Density, Viscosity, Vapor−Liquid Equilibrium, and Excess Molar Enthalpy of [Chloroform + Methyl *tert*-Butyl Ether]

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Density and viscosity measurements in the $T = (273.15$ to $318.15)$ K range of pure chloroform and methyl *tert*-butyl ether (MTBE), as well as of the binary system [x_1 chloroform + $(1 - x_1)$ MTBE] over the whole concentration range at $T = 293.15$ K, were made. The experimental results for the pure components were fitted to empirical equations, which permit the calculation of these properties in the studied temperature range. Calculated values are in agreement with the experimental ones. Data of the binary mixture were further used to calculate the excess molar volume and viscosity deviations. The excess molar enthalpy at $T = (303 \pm 1)$ K and vapor−liquid equilibrium measurements at $T = (303.15 \pm 0.05)$ K were also measured for the binary system. These last experimental results were used to calculate activity coefficients, the excess molar Gibbs energy, and excess molar entropy. This binary system shows strong negative deviations from ideality and exhibits a minimum pressure azeotrope, whose coordinates are: $P = (26.30 \pm 0.05)$ kPa and $x_1 = (0.586 \pm 0.002)$. Excess or deviation properties were fitted to the Redlich−Kister polynomial relation to obtain their coefficients and standard deviations. The vapor pressure of pure MTBE over the $P = [(20.00$ to $97.20) \pm 0.05]$ kPa range was also measured.

Introduction

Properties such as density, viscosity, and vapor pressure of pure chemicals at several temperatures together with the study of several properties for the binary liquid mixture over the whole composition range, where these chemicals are included, 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 nonthermodynamic ones of binary liquid mixtures are fundamental to understand the interactions between molecules in this type of mixtures, particularly when polar components are involved.

In this paper we report density ρ and viscosity η data in the $T = [(273.15$ to $318.15) \pm 0.01]$ K range of pure chloroform and methyl *tert*-butyl ether (MTBE), as well as for the binary system constituted by these two chemicals in the whole mole fraction range at $T = (293.15 \pm 0.01)$ K. The excess enthalpy at $T = (303 \pm 1)$ K and vapor−liquid equilibrium (VLE) data at $T = (303.15 \pm 0.05)$ K for this binary system are also reported. The vapor pressure of MTBE over the $P = [(20.00$ to $97.20) \pm 0.05]$ kPa range was also measured and the Antoine's constants calculated. From the experimental result for the binary system, excess molar volume V^E, viscosity deviations from the ideal behavior $\Delta\eta$, activity coefficients γ_i, excess molar Gibbs energy G^E, and excess molar entropy TS^E were calculated.

Empirical equations for density and viscosity of both pure components as a function of temperature, as well as for the binary system as a function of composition, were deduced.

On the other hand, the excess thermodynamic properties and nonthermodynamic ones were fitted to a Redlich−Kister[1] type equation, using least-squares to obtain its respective dependency on concentration.

Although this binary system, as far as we know, does not have any technological interest, few experimental data can be found in the literature, which justify its study. Only isothermal vapor−liquid equilibrium data at 313.15 K together with excess molar volumes at 298.15 K, excess enthalpy data at 298.15 K, and excess molar volumes at 303.15 K were reported in the literature.[2−4]

Experimental Section

Materials. Chloroform (p.a.) and MTBE (p.a.) were supplied by Cicarelli (Argentina) and Riedel-de Haën (Germany), respectively. Chromatographic analysis of these commercial chemicals reveals that they had the following chemical purities (expressed in mass fraction): 0.998 and 0.995, respectively. A Hewlett-Packard 6890 gas chromatograph with an automatic injector (Agilent G2613A) directly connected to a ChemStation (HP G2070AA) with a flame ionization detector (FID) and a 30 m × 0.25 mm × 0.5 μm (length × inner diameter × thickness) capillary column (INNOWax, cross-linked polyethylene glycol, HP 19091N-233) was used for this purpose. The pure components were stored over 0.3 nm molecular sieves to prevent water absorption, and their water contents were periodically checked by Karl Fischer titration using an automatic Mettler DL18 Karl Fischer titrator. The water content never surpassed 80 ppm.

Apparatus and Procedure. The same methodology previously applied for the preparation of mixtures was used in this work.[5] All weighing was performed 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 $\pm 1 \cdot 10^{-4}$.

