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Isothermal Vapor−Liquid Equilibrium of Binary Mixtures Containing 1-Chlorobutane, Ethanol, or Acetonitrile[†]

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Vapor−liquid equilibrium has been measured at 333.15 K for the following binary mixtures: acetonitrile (3) + 1-chlorobutane (1), ethanol (2) + 1-chlorobutane (1), and ethanol (2) + acetonitrile (3) at 333.15 K. Values of the maximum of G^E ranging from 700 $J \cdot mol^{-1}$ to 1150 $J \cdot mol^{-1}$ were found for the three systems. Consistency with data already published at different temperatures has been demonstrated as well as with experimental excess enthalpy for the ethanol + acetonitrile mixture. The results have been used to test the ability of a lattice-fluid theory to fit the G^E and to predict the H^E and V^E excess functions. Although reasonable fits were found for the systems containing ethanol, worse results were found for 1-chlorobutane + acetonitrile. In general, the theoretical predictions of H^E and V^E are rather poor when the binary energy parameter of the theory is fitted to G^E.

Introduction

Information on phase equilibrium of fluid mixtures is required for engineering processing. In spite of the advances made in the field of molecular thermodynamics during the last two decades, our ability to predict with quantitative accuracy the phase equilibria of fluid mixtures is still far from satisfactory.[1]

In the present work, we have selected three binary mixtures in which strong specific interactions, strong hydrogen bonds, as well as dipole−dipole interactions exist between the components. The compounds were chosen because they are poor solvents for some commodity polymers such as poly(methyl methacrylate); however, their binary mixtures are rather good solvents.[2] This phenomenon, called cosolvency, depends on the osmotic susceptibility of the solvent binary mixture, and at the microscopic level it represents the existence of a local solvent composition in the immediate proximity of the polymer segments that may be rather different from the overall solvent composition.[3,4] This phenomenon may also have strong influence on the nanostructures formed by block-copolymers in mixed solvents, although it has not been fully explored yet.[5]

The three binary mixtures studied in this paper (1-chlorobutane (1) + ethanol (2), 1-chlorobutane (1) + acetonitrile (3), and acetonitrile (3) + ethanol (2)) show large excess Gibbs energies, G^E, which seems to be a necessary condition for cosolvency. However, most of the studies are based on a single set of data at one temperature, and no analysis of the thermodynamic consistency of the G^E data was carried out. Furthermore, the analysis was accompanied by the use of some theoretical models for liquid mixtures, the validity of which is strongly dependent on the consistency of the experimental G^E data. The purpose of the present work is to complement the available G^E data for the three mixtures mentioned above and to check for their consistency. We have chosen a relatively high temperature for our measurements because a broad temperature range is convenient when analyzing mixtures in which hydrogen-bond interactions are present. To gather some information about the molecular basis of the cosolvency phenomenon, it is convenient to analyze the data using a theoretical model for mixtures that can incorporate hydrogen bonds. In this paper, we have used a lattice-fluid model that has been shown to be able to fit the G^E versus composition curves but fails in predicting other excess functions.

Experimental

The 1-chlorobutane and the acetonitrile were Carlo Erba, of the highest quality available (RPE). The ethanol was purchased from Aldrich. Water was removed using molecular sieves until a standard analytical method (Karl-Ficher method) showed no presence of water. The purity of the pure substances was higher than 99.9 % in mass according to the gas chromatography analysis. Further test of the purity of the substances was done by measuring the density, the refractive index, and the temperature dependence of the vapor pressure. The densities were measured with a vibrating tube densimeter (Anton Paar DMA601) calibrated as described in a previous paper.[6] The uncertainty of each density measurement was ± 0.02 $kg \cdot m^{-3}$ provided that the temperature of the sample was controlled to within ± 0.002 K during the measurement. The refractive index has been measured with a Zeiss refractometer using a sodium lamp. The uncertainty of each refractive index measurement was ± 0.0001 when the temperature was constant to within ± 0.01 K. The vapor pressures were measured using the same ebulliometer used previously.[7] Table 1 compares the results measured for the pure components with literature data, and the agreement is quite satisfactory. Analysis of the liquid and vapor phases was performed by refractive index measurements. Mixture samples (50 mL) for constructing the calibration curves were made by mass in an analytical balance precise to ± 0.02 mg. The precision of the mole fractions of these calibration mixtures is ± 0.00001. The temperature in the ebulliometer was measured with a Pt resistance thermometer, with a precision of 10^{-3} K. The agreement of the temperature scale on IPTS-90 is ± 0.02 K. The uncertainty of each pressure measurement was ± 0.07 Pa using a mercury manometer. The height of each branch of the manometer was read with a cathetometer precise to ± 1 μm.

