Experimental and Theoretical Study of Excess Molar Enthalpies of Ethyl Propionate + *n*-Hexane + 1-Butanol at 298.15 K

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Excess molar enthalpies at the temperature 298.15 K and atmospheric pressure of the ternary mixture ethyl propionate + *n*-hexane + 1-butanol and the involved binary mixtures ethyl propionate + 1-butanol and *n*-hexane + 1-butanol were measured using a Calvet microcalorimeter. The results were fitted by means of different polynomial expressions. The group contribution models of Nitta-Chao and UNIFAC (in the versions of Tassios, Larsen, and Gmehling) were used to predict ternary excess enthalpy values, as well as several empirical expressions for estimating ternary properties from binary results.

1. Introduction

Continuing our previous studies focused on both experimental and theoretical determination of calorimetric properties of nonelectrolyte ternary liquid mixtures (López et al., 1992, 1993, 1995a,b, 1998), excess molar enthalpies at 298.15 K and atmospheric pressure of the ternary mixture ethyl propionate + *n*-hexane + 1-butanol and the involved binaries ethyl propionate + 1-butanol and *n*-hexane + 1-butanol are presented. The property studied has proved to be meaningful from a thermodynamic point of view, as it provides direct information about the energetic effects arising between the molecules present in the mixture, so it can help to explain the rearranging of bondings that occurs during the mixing process, which is essential when studying new theoretical approaches to the liquid−state matter and its mixtures. The excess enthalpy of the binary ethyl propionate + *n*-hexane was reported in an earlier work (López et al., 1993). The enthalpy change on mixing was determined in every case using a Calvet microcalorimeter. The binary experimental data were fitted using a variable-degree polynomial, due to Redlich Kister (1948). The ternary contribution to the excess enthalpy was correlated using Cibulka (1982) and Nagata and Tamura (1990) equations. Ternary results were also fitted with three equations proposed in an earlier work (Piñeiro et al., 1997).

Experimental values were compared with the predictions obtained by applying the group contribution models of Nitta et al. (1977) and UNIFAC, the latter in the versions of Dang and Tassios (1986), Larsen et al. (1987), and Weidlich and Gmehling (1987). The predicting capability of several empirical methods was also tested. These equations offer reliable estimations of excess properties for a multicomponent mixture using the involved binaries experimental data. The symmetric equations used were those introduced by Kohler (1960), Jacob and Fitzner (1977), Colinet (1967), and Knobeloch and Schwartz (1962) and the asymmetric ones due to Tsao and Smith (1953), Toop (1965), Scatchard et al. (1952), Hillert (1980), and Mathieson and Thynne (1957).

2. Experimental Section

All chemicals employed were supplied by Fluka, ethyl propionate (puriss, >99.5 mass %), *n*-hexane (puriss, >99.5 mass %), 1-butanol (>99.5 mass %), and were used with no other purification than being dried over Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and avoid moisturizing, and degassed by the ultrasound technique.

The experimental measurements were carried out using a Calvet microcalorimeter equipped with a device allowing operation in the absence of a vapor phase. Calibration was performed electrically using a Setaram EJP 30 stabilized current source. The accuracy in excess enthalpy measurements was estimated to be ±1 J·mol^{-1}. The mixtures were prepared by mass using a Mettler H51 balance, ensuring an accuracy in the mole fractions of 10^{-4}. Further details about the experimental method of operation have been previously published (Paz Andrade, 1967; López et al., 1992).

Three experimental series of measurements were carried out for ternary compositions resulting from adding 1-butanol to a binary mixture composed of {x'_1 [ethyl propionate] + x'_2 [*n*-hexane]}, where $x'_2 = 1 - x'_1$. The ternary composition point is then a pseudobinary mixture composed of 1-butanol (x_2) and the mentioned binary mixture (x_1). Thus, the ternary excess molar enthalpy at pseudobinary composition x_1 and x_2 can be expressed as

$$H^{\mathrm{E}}_{m,1+2+3} = H^{\mathrm{E}}_{m,(1+2)+3} + (x_1 + x_2)H^{\mathrm{E}}_{m,1+2} \qquad (1)$$

where $H^{\mathrm{E}}_{m,(1+2)+3}$ is the measured excess molar enthalpy for the pseudobinary mixture and $H^{\mathrm{E}}_{m,1+2}$ is the excess enthalpy of the initial binary mixture {x'_1 [ethyl propionate] + x'_2 [*n*-hexane]}.

