmospheric pressure of (ethyl propanoate + *n*-hexane + *n*-tetradecane) and of the corresponding binary mixtures. Enthalpy mixture was measured using a Calvet microcalorimeter. A variable polynomial has now been fitted to each set of experimental results. The ternary system has been fitted by means of an equation proposed by Cibulka[2]. The excess molar enthalpies obtained were used to test the group-contribution model of Nitta–Chao[3] which is based on the Carnahan–Starling hard-sphere equation of state[4].

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EXPERIMENTAL

The chemical substances employed were supplied by Fluka A.G., and subjected to no further purification other than being dried with Union Carbide 0.4 nm molecular sieves and degasified. The mole-fraction purities were: ethyl propanoate (>99%), *n*-hexane (>99.5%) and *n*-tetradecane (>99.5%). Densities of these compounds, measured at 298.15 K with an Anton–Paar densimeter, agreed with literature values[5].

All experimental measurements were carried out using a Calvet microcalorimeter equipped with a device allowing operation in the absence of vapor phase. Calibration was performed electrically using a Setaram EJP 30 stabilized current source. Details of the employed procedure have been published previously[6,7]. The precision of the excess molar enthalpies is estimated as better than $0.01 \cdot H^E_m$.

Three experimental runs were carried out for ternary mixtures formed by adding *n*-tetradecane to a binary mixture of ethyl propanoate (x'_1) + *n*-hexane (x'_2), been x'_1 and x'_2 the concentrations for the binary mixture. A ternary mixture may be considered as a pseudo binary mixture composed of one binary mixture and *n*-tetradecane x_3. The ternary excess molar enthalpy at x_1, x_2 and x_3 can be given as

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

where $H^E_{m,\psi}$ is the measured excess molar enthalpy for the pseudo binary mixture and $H^E_{12,m}$ is the excess enthalpy of the initial binary ethyl propanoate + *n*-hexane mixtures. Values of $H^E_{12,m}$ at three mole fractions were interpolated by using a spline-fit method. Equation (1) does not involve any approximation[8].

RESULTS AND DISCUSSION

Excess molar enthalpies of the binary mixtures are listed in Table 1. A variable degree polynomial of the form:

$$H^E_{ij,m}/(\mathrm{J \cdot mol^{-1}}) = x_i x_j \sum_{m=1}^{n} A_m (x_1 - x_j)^m \tag{2}$$

was fitted. Least square method has been employed. The number of parameters was determined in each case using an *F*-test[9]. The parameters A_m and the standard deviations of the fits are listed in Table 2.

Figure 1 shows the experimental excess molar enthalpies plotted against x together with the fitted curves and the predictions of the Nitta–Chao model[3].

The differences between the experimental values of the literature[10,11] in the binary mixtures and our results fitted with Eq. (2) where about an 7 per cent. Table 3 lists the ternary excess molar enthalpies $H^E_{123,m}$ and H^E_m at 298.15 K. The values of $H^E_{123,m}$

Table 1 Experimental excess molar enthalpies H_m^E at the temperature 298.15 K.

x	H_m^E / $J \cdot mol^{-1}$	x	H_m^E / $J \cdot mol^{-1}$	x	H_m^E / $J \cdot mol^{-1}$	x	H_m^E / $J \cdot mol^{-1}$
			x ethyl propanoate + $(1-x)$ *n*-hexane				
0.0867	350.0	0.4068	1010.6	0.6050	981.4	0.8284	575.0
0.1597	595.3	0.4629	1029.0	0.6619	921.0	0.8652	469.1
0.2088	729.1	0.4797	1034.5	0.6896	875.9	0.9142	310.3
0.2450	805.0	0.5130	1030.3	0.7130	839.4		
0.3168	926.1	0.5407	1023.0	0.7684	729.1		
0.3698	983.2	0.5713	1007.7	0.8076	633.0		
			x ethyl propanoate + $(1-x)$ *n*-tetradecane				
0.0921	481.1	0.3751	1396.0	0.5380	1550.5	0.7881	1165.7
0.1674	793.2	0.3905	1417.6	0.5648	1542.3	0.8152	1073.8
0.1681	797.2	0.4370	1485.3	0.6104	1515.6	0.8778	824.5
0.2587	1105.0	0.4719	1522.7	0.5601	1468.8	0.9386	487.3
0.3021	1227.1	0.4961	1537.1	0.6870	1404.8		
0.3444	1328.9	0.5234	1548.4	0.7401	1297.9		
			x *n*-hexane + $(1-x)$ *n*-tetradecane				
0.0486	6.7	0.2349	42.5	0.4683	66.7	0.7907	37.8
0.0731	11.1	0.2673	50.2	0.5226	67.9	0.8463	25.1
0.0925	15.0	0.3176	55.7	0.5633	65.9	0.8986	13.7
0.1234	20.8	0.3448	60.1	0.5923	64.4		
0.1692	30.5	0.3870	63.6	0.6708	58.1		
0.1932	35.3	0.4349	67.6	0.7415	47.3		