Density and viscosity were simultaneously measured with an Anton Paar Stabinger viscometer (SVM 3000/G2) calibrated

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Table 1. Density ρ and Viscosity η of Pure Compounds at Several Temperatures

	ρ/kg·m^{-3}		η/mPa·s	
T/K	exptl	lit.	exptl	lit.
		Chloroform		
273.15	1526.0		0.713	
283.15	1507.1	1507.3^{a}	0.651	0.629^{a}
293.15	1488.4	1489.11^{b} 1487.58^{c}	0.600	0.573^{a}
298.15	1478.8	1477.3^{d} 1479.70^{b}	0.576	0.5357^{b}
303.15	1469.2	1470.60^{b} 1469.4^{a}	0.552	0.516^{a} 0.514^{b}
313.15	1450.0	1440.7^{e} 1450.0^{a}	0.509	0.468^{a}
318.15	1440.0		0.491	
		MTBE		
273.15	760.4	761.34^{f}	0.390	
283.15	750.1	751.02^{f}	0.360	
293.15	739.9	740.65^{f} 738^{h}	0.333	0.3711^{g}
298.15	734.4	734.915^{i}	0.319	0.3560^{g}
303.15	729.2	730.1^{f}	0.304	0.3359^{g}
313.15	718.5	719.42^{f}	0.278	
318.15^{j}				

[a] From ref 5. [b] From ref 8. [c] From ref 9. [d] From ref 10. [e] From ref 11. [f] From ref 12. [g] From ref 13. [h] From ref 15. [i] From ref 14. [j] The density and viscosity of MTBE could not be measured at 318.15 K, because this temperature is close to its boiling temperature. Therefore, a significant amount of bubbles form inside the measuring cell.

Table 2. Saturated Vapor Pressure Data P_i^{sat} for Pure MTBE at Several Temperatures

T/K	P_i^{sat}/kPa	T/K	P_i^{sat}/kPa
286.50	20.00	315.30	65.00
291.30	25.00	317.40	70.00
295.50	30.00	319.30	75.00
299.20	35.00	321.10	80.00
302.50	40.00	322.90	85.00
305.45	45.00	324.50	90.00
308.20	50.00	325.40	92.50
310.80	55.00	326.20	95.00
313.10	60.00	326.90	97.20

Table 3. Experimental Density ρ and Viscosity η Data for the [x_1 Chloroform + (1 − x_1) MTBE] Binary System at (293.15 ± 0.01) K

x_1	ρ / kg·m^{-3}	η / mPa·s
0.0000	739.9	0.333
0.0527	768.1	0.358
0.0834	785.4	0.372
0.1841	842.6	0.423
0.2714	895.6	0.470
0.3580	951.5	0.514
0.4511	1015.0	0.560
0.5460	1083.8	0.595
0.6303	1148.9	0.612
0.7240	1225.9	0.620
0.8108	1302.9	0.618
0.8948	1381.1	0.613
0.9515	1437.9	0.609
1.0000	1488.4	0.600

by the manufacturer. This equipment is equipped with its own Peltier effect control system, which maintains the temperature at ± 0.01 K. The repeatability of the results, as provided by the manufacturer, is ± 0.1 % of the measured viscosity value, ± 0.1 kg·m^{-3} for density, and ± 0.005 K for temperature, but our uncertainties in this work were ± 0.3 % of the measured viscosity value, ± 0.1 kg·m^{-3} for density, and ± 0.01 K for temperature. The calibration of the apparatus was checked using standard oils provided by the manufacturer. At least three measurements were made at each temperature and for each solution or pure component. The experimental results reported in Tables 1 and 3 are average values.

Vapor pressure data were obtained with a commercial equipment (Labodest, model 602-S) available from Fischer Technology, Germany. This equipment recirculates both the liquid and the vapor phases and is suitable for the determination of either isobaric or isothermal VLE data. The equilibrium temperatures were measured with a digital temperature logging module tmg (Temperaturmesstechnik Geraberg GmbH, Germany), type DTM5080 with a Pt-100 temperature sensor, calibrated by the manufacturer with an accuracy of ± 0.02 K, whereas the total pressure in the still was measured with a precision pressure transmitter (Wika, model P-10) also calibrated by the manufacturer with an accuracy of 0.1 % of span, both connected to the Fischer VLE2+ vacuum and temperature control unit, as previously reported.[6] The observed uncertainties are ± 0.05 K for temperature and ± 0.05 kPa for pressure.

