J. Chem. Eng. Data **2006,** *51,* 1473−1478

Density, Viscosity, Vapor−Liquid Equilibrium, Excess Molar Volume, Viscosity Deviation, and Their Correlations for the Chloroform + 2-Butanone Binary System

René A. Clará, Ana C. Gómez Marigliano, and Horacio N. Sólimo*

Departamento de Física, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán,
Avenida Independencia 1800, 4000 San Miguel de Tucumán, Argentina

Density and viscosity measurements for pure trichloromethane and 2-butanone as well as for trichloromethane (1) + 2-butanone (2) were made at (283.15, 293.15, 303.15, and 313.15) K over the whole concentration range. The experimental results were fitted to empirical equations, which permit the calculation of these properties in the whole concentration range and in the studied range of temperatures. The calculated values are in good agreement with the experimental ones. Data of the binary mixture were further used to calculate the excess molar volume and viscosity deviation. Vapor−liquid equilibrium (VLE) at $T = 303.15$ K for this binary system was also measured in order to calculate the activity coefficients and the excess molar Gibbs function. This binary system shows negative deviations from ideal behavior and forms a minimum pressure azeotrope at $x_1 = 0.199$ and $p = 15.3$ kPa. The excess or deviation properties were fitted by the Redlich−Kister polynomial relation to obtain their coefficients and standard deviations.

Introduction

Properties such as density and viscosity of pure chemicals and of their binary liquid mixtures over the whole composition range measured at several temperatures, are useful for a full understanding of their thermodynamic and transport properties as well as for practical chemical engineering purposes. On the other hand, excess thermodynamic functions and deviations of non-thermodynamic ones of binary liquid mixtures are fundamental for understanding of the interactions between molecules in these types of mixtures, particularly when polar components are involved. These functions have also been used as a qualitative and quantitative guide to predict the extent of complex formation in this kind of mixtures.[1−3]

In this paper we report density ρ and viscosity η data for pure trichloromethane (also called chloroform) and 2-butanone as well as for the binary system constituted by these two chemicals in the whole mole fraction range at temperatures of (283.15, 293.15, 303.15, and 313.15) K. Vapor−liquid equilibrium (VLE) data are also reported at $T = 303.15$ K. From these experimental results, excess molar volume V^{E}, viscosity deviation from the ideal behavior $\Delta\eta$, activity coefficients γ_i, and excess molar Gibbs function G^{E} were calculated.

Empiric equations for the density and viscosity of pure components as a function of the temperature as well as for the binary system as a function of temperature and composition were applied. These equations are useful for interpolation within the studied temperature range. On the other hand, the excess thermodynamic properties and non-thermodynamic ones were fitted to a Redlich−Kister-type equation using least squares to obtain their dependencies on concentration and temperature.[4]

Isobaric VLE data at atmospheric pressure have been previously measured for this binary system,[5] whereas isothermal data at temperatures of (318.15 and 328.15) K have been reported by Ohta et al.[6] together with heats of mixing at $T = 308.15$ K. Furthermore, Camero et al.[7] reported $P-x$ data for VLE at $T = 303.15$ K. However, as far as we know, no other property is available in the literature for this binary system.

Experimental Section

Materials. Chloroform (analytical reagent) and 2-butanone (analytical reagent) were supplied by Sintorgan (Argentina). They were used as received because no impurity was detected by gas chromatography using a HP 6890 gas chromatograph with a FID detector, showing that their mole fractions were higher than 0.998. The pure components were stored over 0.3 nm molecular sieves to prevent water absorption, and their water content was periodically checked by Karl Fischer titration using an automatic Mettler DL18 Karl Fischer titrator.

Apparatus and Procedure. Liquid mixtures were prepared by mass in airtight stoppered bottles, keeping in mind the vapor pressures of the components when establishing the filling sequence. Each mixture was immediately used after it was well-mixed by shaking. All the weighings were preformed on an electronic balance (Mettler Toledo AG-245) accurate to 0.1 mg. The uncertainty in the mole fractions is estimated to be lower than $\pm 1 \times 10^{-4}$.

Density and viscosity were measured with a vibrating-tube densimeter KEM DA-300 (using degassed bidistilled water and dry air as calibrating substances) and a Schott-Geräte AVS 400 viscometer with appropriate Ubbelohde capillary viscometers calibrated by the manufacturer, respectively. The uncertainties were ± 0.1 kg·m^{-3} for density and ± 0.001 mPa·s for viscosity. A Schott CT 1450 thermostatically controlled water bath, uncertain by ± 0.01 K, was used for viscosity measurements.