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10.1021/je9900530 CCC: $18.00

Table 1. Experimental Binary Excess Molar Enthalpies $H^E_{m,i+j}$ at 298.15 K

x	$H^E_{m,i+j}$ /(J mol^{-1})	x	$H^E_{m,i+j}$ /(J mol^{-1})
x[CH$_3$CH$_2$COOCH$_2$CH$_3$] + (1 − x)[CH$_3$(CH$_2$)$_3$OH]			
0.0484	294	0.5051	1560
0.0987	549	0.5412	1578
0.1561	810	0.5651	1563
0.1825	899	0.6041	1554
0.2923	1245	0.6501	1497
0.3216	1318	0.7220	1367
0.3602	1388	0.7807	1221
0.4066	1472	0.8702	858
0.4483	1519	0.9251	540
0.4712	1541		
x[CH$_3$(CH$_2$)$_4$CH$_3$] + (1 − x)[CH$_3$(CH$_2$)$_3$OH]			
0.1168	157	0.6279	572
0.2075	278	0.6681	583
0.2874	350	0.6960	572
0.3623	427	0.7369	570
0.3851	447	0.7918	538
0.4571	498	0.8619	468
0.4987	523	0.8901	454
0.5590	561	0.9359	379
0.6012	560	0.9714	285

Values of $H^E_{m,1+2}$ at three mole fractions were interpolated by using a spline-fit method. Equation 1 does not involve any approximation.

3. Data Correlation

The excess molar enthalpies of the binary mixtures are listed in Table 1. The values corresponding to the mixture ethyl propionate + 1-butanol were fitted to a variable-degree polynomial suggested by Redlich−Kister (1948):

$$H^E_{m,i+j}/(\mathrm{J{\cdot}mol^{-1}}) = x_i x_j \sum_{m=0}^{M} A_m (x_i - x_j)^m \tag{2}$$

while lower deviations for the mixture *n*-hexane + 1-butanol were obtained by fitting experimental binary data to the equation

$$H^E_{m,i+j}/(\mathrm{J{\cdot}mol^{-1}}) = x_i x_j \sum_{m=0}^{M} \frac{A_m}{(1 - x_i)^{m/2}} \tag{3}$$

Due to the asymmetry of the trend of the enthalpy, the maximum in the representation is shifted toward lower concentrations of alcohol, as can be observed in Figure 1, where experimental values of $H^E{}_{m,i+j}$ were plotted against the curves calculated from fitting eqs 2 and 3. For both equations, the fitting parameters A_m were computed using the unweighted least-squares method. The number of parameters, M was determined using the optimization F-test (Bevington, 1969). The coefficients A_m and the corresponding standard deviations s are shown in Table 2.

The measured data for the binary mixture *n*-hexane + 1-butanol were compared with those found in the literature (Brown et al., 1964; Smirnova and Kurtinina, 1969), and the differences were ≈0.06 $|H^E_{m,i+j}|$ and ≈0.04 $|H^E_{m,i+j}|$, respectively, for these references. No data of excess enthalpy were found in currently available literature for the binary mixture ethyl propionate + 1-butanol or for the ternary mixture. Figure 2 shows deviations of the excess molar enthalpies, δH^E_m, that is the difference between the values presented in this work and the literature values, plotted against the curves representing a ±5% deviation with respect to the experimental data presented.