Compositions of both conjugated phases for VLE data were determined by density measurements using the above-mentioned equipment. The uncertainty in the mole fractions is estimated to be ± 0.001.

Excess enthalpy measurements at atmospheric pressure and at T = (303 ± 1) K of the binary system [x_1 chloroform + (1 − x_1) MTBE] were performed using an adiabatic calorimeter previously described and using the same methodology.[7] The uncertainty in the mole fraction is estimated to be lower than ± 0.001 while, for enthalpy of mixing measurements, it is estimated to be lower than 4 % of the measured value. The temperature inside the Dewar flask was measured with a Hart Scientific 1502A platinum resistance thermometer (certified by the National Institute of Standards and Technology, NIST) with an uncertainty of ± 0.01 K. Temperatures are reported in terms of ITS-90.

Results and Discussion

Experimental results of the density and viscosity of the pure compounds in the T = (273.15 to 318.15) K range are summarized in Table 1, along with those found in the literature for comparison,[5,8−15] while saturated vapor pressure data (P_i^{sat}) for MTBE in the T = [(286.50 to 326.90) ± 0.05] K range are listed in Table 2. Experimental results of density and viscosity for the [x_1 chloroform + (1 − x_1) MTBE] binary system in the whole composition range at (293.15 ± 0.01) K are listed in Table 3.

Polynomial equations were used to correlate the density and viscosity of pure components as a function of temperature, as follows:

$$\rho(T)/\text{kg}\cdot\text{m}^{-3} = a_1 + a_2(T/\text{K}) \tag{1}$$

$$\eta(T)/\text{mPa}\cdot\text{s} = b_1 + b_2(T/\text{K}) + b_3(T/\text{K})^2 \tag{2}$$

where a_i and b_i are parameters, while T is the Kelvin temperature and x_1 is the mole fraction of chloroform. These equations were selected because they were the ones that best fit our experimental results. Table 4 lists these equations with the corresponding parameter values together with their standard deviations σ for both pure components. These equations make it possible to estimate the density and viscosity of both pure components at any temperature in the T = (273.15 to 318.15) K range.

Table 4. Equations for Density and Viscosity as a Function of Temperature for Pure Components

equation	σ
Chloroform	
$\rho/\text{kg}\cdot\text{m}^{-3} = 1047.5 - 1.0503(T/\text{K})$	$0.3\ \text{kg}\cdot\text{m}^{-3}$
$\eta/\text{mPa}\cdot\text{s} = 4.491 - 0.02149(T/\text{K}) + 2.801\cdot 10^{-5}(T/\text{K})^2$	$2.10^{-3}\ \text{mPa}\cdot\text{s}$
MTBE	
$\rho/\text{kg}\cdot\text{m}^{-3} = 1047.5 - 1.0503(T/\text{K})$	$0.2\ \text{kg}\cdot\text{m}^{-3}$
$\eta/\text{mPa}\cdot\text{s} = 1.154 - 0.0028(T/\text{K})$	$1.10^{-3}\ \text{mPa}\cdot\text{s}$

Table 5. Equations for Density, Viscosity, Excess Molar Volume, and Viscosity Deviation Properties as a Function of Composition for the [x_1 Chloroform + (1 − x_1) MTBE] Binary System