An equilibrium still, which was described by Boublik and Benson,[8] was used to obtain isothermal vapor−liquid equilibrium data. The equilibrium temperatures were measured with a Hart Scientific 1502A platinum resistance thermometer (certified

---

* Corresponding author. E-mail: hsolimo@herrera.unt.edu.ar.

10.1021/je060150a CCC: $33.50

Table 1. Density (ρ), Refractive Index (n_D), and Viscosity (η) Values of Pure Components at Several Temperatures and Saturated Vapor Pressure (P_i^{sat}) Values at T = 303.15 K

	ρ/kg·m^{-3}		n_D		η/mPa·s		P_i^{sat}/kPa	
T/K	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
				Chloroform				
283.15	1507.3		1.45189		0.629			
293.15	1488.4	1489.11[a]	1.44589	1.4459[a]	0.573			
303.15	1469.4	1470.60[a]	1.43987		0.516	0.514[a]	32.19	32.395[b]
313.15	1450.0		1.43386		0.468			
				2-Butanone				
283.15	815.9		1.38400		0.472			
293.15	805.5	804.9[a]	1.37888	1.3788[a]	0.423	0.399[a]		
303.15	795.1	794.6[a]	1.37383		0.382	0.366[a]	15.74	15.324[b]
313.15	784.3		1.36856		0.347			

[a] From ref 9. [b] From ref 7.

Table 2. Experimental Density (ρ) and Viscosity (η) Values at Several Temperatures for the [Chloroform (1) + 2-Butanone (2)] Binary System

	ρ/kg·m^{-3}				η/mPa·s			
x_1[a]	283.15	293.15	303.15	313.15	283.15	293.15	303.15	313.15
0.0000	815.9	805.5	795.1	784.3	0.472	0.423	0.382	0.347
0.0906	872.7	861.7	850.7	839.3	0.528	0.475	0.419	0.385
0.1806	930.4	918.7	907.1	895.1	0.588	0.526	0.468	0.420
0.2720	990.2	977.9	965.6	952.9	0.627	0.556	0.499	0.451
0.3661	1053.3	1040.2	1027.2	1013.7	0.660	0.594	0.530	0.477
0.4551	1113.9	1100.2	1086.4	1072.3	0.692	0.620	0.553	0.498
0.5490	1179.5	1165.0	1150.5	1135.5	0.711	0.633	0.565	0.510
0.6330	1238.9	1223.7	1208.5	1192.7	0.712	0.636	0.571	0.515
0.7035	1289.3	1273.6	1257.7	1241.3	0.717	0.631	0.566	0.513
0.7973	1357.5	1340.7	1323.9	1306.6	0.701	0.630	0.566	0.510
0.9068	1437.7	1419.8	1401.8	1383.4	0.674	0.610	0.546	0.491
1.0000	1507.3	1488.4	1469.4	1450.0	0.629	0.573	0.516	0.468

[a] Mole fraction of chloroform.

by the National Institute of Standards and Technology; NIST) with an imprecision of ± 0.007 K. All temperatures are reported in terms of ITS-90, whereas total pressures in the still were measured with an Edwards pressure transducer, Datametrics Controller 1501B, attached through a vacuum line with a precision of 13 Pa. Compositions of both conjugated phases were determined by density measurements at 303.15 K. The uncertainty in mole fractions is estimated to be lower than $\pm 1 \times 10^{-3}$, with a confidence uncertainty of 99.5 %.

Results and Discussion

Experimental results for refractive index, density, and viscosity of pure compounds at several temperatures and saturated vapor pressures at T = 303.15 K are summarized in Table 1. For comparison, existing values found in the literature are also included.[9]

From experimental results reported in Table 1, we conclude that the viscosity of the pure components does not have a linear behavior with temperature, while density has a linear plot.

Experimental results of density and viscosity corresponding to temperatures in the range (283.15 to 313.15) K for the system [chloroform (1) + 2-butanone (2)] are listed in Table 2.

To obtain empirical correlations for pure compounds with temperature, the following functional relationships for density and viscosity were used:

$$\rho = a_1 + b_1 \times (T/\mathrm{K}) \tag{1}$$

$$\eta = a_2 + b_2 \times (T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{2}$$

where a_1, b_1, a_2, b_2, and c_2 are constants. These equations were fitted using least squares with all points equally weighted, which allows evaluation of all constants. The appropriate number of significant digits was selected taking into account the experimental error previously reported for density, viscosity, and temperature. These values of the constants and their standard deviations are collected in Table 3.