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Table 1. Physical Constants of Pure Chemicals: Density, ρ, Refractive Index, n_D, and Second Virial Coefficient, B^a

	acetonitrile		ethanol		1-chlorobutane	
	exptl	lit.	exptl	lit.	exptl	lit.
$\rho/\text{kg}\cdot\text{m}^{-3}$ (298.15 K)	776.65 (0.02)	776.49[8]	785.34 (0.03)	785.08[10]	880.86 (0.01)	880.80[9]
n_D (298.15 K)	1341.39 (0.02)	1341.6[9]	1359.17 (0.02)	1359.41[10]	1399.53 (0)	1399.53[9]
$-10^6B/\text{m}^3\cdot\text{mol}^{-1}$ (333.15 K)		550.0[11]		1285.0[11]		1163.1[11]

[a] The values in brackets represent the relative deviation with respect to the literature values in %.

Table 2. Vapor Pressures of the Pure Components as a Function of T^a

	acetonitrile			ethanol			1-chlorobutane		
T/K	exptl	lit.[12]	δ	exptl	lit.[12]	δ	exptl	lit.[12]	δ
313.15	22.758	22.669	0.3	17.922	17.909	0.1	25.974	26.014	0.1
318.15	27.891	27.748	0.5	23.103	23.087	0.1	31.699	31.736	0.1
323.15	33.092	33.728	1.9	29.549	29.490	0.2	38.437	38.437	0
328.15	40.946	40.721	0.5	37.410	37.342	0.2	46.192	46.236	0.1
333.15	49.079	48.851	0.5	46.900	46.899	0.1	55.256	55.256	0
338.15	58.511	58.248	0.5	58.438	58.442	0.1	65.660	65.629	0.1
343.15	69.522	69.057	0.7	72.311	72.287	0.1	77.512	77.496	0.1
348.15	82.040	81.423	0.7	88.765	88.786	0.1	90.966	91.002	0.1

[a] The data are given in kPa. Exptl refers to the experimental values measured in this work, and lit. to data reported in the literature. δ represents the absolute diference with respect the literature values in %.

Table 3. Coefficients A_i, Standard Deviation, $\sigma(n_D)$, and Average Absolute Deviation of Equation 1, $<\Delta(n_D)>$, at 303.15 K

	A_1	A_2	A_3	A_4	A_5	$10^5\cdot\sigma(n_D)$ $10^5\cdot<\Delta(n_D)>$
acetonitrile (3) + 1-chlorobutane (1)	1.39722	−0.03079	−0.01842	0.00422	−0.01297	4 3
ethanol (2) + 1-chlorobutane (1)	1.39720	−0.02783	0.00349	−0.01526		4 4
ethanol (2) + acetonitrile (3)	1.33937	0.01937	0.00348	−0.00456		2 2