equation	T/K	σ
$\rho/\text{kg}\cdot\text{m}^{-3} = 742.6 + 485.559\cdot x_1 + 256.657\cdot x_1^{\,2}$	293.15	$2\ \text{kg}\cdot\text{m}^{-3}$
$\eta/\text{mPa}\cdot\text{s} = 0.335 + 0.340\cdot x_1 + 1.07\cdot x_1^{\,2} - 1.98\cdot x_1^{\,3} + 0.83\cdot x_1^{\,4}$	293.15	$2\cdot 10^{-3}\ \text{mPa}\cdot\text{s}$
$V^{\text{E}}/\text{m}^3\cdot\text{mol}^{-1} = x_1(1 - x_1)[-3.2155\cdot 10^{-6} - 4.914\cdot 10^{-7}(1 - 2x_1)]$	293.15	$2\cdot 10^{-8}\ \text{m}^3\cdot\text{mol}^{-1}$
$\Delta\eta/\text{mPa}\cdot\text{s} = x_1(1 - x_1)[0.444 - 0.149(1 - 2x_1) - 0.19(1 - 2x_1)^2]$	293.15	$2\cdot 10^{-3}\ \text{mPa}\cdot\text{s}$
$G^{\text{E}}/\text{J}\cdot\text{mol}^{-1} = x_1(1 - x_1)[-2970 + 300(1 - 2x_1) + 700(1 - 2x_1)^2]$	303.15	$10\ \text{J}\cdot\text{mol}^{-1}$
$H^{\text{E}}/\text{J}\cdot\text{mol}^{-1} = x_1(1 - x_1)[-8500 - 1000(1 - 2x_1) - 400(1 - 2x_1)^2 - -1000(1 - 2x_1)^3]$	303.15	$70\ \text{J}\cdot\text{mol}^{-1}$

Equations 1 and 2 were fitted using a nonlinear regression method based on the Levenberg−Marquardt algorithm[16] with all points equally weighted, which allows evaluating all constants. The appropriate number of significant digits was selected, taking into account the experimental uncertainty above-reported for each measured property. Values calculated with these equations compare well with experimental data, within the experimental error.

From equations reported in Table 4, we conclude that the density of pure chloroform has a linear behavior with temperature, while its viscosity does not. Furthermore, both the density and the viscosity of MTBE have a linear behavior with temperature.

Polynomial equations were also used to correlate the same properties as a function of mole fraction for the [x_1 chloroform + (1 − x_1) MTBE] binary system, as follows:

$$\rho/\text{kg}\cdot\text{m}^{-3} = c_1 + c_2\cdot x_1 + c_3\cdot x_1^{\,2} \qquad (3)$$

$$\eta/\text{mPa}\cdot\text{s} = d_1 + d_2\cdot x_1 + d_3\cdot x_1^{\,2} + d_4\cdot x_1^{\,3} + d_5\cdot x_1^{\,4} \qquad (4)$$

where c_i and d_i are parameters and x_1 is the mole fraction of chloroform. Equations 3 and 4 were fitted using the same nonlinear regression methodology used for pure components.[16] The resulting equations for the density and viscosity of this binary system are collected in Table 5 together with their standard deviations σ.

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

$$V^{\text{E}}/\text{m}^3\cdot\text{mol}^{-1} = [(x_1M_1 + (1 - x_1)M_2)/\rho] - [x_1(M_1/\rho_1) + x_2(M_2/\rho_2)] \qquad (5)$$

$$\Delta\eta/\text{mPa}\cdot\text{s} = \eta - [x_1\eta_1 + (1 - x_1)\eta_2] \qquad (6)$$

$$G^{\text{E}} = RT[x_1 \ln \gamma_1 + (1 - x_1) \ln \gamma_2] \qquad (7)$$

$$TS^{\text{E}} = H^{\text{E}} - G^{\text{E}} \qquad (8)$$

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

$$\ln \gamma_i = \ln(y_iP/x_iP_i^{\text{o}}) + [(B_{ii} - V_i)(P - P_i^{\text{o}})]/RT + (1 - y_i)^2(P\delta/RT) \qquad (9)$$

Here, y_i is the mole fraction of component i in the vapor phase, P and P_i^{o} are the total pressure and the pure component vapor pressure, respectively, and V_i is the molar volume of component i. The value of δ is given by

$$\delta = 2B_{12} - B_{11} - B_{22} \qquad (10)$$

Table 6. 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 the [x_1 Chloroform + (1 − x_1) MTBE] Binary System at $T = (303.15 \pm 0.05)$ K