were adequately correlated by

$$H^E_{123,m} = H^E_{12,m} + H^E_{13,m} + H^E_{23,m} + x_1 x_2 x_3 \Delta_{123} \tag{3}$$

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

like used by Cibulka[2], in correlating their ternary excess molar volumes results.

Table 2 Parameters A_i, B_i, C_i for Eq. (2) to (5) and standard deviations s.

		x ethyl propanoate + $(1-x)$ *n*-hexane			
$A_0 = 4129$	$A_1 = -220.3$	$A_2 = 550.8$	$A_3 = -131.3$	$A_4 = -672.6$	$s = 1.7$
		x ethyl propanoate + $(1-x)$ *n*-tetradecane			
$A_0 = 6161$	$A_1 = 848.5$	$A_2 = -18.48$	$A_3 = 779.5$	$A_4 = 1689$	$s = 2.4$
		x *n*-hexane + $(1-x)$ *n*-tetradecane			
$A_0 = 275.3$	$A_1 = -6.821$	$A_2 = -147.9$	$A_3 =$ ——	$A_4 =$ ——	$s = 1.1$
		$x_1$ethyl propanoate + x_2*n*-hexane + x_3*n*-tetradecane			
$B_0 = 1551.1$	$B_1 = -1816.1$	$B_2 = -2386.4$			$s = 3.8$

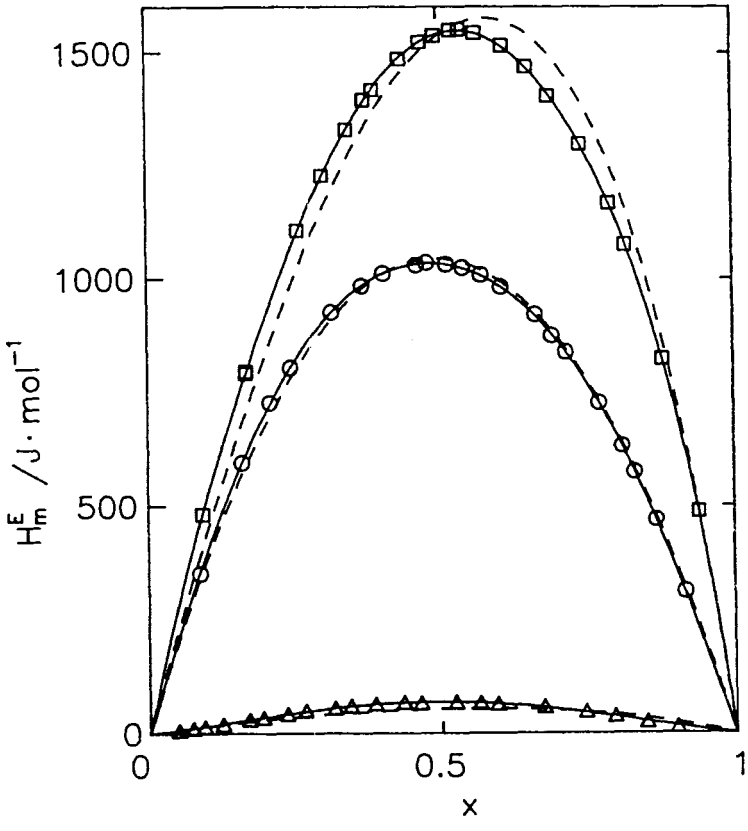

Figure 1 Excess molar enthalpies for (○), (x ethyl propanoate + (1 − x) n-hexane); (□), (x ethyl propanoate + (1 − x) n-tetradecane); and (△), (x n-hexane + (1 − x) n-tetradecane) at the temperature 298.15 K. Continuous curves were calculated from Eq. (2). Broken lines were calculated by means of the Nitta–Chao model.