Results and Discussion

The refractive index, n_D, of 50 liquid mixtures spanning the whole mole fraction range was measured at 303.15 K for each of the three binary mixtures studied. The experimental results were fitted to a polynomial

$$n_D = \sum_{i=0}^{m} A_i x_1^i \qquad (1)$$

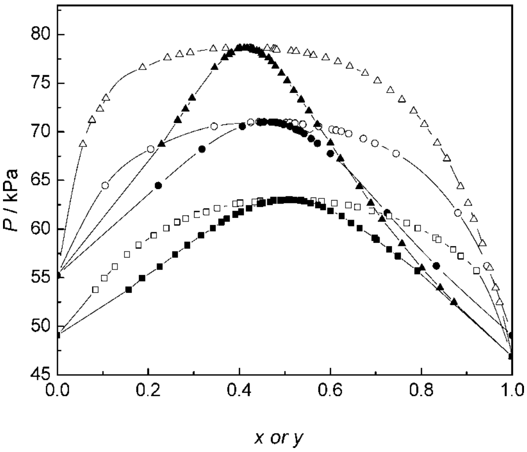

Figure 1. Composition dependence of the total vapor pressure, P, for the three mixtures studied at 333.15 K. x and y are the mole fraction of the liquid and vapor phases, respectively, of the component written in the first place in the binary mixture. The symbols are the experimental data of Table 4, and the curves are the predictions based on the correlation of G^E with eq 2 and the parameters included in Table 5. From top to bottom, the systems correspond to: ethanol (2) + acetonitrile (3), acetonitrile (3) + 1-chlorobutane (1), and ethanol (2) + 1-chlorobutane (1).

where $x_1$is the mole fraction of component 1 and the adjustable parameters A_i are shown in Table 2, together with the standard deviation of the fitting, $\sigma(n_D)$. From the values of $\sigma(n_D)$, the estimated uncertainties in the determination of the compositions of the coexisting phases (expressed as mole fractions) were $\pm 1\cdot10^{-3}$ for the two systems with 1-chlorobutane and $\pm 3\cdot10^{-4}$ for the system acetonitrile (3) + ethanol (2). The activity coefficients, γ_i, of the two components of the mixture and the excess Gibbs energy, G^E, have been calculated from the vapor pressure, the temperature, and the vapor- and liquid-phase compositions using standard thermodynamic methods.[13] The vapor-phase nonideality was accounted for using the second virial coefficients.[11] The activity coefficient of component i is given by

$$RT\ln\gamma_i = RT\ln\frac{P_i}{P_i^0} + (B_{ii} - V_i^0)(P - P_i^0) + P\cdot y_j^2\cdot\delta_{12}$$

$$P_i = P\cdot y_i$$

$$\delta_{12} = B_{11} + B_{22} - 2\cdot B_{12}$$

$$B_{12} = \left(\frac{B_{11}^{1/3} + B_{22}^{1/3}}{3}\right)^3$$

$$G^E = RT\sum_i x_i\ln\gamma_i \qquad (2)$$

where P_i^0 is the vapor pressure of pure component i; V_i^0 its molar volume; and B_{ii} is the second virial coefficient. All the variables are measured, thus the G^E can be directly calculated.

Table 3 shows the experimental VLE data: liquid and vapor compositions, vapor pressures, activity coefficients, and excess Gibbs energies. Figure 1 shows the vapor pressure−composition plot for the three systems. The three systems studied present an azeotropic point, and the mole fractions or the azeotropic points are: $x_{1,az} = 0.462$ for 1-chlorobutane (1) + acetonitrile (3); $x_{1,az} = 0.502$ for 1-chlorobutane (1) + ethanol (2); and $x_{3,az} = 0.4133$ for acetonitrile (3) + ethanol (2).

Table 4. Vapor Pressure P, Liquid-Phase Concentration, x, Vapor-Phase Concentration, y, Activity Coefficients, γ_i, and Excess Molar Gibbs Energy, G^E, at 333.15 K