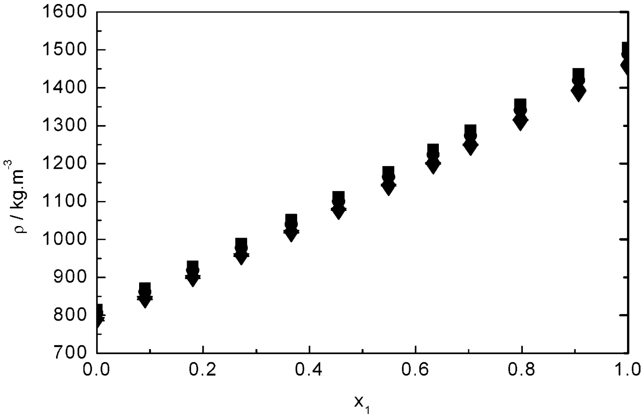

Figure 1. Density against x_1 for [chloroform (1) + 2-butanone (2)]: ■, T = 283.15 K; ●, T = 293.15 K; ▲, T = 303.15 K; ▼, T = 313.15 K.

Table 3. Coefficients and Standard Deviations of Equations 1 and 2

	ρ/kg·m^{-3}			η/mPa·s			
compound	a_1	b_1	σ/kg·m^{-3}	a_2	$10^3 b_2$	$10^5 c_2$	σ/mPa·s
chloroform	2047.7	−1.909	0.2	3.929	−17.32	2	2×10^{-3}
2-butanone	1113.7	−1.052	0.2	4.749	−25.02	3.5	1×10^{-3}

Polynomial equations were used to correlate the same properties for the [x_1 chloroform + $(1 - x_1)$ 2-butanone] binary system, as follows:

$$\rho/\mathrm{kg{\cdot}m^{-3}}(x_1, T) = a_1(T/\mathrm{K}) + b_1(T/\mathrm{K}) \times x_1 + c_1(T/\mathrm{K}) \times x_1^2 \tag{3}$$

$$\eta/\mathrm{mPa{\cdot}s}(x_1, T) = a_2(T/\mathrm{K}) + b_2(T/\mathrm{K}) \times x_1 + c_2(T/\mathrm{K}) \times x_1^2 \tag{4}$$

where a_i, b_i, and c_i are parameters; T is the temperature; and x_1 is the mole fraction of chloroform.

To obtain their respective dependences on composition, density, or viscosity of the mixture, these values were plotted against the mole fraction of chloroform at each temperature, as shown in Figure 1 for the density of [x_1 chloroform + $(1 - x_1)$ 2-butanone], which was taken as an example to indicate the calculation methodology. Equations 3 and 4 were fitted using a nonlinear regression method based on the Levenberg−Marquardt algorithm.[10] This fit shows quadratic behavior for the two studied properties with composition.

Then, the parameters of eq 3 obtained from this fit were plotted against temperature, as can be seen in Figure 2. In this way, the dependence with temperature and composition of each property was obtained. The appropriate number of significant digits was selected taking into account the experimental error previously reported for density, viscosity, and temperature. The plot for viscosity is not presented here because the methodology is the same.

Equations 5 and 6 (included in Table 4) make it possible to predict the density and viscosity of the binary system at any composition and temperature in the temperature range (283.15 to 313.15) K, respectively, within its respective standard deviation σ. Values calculated with these equations compare well with experimental data, and the standard deviations are similar to those obtained in previous works.[11,12]

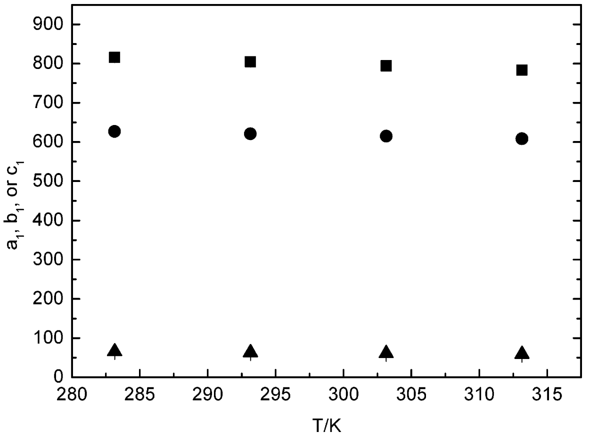

Figure 2. Constants ■, $a_i(T/\text{K})$; ●, $b_i(T/\text{K})$; and ▲, $c_i(T/\text{K})$ in eq 3 against temperature for [chloroform (1) + 2-butanone (2)]. Units: $a_i(T/\text{K})$, kg·m^{-3}; $b_i(T/\text{K})$, kg·m^{-3}·K^{-1}; and $c_i(T/\text{K})$, kg·m^{-3}·K^{-2}.