x_1	y_1	$\frac{P}{\text{kPa}}$	γ_1	γ_2	$\frac{PG^E}{\text{J}\cdot\text{mol}^{-1}}$
0.000	0.000	41.00			
0.057	0.019	38.80	0.39	1.01	−110
0.082	0.026	38.35	0.37	1.02	−170
0.106	0.034	37.85	0.37	1.02	−220
0.119	0.039	37.40	0.37	1.02	−250
0.131	0.046	37.00	0.39	1.02	−270
0.150	0.056	36.45	0.41	1.01	−300
0.164	0.062	36.00	0.41	1.01	−340
0.174	0.069	35.50	0.43	1.00	−360
0.194	0.080	35.00	0.44	1.00	−400
0.196	0.079	34.95	0.43	1.00	−410
0.207	0.087	34.70	0.44	1.00	−420
0.225	0.098	34.10	0.45	0.99	−450
0.230	0.105	33.70	0.47	0.98	−470
0.253	0.117	33.50	0.47	0.99	−490
0.256	0.126	33.10	0.50	0.97	−490
0.275	0.138	32.80	0.50	0.98	−510
0.283	0.140	32.40	0.49	0.97	−550
0.297	0.155	32.05	0.51	0.97	−550
0.317	0.183	30.95	0.55	0.93	−600
0.338	0.210	30.30	0.58	0.90	−620
0.363	0.240	29.60	0.60	0.89	−650
0.381	0.262	29.10	0.62	0.87	−670
0.413	0.306	28.30	0.65	0.84	−700
0.434	0.335	27.80	0.66	0.82	−720
0.456	0.370	27.40	0.69	0.80	−730
0.471	0.396	27.10	0.71	0.78	−740
0.492	0.429	26.85	0.73	0.76	−740
0.513	0.463	26.55	0.74	0.74	−750
0.532	0.496	26.40	0.76	0.71	−750
0.540	0.511	26.35	0.77	0.70	−750
0.552	0.531	26.25	0.78	0.69	−750
0.569	0.558	26.20	0.80	0.67	−740
0.583	0.582	26.20	0.81	0.66	−730
0.586	0.586	26.35	0.82	0.66	−720
0.601	0.610	26.35	0.83	0.64	−710
0.617	0.637	26.35	0.85	0.62	−700
0.626	0.652	26.40	0.86	0.61	−700
0.642	0.677	26.40	0.87	0.60	−690
0.669	0.716	26.70	0.89	0.57	−660
0.698	0.757	26.90	0.91	0.54	−630
0.731	0.801	27.40	0.93	0.50	−580
0.767	0.837	27.90	0.95	0.48	−520
0.797	0.868	28.35	0.96	0.46	−470
0.828	0.899	29.10	0.98	0.42	−400
0.857	0.922	29.60	0.99	0.40	−350
0.880	0.943	30.15	1.00	0.35	−300
0.909	0.961	30.90	1.02	0.33	−220
0.950	0.980	31.50	1.01	0.31	−120
1.000	1.000	32.20			

where B_{11} and B_{22} are the second virial coefficients of the pure components, while B_{12} is the second virial cross coefficient. These coefficients, estimated at $T = 303.15$ K by the Hayden and O'Connell method,[17] are: $B_{11} = -1141.176$, $B_{22} = -1365.587$, and $B_{12} = -1978.134$, all expressed in $\text{cm}^3\cdot\text{mol}^{-1}$.

The VLE data of the binary system [x_1 chloroform + (1 − x_1) MTBE] reported in Table 6 at $T = (303.15 \pm 0.05)$ K were found to be thermodynamically consistent according to the point-to-point Van Ness et al. test,[18] as modified by Fredenslund et al.,[19] since the average absolute deviation between y_i(exp) and y_i(calc) is: $\Delta y = 0.01$, while the average absolute deviation in pressure is: $\Delta P = 0.6$ kPa, using a one-parameter Legendre polynomial.

Table 7 lists the excess molar enthalpy H^E of the binary system [x_1 chloroform + (1 − x_1) MTBE] as a function of the mole fraction of chloroform at $T = (303 \pm 1)$ K.