x_3	y_3	P/kPa	γ_3	γ_1	G^E/J·mol^{-1}	x_3	y_3	P/kPa	γ_3	γ_1	G^E/J·mol^{-1}
Acetonitrile (3) + 1-Chlorobutane (1)											
0.1052	0.2224	64.468	2.738	1.010	319.0	0.5743	0.5120	70.555	1.249	1.458	799.1
0.2058	0.3181	68.216	2.106	1.055	542.4	0.6040	0.5245	70.247	1.212	1.521	781.9
0.3448	0.4070	70.554	1.656	1.149	735.5	0.6132	0.5293	70.154	1.203	1.539	776.7
0.4255	0.4461	70.966	1.478	1.232	793.2	0.6247	0.5348	70.066	1.192	1.566	770.5
0.4434	0.4548	71.019	1.447	1.253	801.7	0.6408	0.5428	69.817	1.175	1.603	756.6
0.4776	0.4697	71.007	1.387	1.298	810.9	0.6730	0.5586	69.301	1.144	1.688	725.0
0.5027	0.4811	70.937	1.348	1.333	812.9	0.6986	0.5725	68.816	1.122	1.762	695.9
0.5116	0.4838	70.938	1.332	1.350	813.6	0.7447	0.6006	67.769	1.088	1.915	634.9
0.5230	0.4897	70.889	1.318	1.366	813.0	0.8811	0.7247	61.671	1.017	2.590	355.7
0.5397	0.4966	70.797	1.294	1.395	810.0	0.9446	0.8339	56.225	1.002	3.068	177.9
0.5401	0.4972	70.754	1.293	1.394	808.6						
Ethanol (2) + 1-Chlorobutane (1)											
0.0567	0.2292	68.694	5.858	1.009	303.1	0.5631	0.4521	77.860	1.313	1.749	1101.4
0.0767	0.2649	71.188	5.180	1.018	468.4	0.5900	0.4645	77.607	1.275	1.826	1081.2
0.0941	0.2822	72.330	4.568	1.029	468.4	0.6171	0.4711	77.164	1.237	1.910	1050.9
0.1071	0.2967	73.446	4.282	1.033	524.8	0.6433	0.4794	76.722	1.201	2.007	1015.5
0.1877	0.3462	76.582	2.968	1.104	790.1	0.6771	0.4930	75.995	1.163	2.139	963.8
0.2421	0.3680	77.600	2.477	1.159	918.9	0.7038	0.5053	75.240	1.136	2.253	915.4
0.2686	0.3769	77.923	2.296	1.189	969.6	0.7321	0.5196	74.244	1.108	2.389	855.5
0.2924	0.3829	77.150	2.149	1.220	1010.6	0.7579	0.5362	73.281	1.091	2.520	803.4
0.3433	0.3966	78.509	1.904	1.291	1078.4	0.7835	0.5534	72.134	1.073	2.672	742.7
0.3702	0.4022	78.567	1.792	1.335	1103.0	0.8073	0.5717	70.746	1.055	2.826	676.2
0.4006	0.4111	78.597	1.693	1.382	1122.8	0.8356	0.6003	68.829	1.043	3.010	599.6
0.4223	0.4175	78.603	1.631	1.419	1133.0	0.8564	0.6224	67.221	1.031	3.182	533.8
0.4615	0.4256	78.568	1.521	1.500	1142.0	0.8863	0.6645	64.367	1.020	3.423	436.9
0.4754	0.4283	78.511	1.485	1.532	1141.0	0.9033	0.6890	62.665	1.011	3.635	374.2
0.4788	0.4305	78.491	1.481	1.536	1141.2	0.9161	0.7139	60.990	1.006	3.754	323.8
0.4822	0.4314	78.415	1.473	1.542	1138.7	0.9348	0.7577	58.484	1.006	3.928	260.2
0.5141	0.4388	78.313	1.403	1.620	1132.2	0.9511	0.8015	55.985	1.001	4.112	195.5
0.5248	0.4439	78.240	1.339	1.639	1129.5	0.9638	0.8415	53.942	1.000	4.277	147.5
0.5500	0.4495	78.072	1.340	1.710	1115.2	0.9724	0.8721	52.458	1.000	4.406	114.5
Ethanol (2) + Acetonitrile (3)											
0.0839	0.1573	53.786	2.154	1.002	183.7	0.4941	0.4992	62.987	1.349	1.250	722.9
0.1036	0.1872	54.951	2.119	1.007	234.8	0.5116	0.5080	63.019	1.326	1.273	727.0
0.1268	0.2250	56.149	2.124	1.006	280.3	0.5367	0.5205	63.001	1.295	1.307	728.8
0.1538	0.2592	57.390	2.060	1.013	338.8	0.5631	0.5346	62.927	1.266	1.344	726.6
0.1793	0.2860	58.342	1.981	1.022	390.0	0.5807	0.5435	62.848	1.246	1.372	722.8
0.2126	0.3164	59.355	1.879	1.036	450.4	0.6092	0.5567	62.669	1.213	1.426	711.7
0.2394	0.3428	60.095	1.829	1.043	491.1	0.6404	0.5732	62.471	1.185	1.488	697.6
0.2637	0.3607	60.723	1.765	1.059	532.4	0.6604	0.5844	62.252	1.167	1.530	683.6
0.2821	0.3732	61.062	1.716	1.070	557.9	0.6914	0.6011	61.884	1.140	1.607	657.5
0.3074	0.3913	61.518	1.663	1.085	590.1	0.7296	0.6255	61.350	1.114	1.709	621.4
0.3278	0.4044	61.782	1.618	1.098	612.1	0.7682	0.6465	60.631	1.081	1.862	566.6
0.3517	0.4220	62.145	1.582	1.111	637.2	0.7927	0.6649	60.096	1.068	1.958	532.2
0.3918	0.4454	62.577	1.509	1.144	673.8	0.8317	0.6977	59.110	1.051	2.143	471.8
0.4019	0.4515	62.697	1.494	1.153	682.8	0.8381	0.7017	58.888	1.045	2.191	456.0
0.4347	0.4673	62.812	1.432	1.186	700.7	0.8702	0.7296	57.891	1.030	2.439	391.8
0.4469	0.4755	62.904	1.419	1.196	707.8	0.8871	0.7490	57.209	1.025	2.575	357.1
0.4750	0.4904	62.967	1.378	1.225	718.0	0.9219	0.7914	55.698	1.015	3.019	278.2