Table 3 Experimental excess molar enthalpies for $x_1$ethyl propanoate + $x_2$$n$-hexane + $x_3$$n$-tetradecane at the temperature 298.15 K.

x_1	x_2	H^E_m / J · mol^{-1}	$H^E_{123,m}$ / J · mol^{-1}	$\delta H^E_{123,m}$ / J · mol^{-1}
x'_1 = 0.2494			$H^E_{12,m}$ = 814.9 J · mol^{-1}	
0.2329	0.7007	45.4	806.2	−2.7
0.2231	0.6713	71.6	800.4	−3.4
0.2133	0.6419	97.8	794.7	−2.6
0.2020	0.6076	125.0	784.7	−2.6
0.1849	0.5563	160.3	764.4	−2.4
0.1706	0.5134	181.6	739.0	−4.1
0.1617	0.4865	192.1	720.3	−4.8
0.1453	0.4370	207.4	681.9	−3.3
0.1347	0.4052	211.6	651.5	−3.2
0.1272	0.3827	217.2	632.7	1.8

Table 3 (*continued*)

x_1	x_2	$\frac{H^E_m}{J \cdot mol^{-1}}$	$\frac{H^E_{123,m}}{J \cdot mol^{-1}}$	$\frac{\delta H^E_{123,m}}{J \cdot mol^{-1}}$
$x'_1 = 0.2494$			$H^E_{12,m} = 814.9\ J \cdot mol^{-1}$	
0.1109	0.3337	212.5	574.8	1.9
0.1039	0.3125	208.2	547.5	2.2
0.0861	0.2591	192.7	474.0	4.3
0.0667	0.2006	159.4	377.1	−0.7
0.0462	0.1390	121.3	272.2	−0.3
0.0255	0.0766	70.6	153.8	−3.3
$X'_1 = 0.4991$			$H^E_{12.m} = 1032.5\ J \cdot mol^{-1}$	
0.4878	0.4895	53.3	1062.3	1.8
0.4602	0.4617	168.3	1120.2	4.2
0.4343	0.4358	258.2	1156.6	2.9
0.4192	0.4206	308.8	1175.9	6.1
0.3994	0.4008	360.9	1187.1	2.8
0.3793	0.3806	411.9	1196.4	4.9
0.3521	0.3533	464.5	1192.8	3.7
0.3343	0.3355	490.5	1182.1	2.4
0.3071	0.3081	520.3	1155.5	2.5
0.2971	0.2981	527.2	1141.8	2.2
0.2782	0.2791	534.8	1110.2	1.5
0.2548	0.2557	534.2	1061.3	0.3
0.2419	0.2427	530.5	1030.9	0.7
0.2189	0.2196	516.8	969.6	1.6
0.1803	0.1809	473.2	846.2	2.0
0.1585	0.1590	437.6	765.4	0.8
0.1460	0.1465	414.5	716.5	0.1
0.1190	0.1194	351.8	598.0	−7.7
0.0843	0.0846	272.0	446.4	−4.8
0.0447	0.0448	156.8	249.2	−6.8
$x'_1 = 0.7498$			$H^E_{12,m} = 769.5\ J \cdot mol^{-1}$	
0.7292	0.2433	124.8	873.2	−3.2
0.6978	0.2329	299.5	1015.6	2.0
0.6743	0.2250	403.7	1095.8	−2.9
0.6412	0.2140	539.2	1197.2	−1.2
0.6166	0.2057	628.9	1261.7	2.8
0.5991	0.1999	683.6	1298.4	2.8
0.5738	0.1915	747.1	1336.0	−4.0
0.5424	0.1810	823.7	1380.4	−1.5
0.5216	0.1740	863.6	1398.9	−2.6
0.4929	0.1645	905.9	1411.7	−6.3
0.4686	0.1564	934.5	1415.4	−7.0
0.4408	0.1471	961.0	1413.4	−3.3
0.4231	0.1412	969.8	1404.0	−3.0
0.3965	0.1323	971.3	1378.2	−5.3
0.3518	0.1174	960.1	1321.1	0.4
0.3111	0.1038	924.5	1243.8	4.5
0.2722	0.0908	871.2	1150.5	9.4
0.2499	0.0834	825.1	1081.6	4.5
0.2081	0.0694	730.5	944.0	1.5
0.1562	0.0521	591.5	751.8	−1.0
0.1254	0.0419	495.1	623.8	−5.0
0.0812	0.0271	344.6	428.0	−6.3

The B_1 parameters were calculated by the unweighted least-squares method using a non-linear optimization algorithm due to Marquardt[12]. Table 2 presents the values of the parameters A_i, B_i, and the corresponding standard deviations.