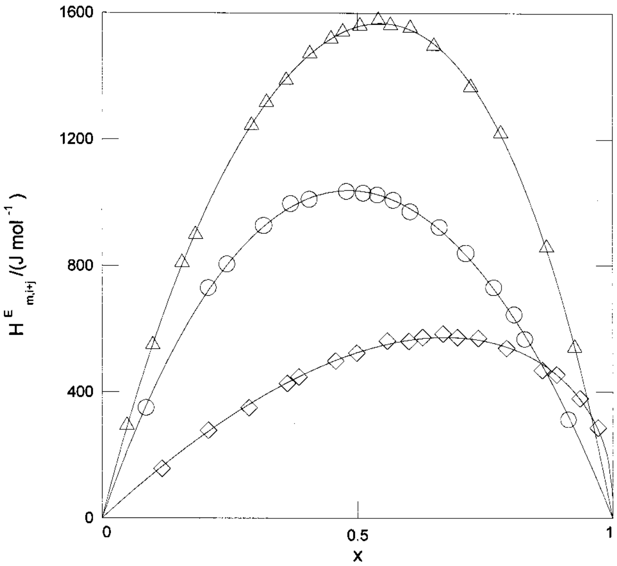

Figure 1. Excess molar enthalpies $H^E{}_{m,i+j}$ at 298.15 K of the binary mixtures: x[ethyl propionate] + (1 − x)[*n*-hexane] (López et al., 1993); (△) x[ethyl propionate] + (1 − x)[1-butanol]; (◇) x[*n*-hexane] + (1 − x)[1-butanol].

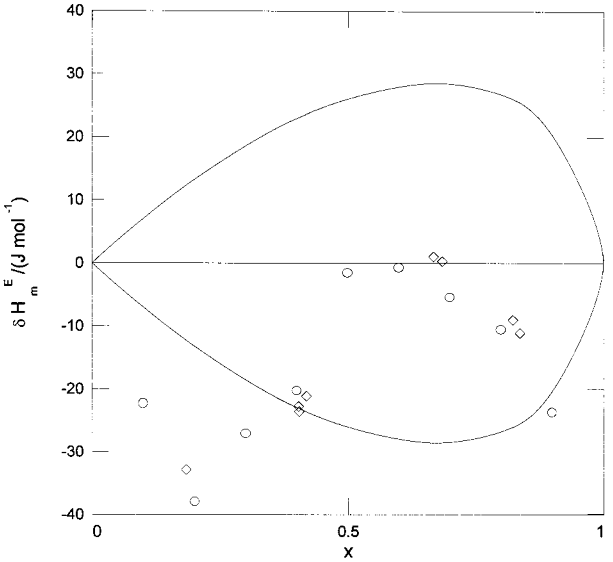

Figure 2. Deviations $\delta H^m_{m,1+2+3}$/(J mol^{-1}) for the binary x[*n*-hexane] + (1 − x)[1-butanol] (the zero value line represents the data presented in this work, and the plotted solid line represents a ±5% deviation), and the values published by (◇) Brown et al. (1964) and (○) Smirnova and Kurtynina (1969).

The measured values of the ternary excess enthalpies, $H^E_{m,1+2+3}$, listed in Table 3, were correlated using the following equation:

$$H^E_{m,1+2+3} = H^E_{m,1+2} = H^E_{m,1+3} + H^E_{m,2+3} + x_1 x_2 (1 - x_1 - x_2)\Delta_{123} \tag{4}$$

where the last term stands for the ternary contribution to the magnitude and was correlated using the equation proposed by Cibulka (1982)

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \tag{5}$$

Table 2. Fitting Coefficients A_m, B_i, and C_i for Eqs 2−8 and Standard Deviations s (J mol^{-1})

eq 2	A_0	A_1	A_2	A_3	A_4	A_5	s
$x[CH_3CH_2COOCH_2CH_3] + (1 - x)[CH_3(CH_2)_4CH_3]$[a]	4129	−220.3	550.8	−131.3	−672.6		1.7
$x[CH_3CH_2COOCH_2CH_3] + (1 - x)[CH_3(CH_2)_3OH]$	6230	944.8	1101				5.8

eq 3	A_0	A_1	A_2	A_3	A_4	A_5	s
$x[CH_3(CH_2)_4CH_3] + (1 - x)[CH_3(CH_2)_3OH]$	132.9	1296	65.38				7.7
$x_1[CH_3CH_2COOCH_2CH_3] + x_2[CH_3(CH_2)_4CH_3] + (1 - x_1 - x_2)[CH_3(CH_2)_3OH]$							

eq 5	B_0	B_1	B_2	s
	2269	6722	8741	21

eq 6	B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
	4.965	13.61	8.065	−20.91	−1.512	−22.02	10.19	−10.44	6.8

eq 7	C_1	C_2	C_3	C_4	C_5	C_6	s
	6679	1592	7960	−2396	1628	−2427	28

eq 8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	s
	6711	1937	9963	−3343	−176.1	10278	453.4	2292	7062	16

[a] López et al. (1993).