It is well-known that measuring simultaneously P, T, and the mole fraction of the liquid phase, x_1, and the mole fraction of the vapor phase, y_1, is an overdetermination, thus allowing the use of thermodynamic consistency tests.[13] To this end, we have assumed that the composition dependence of the excess Gibbs energy, G^E, is given by a Padé approximant of the form

$$\frac{G^E}{RTx(1-x)} = \sum_{i=0}^{n} C_i(2 \cdot x - 1) \qquad (3)$$

The adjustable parameters C_i were obtained using a method based on the maximum likelihood principle (ML) as described previously.[14] Contrary to standard least-squares methods, the ML method does not make any distinction between dependent and independent variables. As a consequence, the method calculates residuals for all the variables and weights them according to their respective experimental uncertainties. This method seems better suited for the analysis of vapor−liquid equilibrium results because all the variables measured (P, T, x, and y) are subject to experimental error. Hence, there is no statistical reason for choosing one of them (most frequently P) as an error-free independent variable in the fits. A detailed description of the method is given in the book of Bryson and Ho.[15] Table 4 shows the parameters C_i together with the mean standard deviation and the average absolute deviation for the experimental variables. Even though the values of the standard deviations are higher than the uncertainties of each of the experimental measurements of P and y_1, the residuals of the fits are randomly distributed around zero, thus it can be concluded that the VLE data are consistent from the thermodynamic point of view.