The experimental excess molar enthalpies of ternary mixtures plotted against x together with the curves fitted and the predictions of the Nitta–Chao model are at the Figure 2. The Nitta–Chao model shows a $0.02 \cdot H_m^E$ deviation for (ethyl propanoate + n-hexane); $0.06 \cdot H_m^E$ for (ethyl propanoate + n-tetradecane); $0.03 \cdot H_m^E$ for (n-hexane + n-tetradecane) whereas the ternary mixtures show $0.08 \cdot H_m^E$.

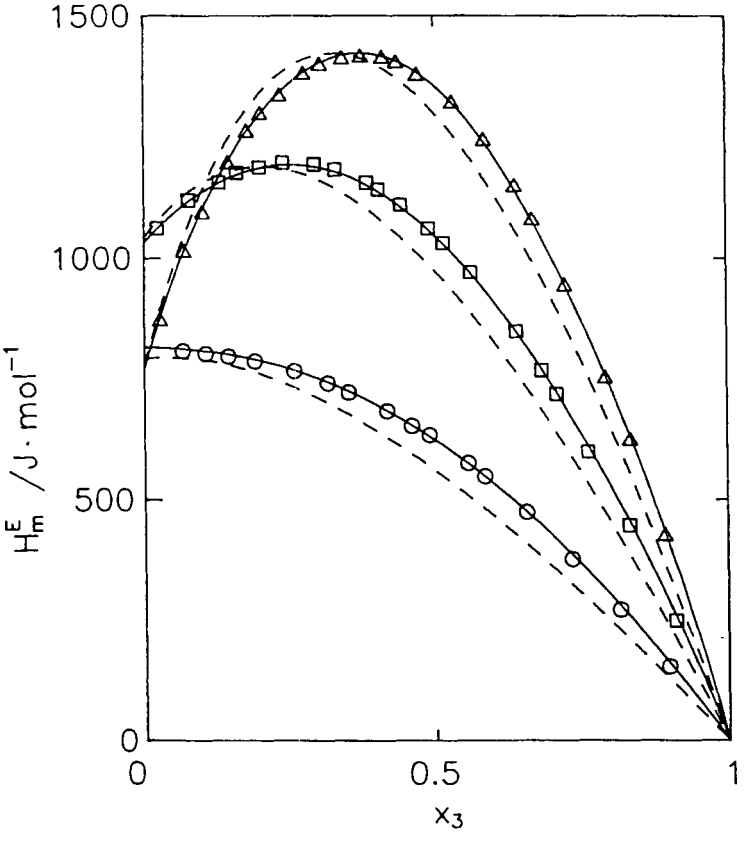

Figure 2 Excess molar enthalpies $H^E_{123,m}$ at the temperature 298.15 K of the pseudo binary (○), (x (0.2494 ethyl propanoate + 0.7306 n-hexane) + (1 − x) n-tetradecane); (□), {x (0.4991 ethyl propanoate + 0.5009 n-hexane) + (1 − x) n-tetradecane); (△), {x (0.7498 ethyl propanoate + 0.2502 n-hexane) + (1 − x) n-tetradecane). Continuous curves were calculated from Eq. (3) and broken lines were calculated by using thje Nitta–Chao model.