Table 3. Excess Molar Enthalpies $H^E_{m,1+2+3}$ for the Ternary Ethyl Propionate + *n*-Hexane + 1-Butanol

x_1	x_2	$H^E_{m,(1+2)+3}$ (J mol^{-1})	$H^E_{m,(1+2)+3}$ (J mol^{-1})	x_1	x_2	$H^E_{m,(1+2)+3}$ (J mol^{-1})	$H^E_{m,(1+2)+3}$ (J mol^{-1})
$x'_1 = 0.2494$, $H^E_{m,1+2} = 815$ J mol^{-1}							
0.2369	0.7127	408	1182	0.1447	0.4352	749	1222
0.2314	0.6962	491	1247	0.1288	0.3876	715	1135
0.2242	0.6745	580	1312	0.1135	0.3416	656	1027
0.2206	0.6637	610	1330	0.1068	0.3214	637	986
0.2128	0.6403	664	1360	0.0935	0.2814	596	901
0.2015	0.6063	730	1388	0.0681	0.2049	465	688
0.1888	0.5679	750	1367	0.0526	0.1582	382	554
0.1809	0.5443	758	1349	0.0342	0.1030	257	369
0.1537	0.4623	758	1260				
$x'_1 = 0.7494$, $H^E_{m,1+2} = 770$ J mol^{-1}							
0.4690	0.4706	467	1437	0.3216	0.3227	997	1663
0.4544	0.4559	608	1548	0.2790	0.2799	980	1557
0.4419	0.4434	698	1612	0.2324	0.2332	920	1400
0.4339	0.4353	749	1647	0.2057	0.2064	855	1281
0.4202	0.4216	814	1683	0.1657	0.1662	764	1106
0.4004	0.4018	887	1716	0.1313	0.1317	639	911
0.3815	0.3828	924	1713	0.1152	0.1156	589	827
0.3486	0.3498	982	1703	0.0687	0.0689	373	515
0.3307	0.3318	991	1676				
$x'_1 = 0.4991$, $H^E_{m,1+2} = 1032$ J mol^{-1}							
0.7282	0.2433	249	997	0.4678	0.1563	1243	1724
0.6932	0.2316	546	1258	0.4234	0.1415	1250	1685
0.6698	0.2238	695	1383	0.3533	0.1180	1210	1573
0.6510	0.2175	802	1471	0.3253	0.1087	1173	1507
0.6228	0.2081	946	1585	0.2933	0.0980	1111	1412
0.5958	0.1991	1034	1646	0.2460	0.0822	1014	1266
0.5729	0.1914	1086	1674	0.1956	0.0654	860	1061
0.5495	0.1836	1163	1727	0.1214	0.0406	604	728
0.4930	0.1647	1225	1731	0.0711	0.0238	373	446
0.4872	0.1628	1243	1743				

and that proposed by Nagata-Tamura (1990)

$$\Delta_{123}/RT = B_0 - B_1x_1 - B_2x_2 - B_3x_1^2 - B_4x_2^2 - B_5x_1x_2 - B_6x_1^3 - B_7x^3{}_2 \quad (6)$$

The following equations, introduced in an earlier work (Piñeiro et al., 1997), were also used to correlate the ternary excess enthalpies. The first uses six adjustable coefficients C_i

$$H^E_{m,1+2+3} = C_1x_1x_2 + C_2x_2x_3 + C_3x_1x_3 + C_4x_1^2x_2 + C_5x_2^2x_3 + C_6x_1x_3^2 \quad (7)$$

and the second includes nine coefficients

$$H^E_{m,1+2+3} = C_1x_1x_2 + C_2x_2x_3 + C_3x_1x_3 + C_4x_1^2x_2 + C_5x_2^2x_3 + C_6x_1x_3^2 + C_7x_1^3x_2 + C_8x_2^3x_3 + C_8x_1x_3^3 \quad (8)$$

Equations 7 and 8 can be expressed in a condensed way using the Levi Civita tensor ϵ_{ijk}:

$$H_{m,1+2+3} = \sum_{m=1}^{p}\sum_{i,j,k=1}^{3} C_{m\cdot i}\left(\frac{1+\epsilon_{ijk}}{2}\right)x_i^m x_j \quad (9)$$

where $p = 2$ for eq 7 and $p = 3$ for eq 8.