Table 7. Experimental Results for the Molar Enthalpy H^E for the [x_1 Chloroform + (1 − x_1) MTBE] Binary System at $T = (303 \pm 1)$ K

x_1	$\frac{H^E}{\text{J}\cdot\text{mol}^{-1}}$	x_1	$\frac{H^E}{\text{J}\cdot\text{mol}^{-1}}$
0.000	0	0.390	−2100
0.038	−342	0.516	−2100
0.068	−664	0.669	−1800
0.097	−920	0.780	−1500
0.101	−1020	0.864	−800
0.118	−1100	0.899	−650
0.154	−1200	0.931	−480
0.172	−1300	0.958	−280
0.219	−1600	0.986	−150
0.251	−1900	1.000	0

The excess molar volume V^E, excess molar Gibbs energy G^E, excess molar enthalpy H^E, excess molar entropy TS^E, and viscosity deviation $\Delta\eta$ were fitted by means of a Redlich−Kister type eq 1 with the above-mentioned fitting procedure.

$$Y^E = x_1(1 - x_1)\sum_{j=0}^{n} a_j(1 - 2x_1)^j \tag{11}$$

where Y^E represents V^E, $\Delta\eta$, H^E, TS^E, or G^E.

The equations arising from this fit are also summarized in Table 5, together with the standard deviation σ, defined as:

$$\sigma = [\sum(Y^E_{\text{exp}} - Y^E_{\text{calc}})^2/(N - p)]^{1/2} \tag{12}$$

where *N* and *p* are the experimental point and parameter numbers, respectively.

Experimental results of the vapor pressure of MTBE reported in Table 2 were used to calculate the parameter values of the Antoine's equation, plotting the logarithm of the vapor pressure as a function of the reciprocal temperature (plot not shown).

$$\ln(P/\text{kPa}) = A - B/[(T/\text{K}) + C] \tag{13}$$

where *A*, *B*, and *C* are parameters, whose values are: 13.145, 2226.6, and −67.04, respectively, with a standard deviation for $\ln P = 2.1\cdot10^{-3}$ and $P = 0.1$ kPa.

Numerical values of the parameters in eq 13 were obtained from a least-squares analysis of the data. The number of significant digits was determined as the minimum number needed to adequately represent the data.

Differentiating eq 13 with respect to *T* and using the Clausius−Clapeyron equation, the dependence of the molar enthalpy of vaporization ΔH_V of MTBE with temperature can be obtained:

$$\Delta H_V/\text{kJ}\cdot\text{mol}^{-1} = 10^{-3}R\cdot B(T/\text{K})^2/[(T/\text{K}) + C]^2 \tag{14}$$

where *R* is the universal gas constant (= 8.31451 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). Appling eq 14 at $T = 298.15$ K, we obtain $\Delta H_V = 30.8$ $\text{kJ}\cdot\text{mol}^{-1}$, which is in very good agreement with the reported value at a nonspecified temperature [= (28.58 ± 3.0) $\text{kJ}\cdot\text{mol}^{-1}$].[20]

Figures 1 and 2 show the excess molar volume and viscosity deviation plotted against the mole fraction of chloroform for the [x_1 chloroform + (1 − x_1) MTBE] binary system at 293.15 K, respectively, while Figure 3 shows the total vapor pressure

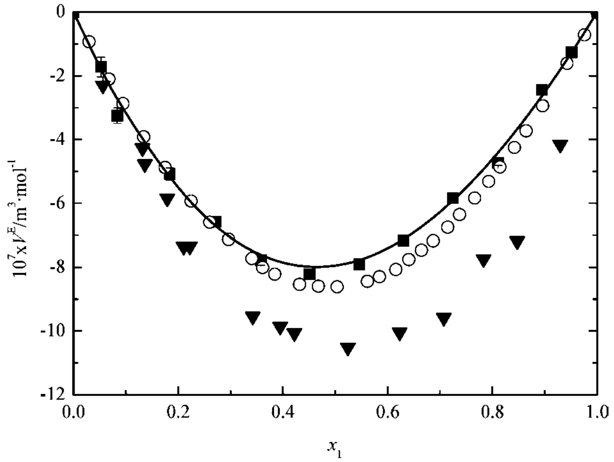

Figure 1. Excess molar volume V^E against x_1 for the [x_1 chloroform + (1 − x_1) MTBE] binary system at T = 293.15 K. ■, this work; ○, from ref 4 at 303.15 K; ▼, from ref 2 at 298.15 K. The solid line corresponds to the least-squares fit using eq 11. Some error bars are hidden within the signs.