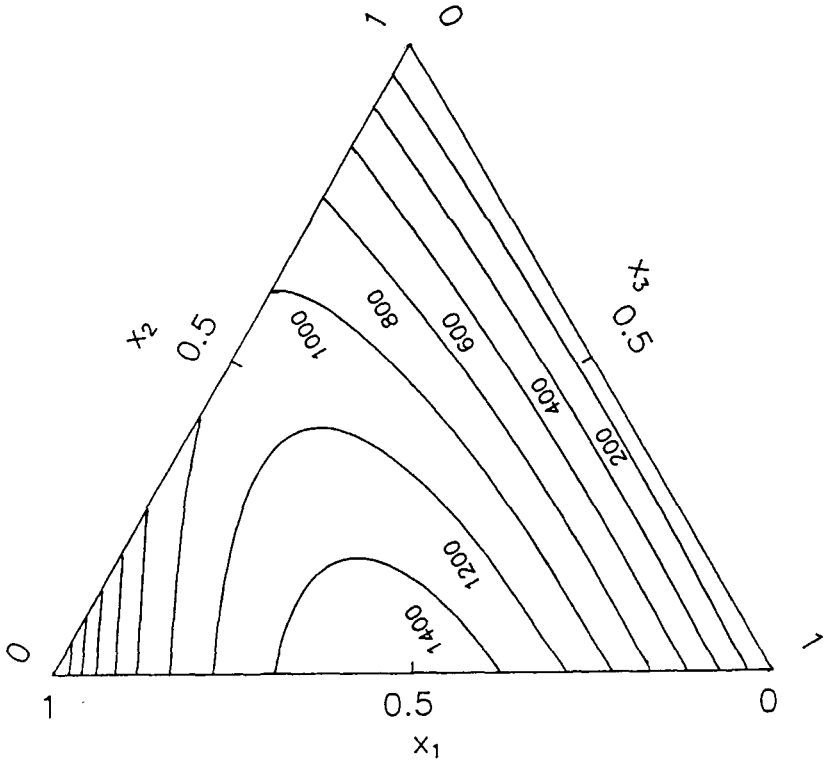

Figure 3 Curves of constant $H^E_{123,m}/(J \cdot mol^{-1})$ for (x_1 ethyl propanoate + x_2 *n*-hexane + x_3) *n*-tetradecane) calculated from Eq. (3) at the temperature 298.15 K.

Figure 3 shows lines of constant ternary excess molar enthalpies (isolines) calculated by using Eq. (3). The called "ternary contribution" Δ_{123}, represents the difference between the experimental H^E_{123} and that predicted values H^E_{123}, from the binary mixtures by employing Eq. (2), (Figure 4). This contribution is described by only three adjustable parameters B_i, and shows a maximum of $10.10\ J \cdot mol^{-1}$ at $x_1 = 0.2380$, $x_2 = 0.1820$ and a minimum of $-5.28\ J \cdot mol^{-1}$ at $x_1 = 0.240$, $x_2 = 0.630$. These values are similar to those found for other ternary systems containing alkanes or solvents of low polarity[13,14], but substantially lower than those due to ternary contributions of mixtures containing one or two alkanols[1,15–19]. In these, according to various successive solvation reactions the solution contains multisolvents copolymers, and a free hydroxyl group of alkanols is attached to the tail molecule of these complexes[18]. This effect is not displayed by the alkanes and in a very small extent by the esters, which agrees the low Δ_{123} experimental values.

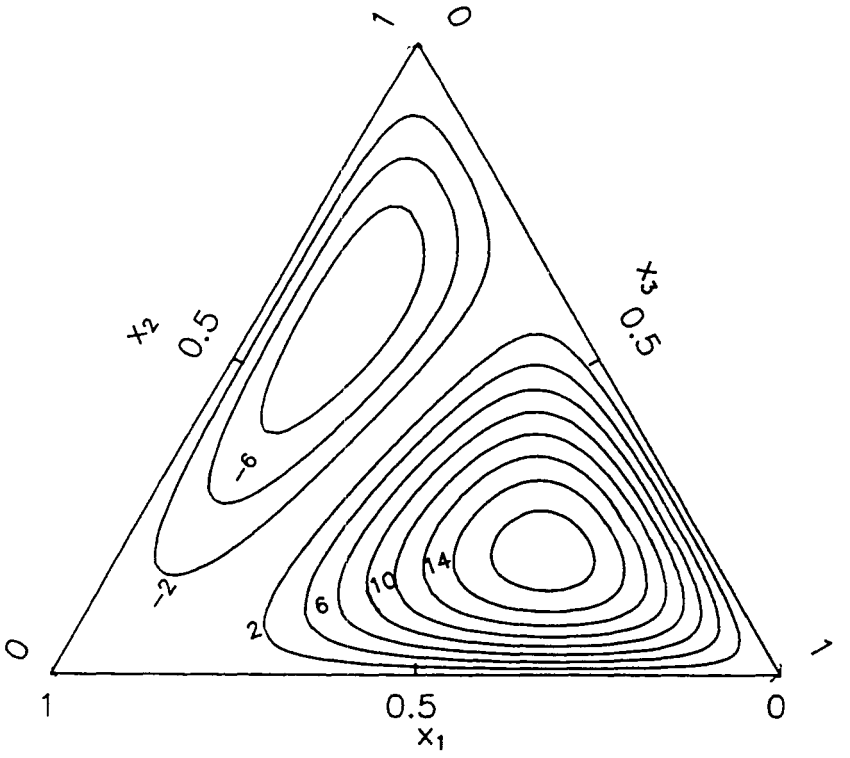

Figure 4 Ternary contributions $x_1x_2x_3\Delta_{123}/(J \cdot mol^{-1})$ to excess molar enthalpy of (x_1 ethyl propanoate + x_2 *n*-hexane + x_3 *n*-tetradecane) at the temperature 298.15 K.

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