On the other hand, the excess molar volume V^E, viscosity deviation $\Delta\eta$, and excess molar Gibbs function G^E were calculated using the following equations:

$$V^E/\text{m}^3\cdot\text{mol}^{-1} = [(x_1M_1 + (1-x_1)M_2)/\rho] - \left(x_1\frac{M_1}{\rho_1} + x_2\frac{M_2}{\rho_2}\right) \quad (7)$$

$$\Delta\eta/\text{mPa}\cdot\text{s} = \eta - \exp[x_1 \ln \eta_1 + (1 - x_1) \ln \eta_2] \quad (8)$$

$$G^E/\text{J}\cdot\text{mol}^{-1} = RT[x_1 \ln \gamma_1 + (1 - x_1) \ln \gamma_2] \quad (9)$$

where x_1 is the mole fraction of chloroform; M_1 and M_2 are the molar masses of chloroform and 2-butanone; ρ and η are the density and viscosity of the mixture; ρ_1, ρ_2, η_1, and η_2 are the densities and viscosities of the pure components; whereas γ_1 and γ_2 are activity coefficients of chloroform and 2-butanone, which, in the liquid phase, are related to vapor−liquid equilibrium by

$$\gamma_i = \frac{y_iP}{x_iP_i^o} \quad (10)$$

Here, x_i and y_i are the mole fractions in the liquid and vapor phases of component i, while P and P_i are the total pressure and the pure component vapor pressure, respectively. In eq 10, the vapor phase is assumed to be an ideal gas, and the pressure dependence of the liquid-phase fugacity is neglected. This equation was selected to calculate activity coefficients because the low pressures observed in the present VLE data makes this simplification reasonable. Calculation without this simplification gave similar results, within the experimental error.

Table 5. Experimental Results for the Mole Fraction of Chloroform in the Liquid (x_1) and Vapor (y_1) Equilibrium Phases, Total Pressure (P), and Calculated Activity Coefficients (γ_i) for [Chloroform (1) + 2-Butanone (2)] at T = 303.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	15.74	0.317[a]	1.000
0.074	0.063	15.59	0.409	1.003
0.142	0.119	15.47	0.402	1.009
0.252	0.281	15.35	0.532	0.938
0.252	0.274	15.33	0.518	0.945
0.363	0.443	15.89	0.602	0.883
0.377	0.469	16.13	0.622	0.875
0.444	0.573	16.69	0.669	0.814
0.474	0.617	17.17	0.694	0.795
0.507	0.673	17.69	0.729	0.746
0.560	0.747	18.75	0.778	0.684
0.571	0.751	19.26	0.787	0.710
0.602	0.799	19.86	0.819	0.637
0.630	0.823	20.41	0.828	0.621
0.631	0.830	20.58	0.841	0.603
0.678	0.868	21.74	0.864	0.566
0.732	0.905	23.37	0.897	0.528
0.757	0.929	24.66	0.940	0.456
0.823	0.958	27.26	0.985	0.411
0.880	0.976	29.22	1.006	0.380
0.913	0.984	30.00	1.004	0.360
1.000	1.000	32.19	1.000	0.261[a]

[a] Extrapolated to infinite dilution.

The VLE data reported in Table 5 for [chloroform (1) + 2-butanone (2)] was found to be thermodynamically consistent according to the point-to-point test of Van Ness et al.,[13] as modified by Fredenslund et al.[14] Consistency criteria ($\Delta y \leq 0.01$) were met using a one-parameter Legendre polynomial, which reduces the expression for the excess Gibbs Function to

$$G^E = Ax_1x_2 \quad (11)$$

In this equation, A is the parameter in the Legendre polynomial, which is equal to −1.20975 for this binary system, while the average absolute deviations in vapor-phase mole fractions and pressure are $\Delta y = 0.005$ and $\Delta P = 0.27$ kPa. However, as stated by Fredenslund et al.,[14] a positive result of the consistency test for a first-order Legendre polynomial may be fortuitous.