A further consistency test may be done by comparing the present data with some results which previously appeared in

Table 5. Best Values of the Parameters C_i Fitting Equation 2, Standard Deviations σ, and Average Absolute Deviation $<\Delta>$ for the Different Variables at 333.15 K

	C_1	C_2	C_3	C_4	σ (G^E/J·mol^{-1}) $<\Delta(G^E/\mathrm{J\cdot mol^{-1}})>$	$10^3\cdot\sigma(y)$ $10^3\cdot<\Delta(y)>$	$10^2\cdot\sigma(P/\mathrm{kPa})$ $10^2\cdot<\Delta(P/\mathrm{kPa})>$
acetonitrile (3) + 1-chlorobutane (1)	3252.45	73.36	223.12	−121.64	6	5	2
					5	3	2
ethanol (2) + 1-chlorobutane (1)	4548.75	−524.25	533.81	−354.48	4	2	6
					3	2	5
ethanol (2) + acetonitrile (3)	2890.79	259.60	258.09	742.11	11	8	6
					9	6	4

the literature. Khurma et al. have reported VLE data for 1-chlorobutane + acetonitrile at (298.15, 348.15, and 398.15) K.[16] The vapor pressure of the 1-chlorobutane + ethanol system has been reported by Martínez et al. in the (278.15 to 323.15) K range.[17] Finally, G^E values for the acetonitrile + 1-chlorobutane system at 298.15 K were reported by Fernández-Piérola and Horta from light-scattering experiments.[18] In Figure 2, we compare the values of G^E ($x_1 = 0.5$) obtained in the different laboratories. Also, the experimental excess enthalpies of Pérez et al. for 1-chlorobutane + ethanol are plotted to test the consistency with the temperature dependence of G^E.[19] It can be observed that the present results are consistent with those reported in the literature at other temperatures and that only the result of Fernandez-Pierola and Horta[17] is well outside the trend of the other data for the acetonitrile (3) + 1-chlorobutane (1) system. It must be remarked that the results for this system indicate that H^E shows a negligible change with T and the system 1-chlorobutane (1) + ethanol (2) presents a noticeable curvature in the G^E/T vs $1/T$ plot, thus indicating a temperature dependence of the excess enthalpy.

Comparison with the Predictions of a Lattice-Fluid Model. In this work, we have tested the ability of the lattice-fluid model developed by Panayiotou and Sanchez for hydrogen-bonded mixtures to fit the experimental G^E vs x_1 curves, as well as its capacity to predict other excess properties.[20] The model leads to the following equation of state

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}\left(1 - \frac{1}{\bar{r}}\right)\right] = 0 \qquad (4)$$

where the reduced pressure, $\tilde{P}$, temperature, $\tilde{T}$, and density, $\tilde{\rho}$, are defined by: $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{\rho} = \rho/\rho^*$. $P^* = \varepsilon^*/V^*$, $T^* = \varepsilon^*/R$, and $\rho^* = 1/V^*$ are substance dependent parameters that define the van der Waals type interaction between molecules (ε^*) and their size (V^*). Each molecule is assumed to be formed by an effective number of segments $\bar{r}$, defined by

$$\frac{1}{\bar{r}} = \frac{1}{r} - \nu_H \qquad (5)$$

where ν_H is the fraction of hydrogen bonds in the system and r is the average number of segments per molecule. For ethanol, we have assumed that the molecules have $d = 1$ donor groups and $a = 1$ acceptor group. We have assumed that in the mixtures with ethanol the acetonitrile molecule has $a = 1$ so that hydrogen bonds can be formed with the hydroxyl group of the alcohol. The model leads to the following equation for the fraction of hydrogen bonds

$$r\cdot\nu_H = \frac{1}{2}\{d + a - [D_{ij}(D_{ij} + 2(d+a))^2]^{1/2}\} \qquad (6)$$

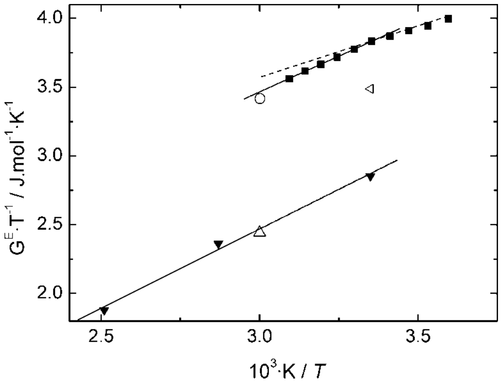

Figure 2. Temperature dependence of the G^E data for $x_1 = 0.5$. The symbols correspond to experimental results: acetonitrile + 1-chlorobutane, ▼, from Khurma et al.;[15] open triangle pointing left, from Fernández-Piérola and Horta;[17] △, this work; 1-chlorobutane + ethanol, ■, from Martinez et al.[16] Circles, ○, correspond to the data measured in the present work. The slope of the dashed straight line corresponds to the experimental H^E value of Thacker and Rowlinson at 298.15 K.[22]