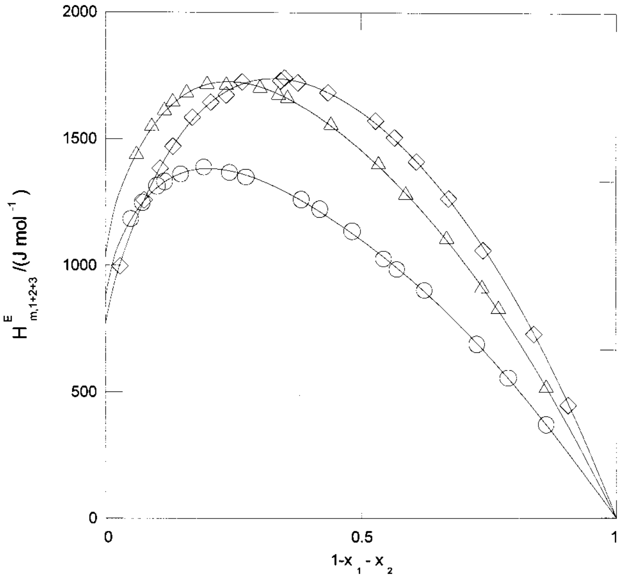

Figure 3. Pseudobinary representation of the excess molar enthalpies $H^{E}_{m,1+2+3}$/(J mol^{-1}) at 298.15 K of {$(x_1 + x_2)(x'_1$[ethyl propionate] + x'_2[*n*-hexane]) + $(1 - x_1 - x_2)$[1-butanol]}: (○) $x'_1 = 0.2494$, $x'_2 = 0.7506$; (△) $x'_1 = 0.4991$, $x'_2 = 0.5009$; (◇) = 0.7494, $x'_2 = 0.2506$; (—) correlated using eqs 3 and 5.

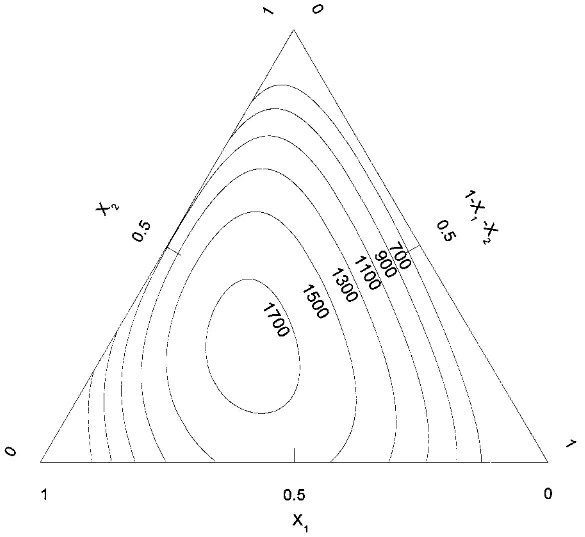

Figure 4. Curves of constant $H^{E}_{m,1+2+3}$/(J mol^{-1}) for the ternary mixture x_1[ethyl propionate] + x_2[*n*-hexane] + $(1 - x_1 - x_2)$[1-butanol], calculated with eqs 3 and 5, at 298.15 K.

The C_i parameters corresponding to eqs 7 and 8 were calculated with the unweighted least-squares method using a nonlinear optimization algorithm due to Marquardt (1963). These parameters and the corresponding standard deviations are also enclosed in Table 2. It can be observed that eqs 7 and 8 provide deviations for the ternary magnitude similar to that obtained after correlating the binary magnitude with the Redlich Kister equation and the ternary contribution with the expression of Cibulka, requiring a more reduced set of correlation parameters.

Figure 3 shows the pseudobinary representation of the measured experimental values of the ternary excess enthalpies together with the correlated curves, where eq 5 was applied to fit the ternary contribution.