The dependence of the excess Gibbs Function with mole fractions given by eq 11 is satisfied when the two components

Table 4. Equations for Density, Viscosity, Excess Molar Volume, Excess Molar Gibbs Function, and Viscosity Deviation as Functions of Temperature and Composition for [Chloroform (1) + 2-Butanone (2)]

Equations	***n°***	***σ***
$\rho/\text{kg}\cdot\text{m}^{-3}(x_1,T) = 1114.0 - 1.0544\times T/\text{K} + (800.8 - 0.6133\times T/\text{K})\times x_1 + (130.8 - 0.2308\times T/\text{K})\times x_1^2$	(5)	0.7/kg·m^{-3}
$\eta/\text{mPa}\cdot\text{s}(x_1,T) = 1.642 - 0.00416\times T/\text{K} + (3.101 - 0.0083\times T/\text{K})\times x_1 + (-2.422 - 0.00652\times T/\text{K})\times x_1^2$	(6)	0.008/mPa·s
$V^E/\text{m}^3\cdot\text{mol}^{-1} = x_1(1-x_1)\left\{\begin{matrix} 3.19\times10^{-6} - 1.383\times10^{-8}\times T/\text{K} + \begin{bmatrix} -1.552\times10^{-5} + 1.0847\times10^{-7}\times T/\text{K} - \\ -1.814\times10^{-10}\times(T/\text{K})^2 \end{bmatrix}(1-2x_1) + \\ + [4.6\times10^{-7} - 1.10\times10^{-9}\times T/\text{K}](1-2x_1)^2 \end{matrix}\right\}$	(15)	1×10^{-8}/m^3·mol^{-1}
$\Delta\eta/\text{mPa}\cdot\text{s} = x_1(1-x_1)\left\{11.0752 - 0.06366\times T/\text{K} + 9.441\times10^{-5}\times(T/\text{K})^2 + \begin{bmatrix} -7.99276 + 0.0523\times T/\text{K} - \\ -8.597\times10^{-5}\times(T/\text{K})^2 \end{bmatrix}(1-2x_1)\right\}$	(16)	0.003/mPa·s
$G^E/\text{J}\cdot\text{mol}^{-1} = x_1(1-x_1)[-3065 + 413(1-2x_1) - 618(1-2x_1)^2]$	(17)	20/J·mol^{-1}

of the binary system form a regular solution. In this case, the activity coefficients are given by[15]

$$RT \ln \gamma_1 = A{x_2}^2$$

$$RT \ln \gamma_2 = A{x_1}^2$$

To verify if this is, or not, fortuitous, plots of the logarithm of the activity coefficients against x_i^2 were made. Since these plots, not shown, display a nonlinear dependence, we conclude that this binary system cannot be considered as a regular solution. This behavior was expected since H^{E} is clearly greater than G^{E} (see Figure 6 and Ohta et al.[6]), and this corresponds to $S^{\mathrm{E}} < 0$ due to a volume change on mixing.

The excess molar volume, excess molar Gibbs function, and viscosity deviation were fitted by means of a Redlich−Kister-type equation[4] with the same above indicated fitting procedure:

$$Y^{\mathrm{E}} = x_1(1 - x_1)\sum_{j=0}^{n} a_j(1 - 2x_1)^j \qquad (12)$$

where Y^{E} represents either V^{E}, G^{E}, or $\Delta\eta$.

Since the coefficients a_j are functions of the temperature, they were plotted against this variable in order to obtain equations that represent each property in the studied temperature range. We propose the following dependence with temperature T for these coefficients:

$$a_j = \sum_{i=0}^{n} a_i \times T^i \qquad (13)$$

Using this temperature dependence, eq 12 can be rewritten as follows:

$$Y^{\mathrm{E}} = x_1(1 - x_1)\sum_{j=0}^{n}\sum_{i=0}^{m} a_{ji}T^i(1 - 2x_1)^j \qquad (14)$$

The equations arising of this fit are also summarized in Table 4 (reported as eqs 15, 16, and 17, respectively), together with their standard deviations σ, defined as

$$\sigma = [\sum (Y^{E}_{\mathrm{exp}} - Y^{\mathrm{E}}_{\mathrm{calc}})^2/(N - p)]^{1/2} \qquad (18)$$

where N and p are the numbers of experimental points and parameters, respectively. The choice of the appropriate number of constants in eq 14 was based on the variation with n and m of the standard error of the estimated value. Their significant digits were determined taking into account each experimental error.

Figures 3 and 4 show the excess molar volume and viscosity deviation, plotted against the mole fraction of chloroform for [chloroform (1) + 2-butanone (2)] at several temperatures, while Figure 5 shows a similar plot for the excess molar Gibbs function at T = 303.15 K. The total pressure P, liquid-phase x_1, and vapor-phase y_1 mole fraction measurements at T = 303.15 K are reported in Table 5 and plotted in Figure 6.