Table 6. Parameters of the Lattice-Fluid Theory for the Pure Components

	P^*/MPa	T^*/K	ρ^*/kg·mol^{-1}	r
acetonitrile	455.2	574.5	866.9	4.51
1-chlorobutane	413.7	509.8	1006.0	8.98
ethanol[a]	380.7	483.1	897.5	4.86

[a] The parameters for the hydrogen bonds: $E° = -25.1$ kJ·mol^{-1}; $S° = -26.5$ kJ·mol^{-1}·K^{-1}; $V° = -5.6\cdot10^{-6}$ m^3·mol^{-1}.

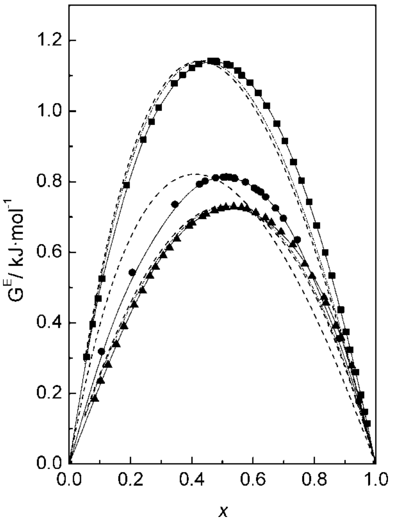

Figure 3. Composition dependence of the excess Gibbs energy at 333.15 K for the three systems studied. The symbols correspond to experimental data: ■, ethanol (2) + 1-chlorobunate (1); ●, acetonitrile (3) + 1-chlorobutane (1); ▲, ethanol (2) + acetonitrile (3). The continuous curves are the fits to the Padé approximants, eq 2. The dashed curves correspond to the fits to the lattice-gas theory with $\zeta_{12} = 0$, and the dashed-dotted lines correspond to $\zeta_{12} \neq 0$. In the case of the acetonitrile (3) + 1-chlorobutane (1) system, the theory used does not include hydrogen bond contributions. X represents the mole fraction of the first component written for each binary mixture in the liquid phase.

Table 7. Experimental and Predicted Values for the Different Excess Functions for the Composition Corresponding to the Maximum of the Experimental G^E Curves[a]

	ξ	x_{max}	$G^E{}_{exptl}$	$G^E{}_{calcd}$	$H^E{}_{exptl}$	$H^E{}_{calcd}$
acetonitrile (3) + 1-chlorobutane (1)	0.918	0.5116	813.64	799	1152[16]	1431
ethanol (2) + 1-chlorobutane (1)	0.882	0.4822	1138.70	1128	702[19]	1954
ethanol (2) + acetonitrile (3)	0.916	0.5367	728.79	730	1505[22]	1147

[a] ξ_{12} is the binary energy parameter of the lattice-fluid theory that best fits the experimental G^E curves.

with $D_{ij} = (r/\tilde{\rho}) \exp(G^0_{ij}/RT)$ and $G^0_{ij} = E^0_{ij} - TS^0_{ij} + PV^0_{ij}$ where the E^0_{ij}, S^0_{ij}, and V^0_{ij} are the energy, entropy, and volume characteristic of the formation of a hydrogen bond between molecules i and j. We have used for these parameters the same values given by ref 20. The pure component parameters P^*, T^*, and V^* have been obtained from the fit of the density, the isothermal compressibility κ_T, and the isobaric expansivity α_P according to the equation of state and the following two ancillary equations

$$\tilde{P} = \frac{P \cdot \kappa_T \cdot \tilde{\rho}^2}{T \cdot \alpha_P - P \cdot \kappa_T}$$

$$\tilde{T} = (1 - \tilde{\rho})\left[2 + \frac{1 - \kappa_T\left(\frac{RT}{V}\right)}{T \cdot \alpha_P - P \cdot \kappa_T}\right] \tag{7}$$