Figure 4 represents the lines of constant ternary excess molar enthalpy calculated using eqs 3 and 5. The excess molar enthalpy is positive over the whole range of concentrations and shows a maximum of 1770 J·mol^{-1} at $x_1 = 0.455$ and $x_2 = 0.266$. Figure 5 shows the ternary contribution to the excess enthalpy correlated with eq 5. The ternary contribution is also positive and shows a maximum of 272 J·mol^{-1} at $x_1 = 0.394$ and $x_2 = 0.386$.

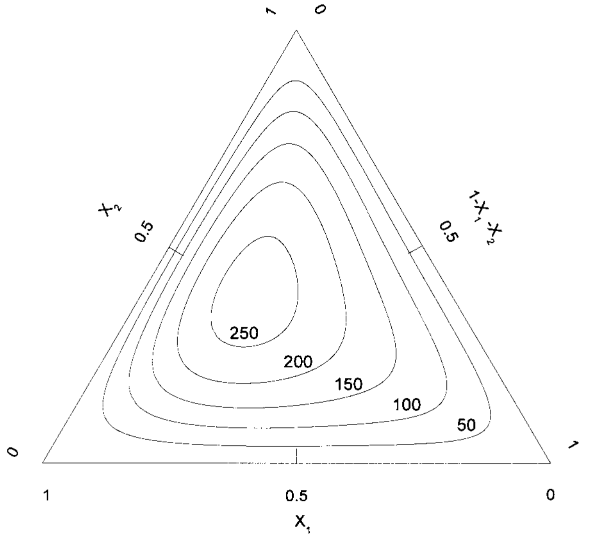

Figure 5. Curves of the constant ternary contribution (J mol^{-1}) to the excess molar enthalpy $H^{E}_{m,1+2+3}$ for the ternary x_1[ethyl propionate] + x_2[*n*-hexane] + $(1 - x_1 - x_2)$ [1-butanol], at 298.15 K, correlated using eq 5.

Table 4. Average Percent Deviations from the Experimental Values Obtained with the Empirical Predictive Methods Listed above[a]

predictive method	percent deviation		
Kohler		12.9	
Jacob−Fitzner		14.4	
Colinet		12.9	
Knobeloch−Schwartz		7.3	
Tsao−Smith	8.3	1.9	4.8
Toop	13.8	15.6	13.1
Scatchard	11.3	16.2	13.2
Hillert	6.7	15.7	13.1
Mathieson−Thynne	11.4	15.4	12.6

[a] For the asymmetric equations, three numberings of the components have been compared, being, in this order, 123, 231, and 312.

4. Excess Enthalpy Theoretical Prediction

Several empirical methods have been proposed to estimate ternary excess properties from experimental results on constituent binaries. These methods can be divided into symmetric and asymmetric, depending on whether the assumption of the three binaries contributing equally to the ternary mixture is accepted or not. Asymmetry is usually understood to be caused by the strongly polar or associative behavior of any of the compounds in the mixture. In these cases, different geometric criteria are applied to match each point of the ternary composition with the contributing binary compositions.

The equations tested in this work were listed in the Introduction. The average percent deviations from the experimental data are listed in Table 4. For the asymmetric equations, three different numberings of the compounds have been tested, the first element considered in each case being ethyl propionate, *n*-hexane, or 1-butanol. The deviations obtained are rather high, and this fact can be attributed to the comparatively important significance of the ternary contribution to the studied magnitude. The best agreement with experimental data was achieved by the

Table 5. Average Percent Deviations, of the Estimated Ternary Molar Excess Enthalpies Using the Described Group Contribution Models, Compared with the Experimental Data

model	percent deviation
Nitta−Chao	3.7
UNIFAC (Tassios)	17.1
UNIFAC (Larsen)	22.4
UNIFAC (Gmehling)	15.7

symmetric equation of Knobeloch and Schwartz, while the best asymmetric equation was that of Tsao Smith, choosing the alkane as the first component in the numbering. It can be observed that the dependence on the arrangement of the components varies in each asymmetric equation.