Figure 7 shows the logarithm of the activity coefficients against the mole fraction of chloroform for [chloroform (1) + 2-butanone (2)] at T= 303.15 K. The lines in Figure 7 were obtained with a nonlinear regression fit, which produces the following equations for the activity coefficients at infinite dilution of both components:

$$\gamma_{1\infty} = \lim_{x_1 \to 0} \exp(\ln \gamma_1) = \lim_{x_1 \to 0} \exp(-1.150 + 2.158 \times x_1 - 0.982 \times {x_1}^2) \qquad (19)$$

$$\gamma_{2\infty} = \lim_{x_1 \to 1} \exp(\ln \gamma_2) = \lim_{x_1 \to 1} \exp(-0.002 + 0.209 \times x_1 - 1.532 \times {x_1}^2) \qquad (20)$$

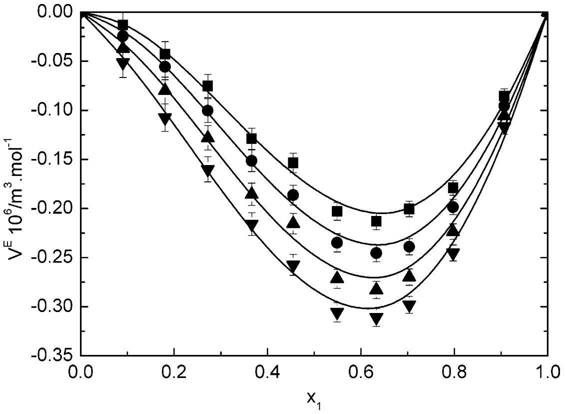

Figure 3. Excess molar volume for [chloroform (1) + 2-butanone (2)]: ■, T = 283.15 K; ●, T = 293.15 K; ▲, T = 303.15 K; ▼, T = 313.15 K. Solid lines correspond to the least-squares fit using eq 12.

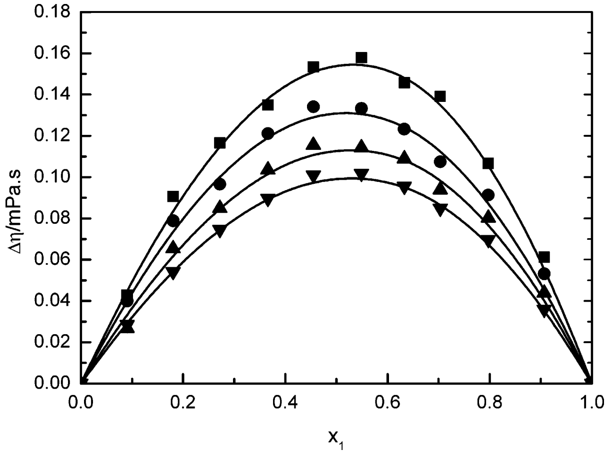

Figure 4. Viscosity deviation for [chloroform (1) + 2-butanone (2)]: ■, T = 283.15 K; ●, T = 293.15 K; ▲, T = 303.15 K; ▼, T = 313.15 K. Solid lines correspond to the least-squares fit using eq 12.

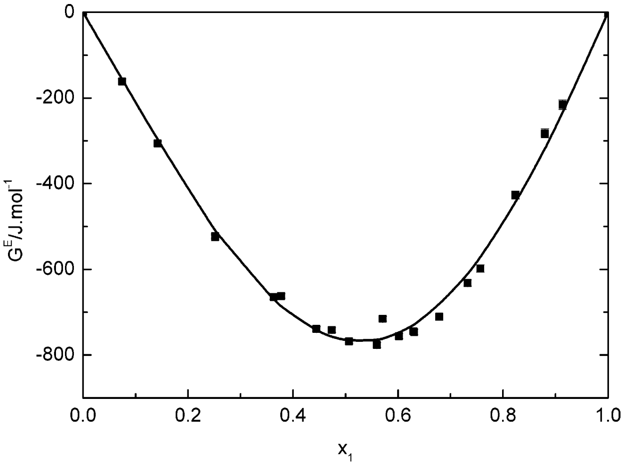

Figure 5. Excess molar Gibbs function for [chloroform (1) + 2-butanone (2)] at T = 303.15 K. Solid line corresponds to the least-squares fit using eq 12.