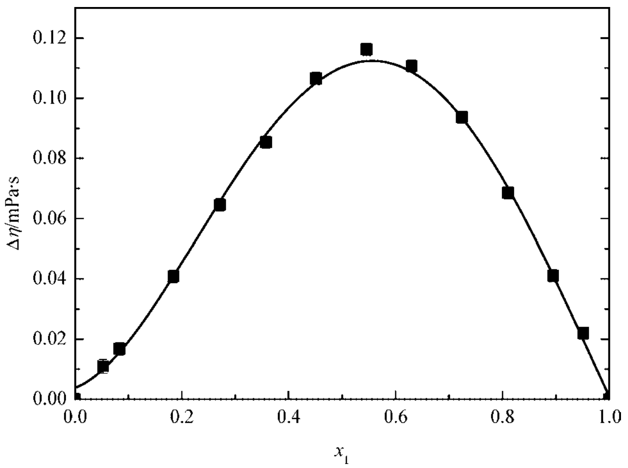

Figure 2. Viscosity deviation $\Delta\eta$ against x_1 for the [x_1 chloroform + (1 − x_1) MTBE] binary system at T = 293.15 K. The solid line corresponds to the least-squares fit using eq 11. Some error bars are hidden within the signs.

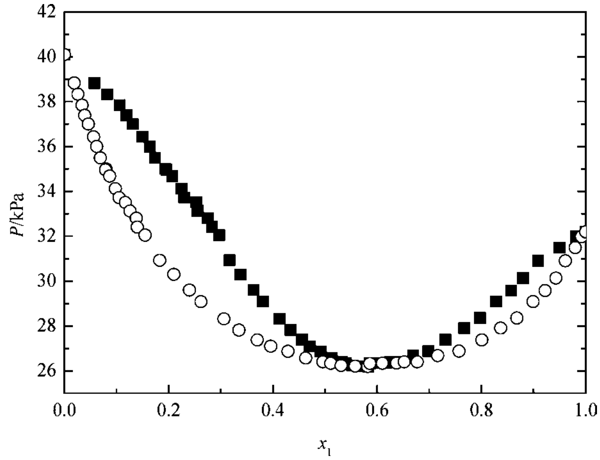

Figure 3. Isothermal VLE for the [x_1 chloroform + (1 − x_1) MTBE] binary system at T = 303.15 K. ○, vapor phase; ■, liquid phase.

P, liquid-phase x_1, and vapor-phase y_1 mole fraction measurements, plotted against the mole fraction of chloroform at 303.15 K. Furthermore, Figure 4 shows the logarithm of the activity coefficients against the mole fraction of chloroform at the same temperature.

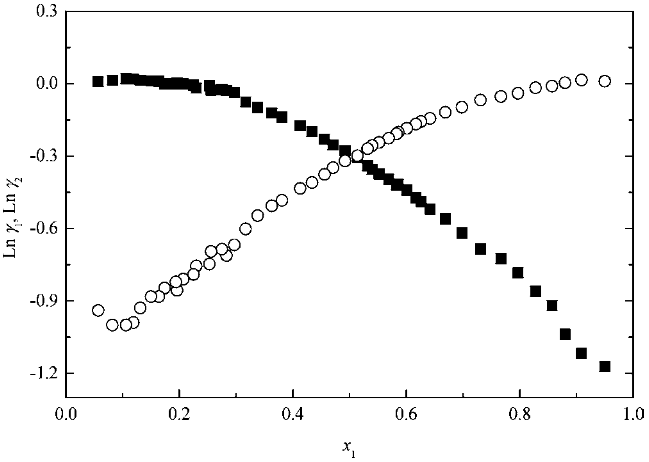

Figure 4. Logarithm of γ_i against x_1 for the [x_1 chloroform + (1 − x_1) MTBE] binary system at 303.15 K. ○, ln γ_1; ■, ln γ_2.