The Nitta et al. (1977) group contribution model is based on the cell theory for thermodynamic properties of polar and nonpolar liquids and their solutions, including excess properties, activity coefficients, and *PVT* relations. The basis of this model is the cell theory, where the repulsive forces between molecules are expressed by means of a cell partition function, derived from the rigid spheres equation of state of Carnahan and Starling (1969), and the quasi-chemical approximation of Guggenheim (1952) is used. The interaction parameters for the groups involved were calculated by Fernández et al. (1990) for the alkane−hydroxyl interaction, Ortega and Legido (1994) for the ester−alkane interaction, and Legido et al. (1998) for the ester−hydroxyl interaction.

The UNIFAC group contribution model was originally developed by Fredenslund et al. (1975), using the UNIQUAC equation by Abrams and Praustniz (1975) for a multicomponent mixture. The Dang and Tassios (1986) version predicts only values for H^E. In the version of Larsen et al. (1987) the interaction parameters become temperature dependent. As a result, this version can predict other properties, such as G^E, and phase equilibria. Weidlich and Gmehling (1987) modified the temperature dependence of the parameters and fitted them simultaneously to phase equilibria, H^E and γ^∞.

Table 5 shows the percent deviations of the values predicted by the mentioned models. The best accuracy was obtained with the Nitta Chao model, with a 3.7% deviation from experimental data, improving definitely the results provided by the other models considered.

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures. A New Expression for the Excess Gibbs Energy of Partly and Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill, New York, 1969.

Brown, I.; Fock, W.; Smith, F. Heats of Mixing. V. Systems of *n*-Alcohols with *n*-Hexane. *Aust. J. Chem.* **1964**, *17*, 1106−1118.

Carnahan, N. F.; Starling, K. E. Equation of State for Nonattracting Rigid Spheres. *J. Chem. Phys.* **1969**, *51*, 635−636.

Cibulka, I. Estimation of Excess Volume and Density of Ternary Liquid Mixtures of Non Electrolytes from binary Data. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1414−1419.

Colinet, C. Thesis, University of Grenoble, France, 1967.

Dang, D.; Tassios, D. P. Prediction of Enthalpies of Mixing with a UNIFAC model. *Ind. Eng. Chem. Process. Des. Dev.* **1986**, *25*, 22−31.

Fernández, J.; Legido, J. L.; Paz Andrade, M. I.; Pías, L.; Ortega, J. Analysis of Thermodynamic Properties of 1-Alkanol + *n*-Alkane Using the Nitta-Chao Group Contribution Model. *Fluid Phase Equilib*, **1990**, *55*, 293−308.

Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21* (6), 1086−1098.

Guggenhein, E. A. *Mixtures*; Clarendon Press: Oxford, U.K., 1952.

Hillert, M. Empirical Methods of Predicting and Representing Thermodynamic Properties of Ternary Solution Phases. *Calphad* **1980**, *4*, 1−12.

Jacob, K. T.; Fitzner, K. The Estimation of the Thermodynamic Properties of Ternary Alloys from Binary Data using the Shortest Distance Composition Path. *Thermochim. Acta* **1977**, *18*, 197−206.

Knobeloch, J. B.; Schwartz, C. E. Heats of Mixing of Ternary Systems: Sulphuric Acid−Phosphoric Acid−Water. *J. Chem. Eng. Data* **1962**, *7*, 386−387.

Kohler, F. Zur Berechnung der thermodynamischen Daten eines ternären Systems aus den zugehörigen binären Systemen. *Monatsh. Chem.* **1960**, *91*, 738−740.

Larsen, B. L.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286.

Legido, J. L.; Vijande, J.; Cominges, B. E.; García, J.; Iglesias, T. P.; García Garabal, S.; Fernández, J. Estimation of Parameters of Nitta-Chao Model for Ester + 1-Alkanol Mixtures. *Fluid Phase Equilib.* **1998**, *148*, 49−68.

Lopez, M.; Legido, J. L.; Romani, L.; Carballo, E.; Perez Martell, E.; Jimenez, E.; Paz Andrade, M. I. Excess Molar Enthalpies for (Propan-1-ol + Pentan-3-one + Hexane) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1992**, *24*, 205−212.

López, M.; Paz Andrade, M. I.; Legido, J. L.; Romaní, L.; Peleteiro, J.; Jiménez, E. Excess Molar Enthalpies for the (Ethyl Propanoate + *n*-Hexane + *n*-Tetradecane) System at the Temperature 298.15 K. *Phys. Chem. Liq.* **1993**, *25*, 145−152.