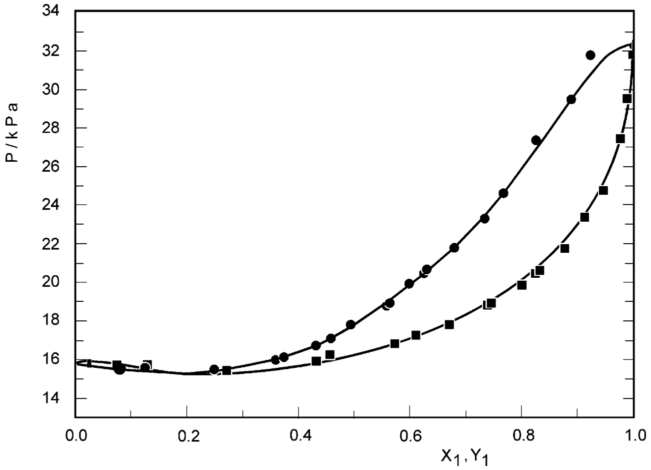

Figure 6. Total pressure P against liquid-phase mole fractions x_1 (●) or vapor phase mole fractions y_1 (■) for [chloroform (1) + 2-butanone (2)] at $T = 303.15$ K.

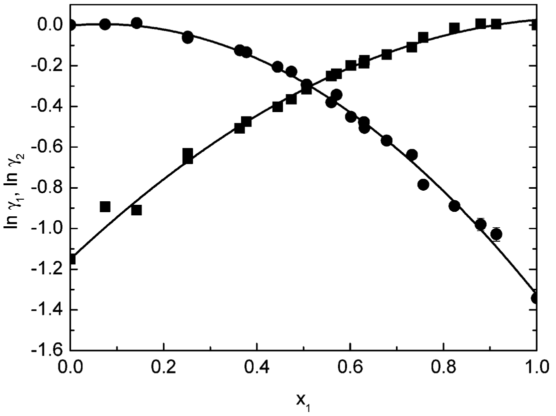

Figure 7. Logarithm of the activity coefficients γ_1 (■) and γ_2 (●) against x_1 for [chloroform (1) + 2-butanone (2)] at $T = 303.15$ K.

where $\gamma_{1\infty}$ and $\gamma_{2\infty}$ are the activity coefficients of chloroform and 2-butanone at infinite dilution, respectively, and x_1 is the mole fraction of chloroform. Equations 19 and 20 lead to the values 0.317 and 0.261 for $\gamma_{1\infty}$ and $\gamma_{2\infty}$, respectively.

Since, in the infinite dilution limit, solute−solute interactions disappear, the values of the infinite dilution activity coefficients provide a valuable way to analyze solute−solvent interactions. A larger value means that solute−solvent interactions are more important. Therefore, the values of the calculated infinite dilution activity coefficients reported above show that the interactions between 2-butanone (as solvent) and chloroform (as solute) are stronger than in the opposite situation, probably due to the higher polarity of 2-butanone ($\mu = 2.8$ D) than chloroform ($\mu = 1.15$ D).[9]

On the other hand, Figure 6 indicates that this binary system shows negative deviations from the ideal behavior and forms a minimum pressure azeotrope at $x_1 = 0.199$ and $p = 15.3$ kPa, as can also be seen from Figure 8, which is in agreement with the results reported by Camero et al.[7]

Figure 3 shows that the excess molar volumes are always negative for all the studied temperatures and for any composition. This would indicate that interactions between different molecules are stronger than interactions between molecules in the pure liquids and that associative forces dominate the behavior of the solution. Therefore, in this system, a compression in free volume is considered to occur, making the mixtures more compressible than the ideal mixture, which ultimately culminates into negative values of V^E. From this plot, we can also conclude

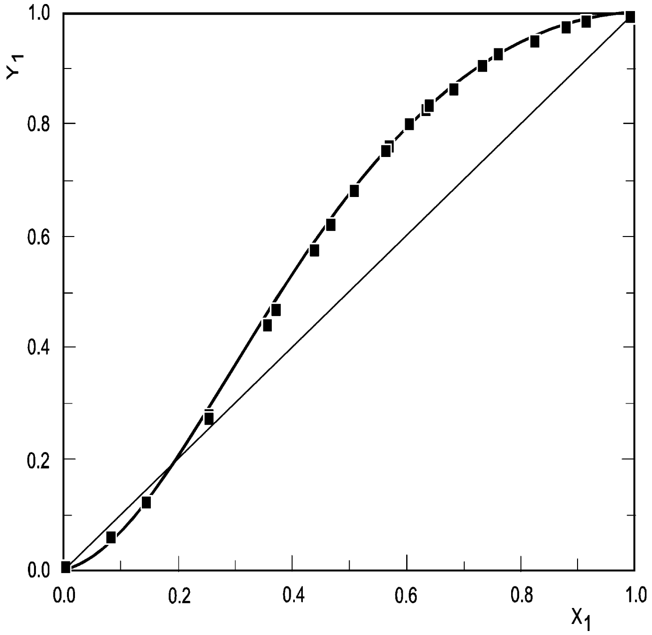

Figure 8. Vapor phase mole fractions y_1 against liquid-phase mole fractions x_1 for [chloroform (1) + 2-butanone (2)] at $T = 303.15$ K.

that increasing the temperature, the V^E values become more negative.