The values of P^*, T^*, and V^* are given in Table 5, together with the E^0, S^0, and V^0 values which have been taken equal for all the molecules studied.[20,21]

For the mixtures, it is necessary to make use of mixing rules to relate the interaction of unlike segments with those of the like ones. We have assumed one-fluid mixing rules

$$\varepsilon^* = \sum_i \sum_j \phi_i \phi_j \varepsilon^*_{ij}; \qquad \varepsilon^*_{ij(j \neq i)} = \xi_{ij}\sqrt{\varepsilon^*_{ii}\varepsilon^*_{jj}} \tag{8a}$$

$$V^* = \sum_i \sum_j V^*_{ij}; \qquad V^*_{ij(j \neq i)} = \xi_{ij}\sqrt{V^*_{ii}V^*_{jj}} \tag{8b}$$

where ϕ_i is the segment fraction of component i. Also, self- and cross-association in the case of ethanol (2) + acetonitrile (3) has been taken into account, which leads to the following system of coupled equations[20]

$$v_{ij}C_{ij} = r\left(\frac{N^i_d}{rN} - \sum_{k=i}^{n} v_{ik}\right)\left(\frac{N^i_a}{rN}\sum_{k=j}^{m} v_{kj}\right) \tag{9}$$

ξ_{ij} takes into account the difference of the strength of the binary interactions with respect to geometric mean of the interaction strengths between like molecules. ζ_{ij} takes into account the change in the core volume (V^*) in the mixture with respect to a linear combination of the pure component values. The corresponding expressions for the excess functions G^E, H^E, and V^E can be derived from eqs 3 to 6 following standard thermodynamic methods.[21] The binary parameters ξ_{ij} and ζ_{ij} were fitted to G^E curves and are given in Table 7.

Figure 3 shows the best fits of the G^E vs x_1 curves using the lattice-fluid theory. Although the fit for ethanol (2) + acetonitrile (3) is satisfactory, for ethanol (2) + 1-chlorobutane (1), the symmetry of the curve is not well reproduced. As can be observed, there is no significant difference in considering ζ_{12} null or not. No hydrogen-bond interactions are considered in acetonitrile (3) + 1-chlorobutane (1), and the theory leads to an unsymmetrical G^E curve, which does not agree with the experiment. A more rigorous test of the theory is to test its ability to predict other excess functions using the same ξ_{12} parameter. Table 7 compares the predicted and experimental values for the composition that corresponds to the maximum of each of the G^E curves. In the most favorable case, the ethanol (2) + acetonitrile (3) system, the difference between the experimental and predicted excess enthalpy amounts to 23 %, while for ethanol (2) + 1-chlorobutane (1), the prediction is almost 3-fold the value calculated from the temperature dependence of G^E. These conclusions are independent of whether ζ_{12} is fitted or kept equal to zero. The predictions are even poorer for the excess volume, where very high values of V^E (between five and seven times the experimental values) are predicted. It is somewhat surprising that the predictions for the acetonitrile (3) + 1-chlorobutane (2) system (for which no hydrogen bonds exist) are equally unsatisfactory to those for the systems with ethanol.

Conclusions

The vapor−liquid equilibrium of the systems acetonitrile (3) + 1-chlorobutane (1), ethanol (2) + 1-chlorobutane (1), and ethanol (2) + acetonitrile (3) has been studied at 333.15 K. The data have been found to be thermodynamically consistent, and they compare well with others found in the literature at other temperatures. The three systems are highly nonideal. A lattice-fluid theory has been found to be able to fit reasonably well the composition dependence of G^E, but the predictions of other excess functions, H^E and V^E, are rather unsatisfactory.

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