López, M.; Carballo, E.; Legido, J. L.; Salgado, J.; Vijande, J.; Paz Andrade M. I. Excess Molar Enthalpies of $\{x_1\ CH_3CH_2COCH_2CH_3 + x_2\ CH_3(CH_2)_4CH_3 + (1\text{-}x_1\text{-}x_2)\ CH_3(CH_2)_{n-2}CH_3\}$, ($n$ = 9 and 12) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1995a**, *27*, 879−886.

López, M.; Carballo, E.; Legido, J. L.; Salgado, J.; Vijande, J.; Paz Andrade, M. I. Excess Molar Enthalpies of $\{x_1\ CH_3CH_2COOCH_2\text{-}CH_3 + x_2\ CH_3(CH_2)_4CH_3 + (1\text{-}x_1\text{-}x_2)\ CH_3(CH_2)_{n-2}CH_3\}$, ($n$ = 10, 12) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1995b**, *27*, 1281−1290.

López, M.; Piñeiro, M. M.; Salgado, J.; Cominges, B. E.; Legido, J. L.; Paz Andrade, M. I. Excess molar enthalpies of the ternary system $\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1\text{-}x_1\text{-}x_2)\ CH_3CH_2\text{-}CH_2OH\}$ at 298.15 K, and prediction using different theoric methods. *Phys. Chem. Liq.*, in press.

Marquardt, D. W. An Algorithm for Least-Squares Estimation for Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *2*, 431−441.

Mathieson, A. R.; Thynne, J. C. J. Heats of Mixing of Ternary, Quaternary, and Quinary Mixtures formed by Benzene, Cyclohexane, Heptane, Toluene and Hexane. *J. Chem. Soc.* **1957**, 3713−3716.

Nagata, I.; Tamura, K. Excess Molar Enthalpies of {Methanol or Ethanol + (2-Butanone + Benzene)} at 298.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 279−283.

Nitta, T.; Turek, E.; Greenkorn, R. A.; Chao, K. C. A Group Contribution Model of Liquids and Solutions. *AIChE J.* **1977**, *23*, 144−160.

Ortega, J.; Legido, J. L. Application of the UNIFAC and Nitta-Chao Models to Describing the Behavior of Methyl Ester/Alkane Mixtures, and Experimental Data for (Methyl *n*-Alkanoates + *n*-Heptadecane) Binary Mixtures. *Fluid Phase Equilib.* **1994**, *95*, 175−214.

Paz Andrade, M. I. *Les Développements Récents de la Microcalorimétrie et de la Thermogenése*, 1st ed.; CNRS: Paris, 1967.

Piñeiro, M. M.; Cominges, B. E.; Legido, J. L.; García-Garabal, S.; López, M.; Paz Andrade, M. I. Application of different group contribution models and empirical methods to excess enthalpies of ternary mixtures. *J. Therm. Anal.* **1998**, *52*, 799−814.

Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Scatchard, G.; Ticknor, L. B.; Goates, J. R.; McCartney, E. R. Heats of Mixing in Some Nonelectrolyte Solutions. *J. Am. Chem. Soc.* **1952**, *74*, 3721−3724.

Smirnova, N. A.; Kurtynina, L. M. Thermodynamic Functions of Mixing for a Number of Binary Alcohol−Hydrocarbon Solutions. *Russ. J. Phys. Chem. (Engl. Transl.)* **1969**, *43* (7), 1059−1060.

Toop, G. W. Predicting Ternary Activities Using Binary Data. *Trans. TMS-AIME.* **1965**, *223*, 850−855.

Tsao, C. C.; Smith, J. M. Heats of Mixing of Liquids. *Chem. Eng. Prog. Symp. Ser.* **1953**, *49*, 107−117.

Weidlich, U.; Gmehling, J. A Modified UNIFAC Model. 1, Prediction of VLE, h^E, and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372−1381.

Received for review February 17, 1999. Accepted April 26, 1999. M. M. Piñeiro wishes to acknowledge Secretaría Xeral de Investigación e Desenvolvemento da Xunta de Galicia for financial support.

JE9900530