According to Kauzman and Eyring[16] the viscosity of a mixture strongly depends on the entropy of the mixture, which is related with the liquid's structure and enthalpy (and consequently with molecular interactions between the components of the mixture). Therefore, the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules. Vogel and Weiss[17] affirm that mixtures with strong interactions between different molecules ($H^E < 0$ and negative deviation from Raoult's law) present positive viscosity deviations; whereas, for mixtures with positive deviation of Raoult's law and without strong specific interactions, the viscosity deviations are negative. Then, viscosity deviations can be used to detect molecular interactions.

As can be seen in Figure 4, the viscosity deviations are positive for all studied temperatures over the whole composition range, which would correspond to binary systems that exhibit negative deviations from Raoult's law and an exothermic behavior[6] as this binary system. The sign of $\Delta\eta$ for this system is also in agreement with the conclusion reported by Fort and Moore,[18] who proposed that positive values of this property are characteristic of systems where association forces are predominating. As can be observed in Figure 4, increasing the temperature, the $\Delta\eta$ values become less positive due to the increase of the thermal energy, which diminishes the chloroform + 2-butanone heteroassociation in the mixture.

Literature Cited

(1) Battino, R. Volumes change on mixing for binary mixtures of liquids. *Chem. Rev.* **1971**, *71*, 5−45.
(2) Rowlinson, J. S. *Liquids and Liquid Mixtures*; Butterworth: London, 1969.
(3) Prigogine, I. *The Molecular Theory of Solutions*; North-Holland: Amsterdam, 1957.
(4) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solution. *Ind. Eng. Chem.* **1948**, *40*, 345−348.
(5) Krishnamurty, V. V. G.; Venkata Rao, C. Vapor−liquid equilibria: system chloroform−methyl ethyl ketone. *J. Sci. Ind. Res.* **1955**, *14B*, 55−62.

(6) Otha, T.; Asano, H.; Nagata, I. Thermodynamic study of complex formation in four binary liquid mixtures containing chloroform. *Fluid Phase Equilib.* **1980**, *4*, 105−114.
(7) Camero, C. G.; Bhethanabotla, V. R.; Campbell, S. W. Total pressure measurements for chloroform + acetone + 2-butanone at 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 210−213.
(8) Boublik, T.; Benson, G. C. Molar excess Gibbs free energies of benzene−*m*-xylene mixtures. *Can. J. Chem*. **1969**, *47*, 539−542.
(9) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
(10) Press: W. H.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes in C*, 2nd ed.; Cambridge University Press: 1992.
(11) Cases, A. M.; Gómez Marigliano, A. C.; Bonatti, C. M.; Sólimo, H. N. Density, viscosity, and refractive index of formamide, three carboxylic acids, and formamide + carboxylic acid binary mixtures. *J. Chem. Eng. Data* **2001**, *46*, 712−715.
(12) Cases, A. M.; Gómez Marigliano, A. C.; Sólimo, H. N. Excess molar volume, viscosity and refractive index deviations for mixtures of formamide + some carboxylic acids at several temperatures. *Phys. Chem. Liq.* **2003**, *41*, 503−508.
(13) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor−liquid equilibrium. Part I. An appraisal of data reduction methods. *AIChE J.* **1973**, *19*, 238−244.
(14) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Liquid−Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
(15) Prigogine, I.; Defay, R. *Chemical Thermodynamics*; Longmans: London, 1954.
(16) Kauzman, W.; Eyring, H. The viscous flow of large molecules. *J. Am. Chem. Soc.* **1940**, *62*, 3113−3125.
(17) Vogel, H.; Weiss, A. Transport properties of liquids. III. Viscosity of athermal liquid mixtures. *Ber. Bunsen-Ges*., *Phys. Chem*. **1982**, *86*, 193−198.
(18) Fort, R.; Moore, W. R. Viscosities of binary liquid mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−1119.

Received for review April 6, 2006. Accepted May 23, 2006. Financial support from the Consejo de Investigaciones de la Universidad Nacional de Tucumán of Argentina, Grant 26/E338, is gratefully acknowledged.

JE060150A