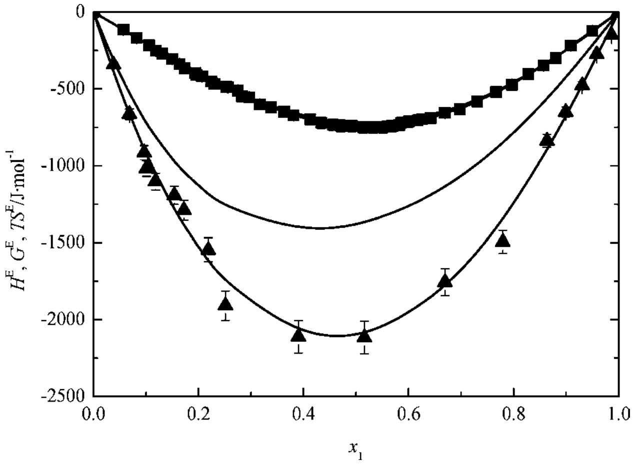

Figure 5. Excess molar Gibbs energy G^E, excess molar enthalpy H^E, and excess molar entropy TS^E against x_1 for the [x_1 chloroform + (1 − x_1) MTBE] binary system at 303.15 K. ■, G^E; ▲, H^E; continuous line without symbols, TS^E. Solid lines correspond to the least-squares fit using eq 11. Some error bars (I) are hidden within the signs.

Figure 5 shows the excess molar Gibbs energy G^E, excess molar enthalpy H^E, and excess molar entropy TS^E against x_1 for the [x_1 chloroform + (1 − x_1) MTBE] binary system at 303.15 K. As can be seen, these three excess molar properties are negative in the whole concentration range at this temperature, with a minimum close to $x_1 = 0.5$.

On the other hand, Figure 1 shows that the excess molar volume is negative in the whole concentration range at 293.15 K, which also has a minimum close to $x_1 = 0.5$. Therefore, in this system, a contraction in free volume is considered to occur, making the mixtures more compressible than the ideal mixture, which ultimately leads to negative values of V^E.

The concentration dependence of these excess properties indicates that the interactions between unlike molecules in the mixture are stronger than between like molecules in the pure liquids and association forces dominate the mixing process.

According to Kauzmann and Eyring,[21] the viscosity of a mixture strongly depends on entropy of mixture, which is related with liquid's structure and enthalpy (and consequently with molecular interactions between the components of the mixture). So, the viscosity deviations are a function of molecular interactions as well as the size and shape of molecules. Vogel and Weiss[22] 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 deviations of Raoult's law and without strong specific interactions, the viscosity deviations are negative.

On the other hand, Figure 2 shows that the viscosity deviation is positive over the whole composition range, which would correspond to binary systems that exhibit negative deviations from Raoult's law. The sign of $\Delta\eta$ is in agreement with the conclusion reported by Fort and Moore[23] who proposed that positive values of this property are characteristic of systems where association forces predominate.

Figure 5 shows that this binary system exhibits an exothermic behavior. This is another consequence of the presence of strong interactions between unlike molecules of both components that lead to the formation of complexes of association through hydrogen bond. This exothermic behavior is also in agreement with the V^E, $\Delta\eta$, and VLE data. Figure 3 also shows that the VLE data at $T = 303.15$ K indicate that this binary system shows negative deviations from ideal behavior in agreement with the statement for V^E, H^E, and $\Delta\eta$, with a minimum pressure azeotrope which has $P = (26.30 \pm 0.05)$ kPa and $x_1 = (0.586 \pm 0.002)$ coordinates at this temperature.

Conclusions

Empirical equations of density and viscosity were deduced, which permit us to estimate these properties both for pure and mixed components within the reported standard deviations. Calculated values are in agreement with the experimental results, within the experimental error.

The excess molar volume, excess molar enthalpy, and viscosity deviation from ideal behavior show that cross interactions in the mixture are stronger than those between like molecules in pure components for this binary system, producing a free volume contraction ($V^E < 0$) and a positive viscosity isotherm ($\Delta\eta > 0$) at $T = 293.15$ K.

Figure 1 shows our results with those reported in the literature, obtained at temperatures higher than this study for comparison. This figure also shows an abnormal trend in behavior with temperature, since the values reported in the literature are both more negative than ours. A plausible explanation for this fact could be the presence of ethanol (as stabilizing agent of chloroform) and other impurities in the chemicals used by Sharma et al.[4] and Mato et al.[2]

Furthermore, the binary system shows an exothermic behavior ($H^E < 0$) as a consequence of the H-bond association between unlike molecules when chloroform and MTBE are mixed. Therefore, association forces are dominant for this binary system. The sign of the excess molar entropy also supports this statement, because values less than zero of this excess property represents a higher molecular order in the mixture.

Isothermal vapor−liquid equilibrium data of the binary system were also obtained at $T = 303.15$ K, which show negative deviations from Raoult's law and a minimum pressure azeotrope.

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