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Density, Viscosity, Refractive Index, Excess Molar Volume, Viscosity, and Refractive Index Deviations and Their Correlations for the (Formamide + Water) System. Isobaric (Vapor + Liquid) Equilibrium at 2.5 kPa

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Density, viscosity, and refractive index measurements for pure formamide and water at $T = (293.15, 303.15, 313.15, \text{and } 323.15)$ K as well as for the binary system $\{x_1$ formamide $+ (1-x_1)$ water$\}$ at the same temperatures were made over the whole concentration range. Isobaric (vapor + liquid) equilibrium at $P = 2.5$ kPa for this binary system was also measured. The experimental results of density, viscosity, and refractive index were fitted to empirical equations, which makes it possible to calculate these properties over the whole studied concentration and temperature ranges. Calculated values are in good agreement with the experimental results. Data of the binary mixture were further used to calculate the excess molar volume, viscosity and refractive index deviations, and the activity coefficients. The excess or deviation properties were fitted to the Redlich–Kister polynomial relation to obtain their coefficients and standard deviations. This binary system shows negative deviations from the ideal behavior and no azeotrope.

Introduction

Excess thermodynamic functions and deviations of nonthermodynamic ones of binary liquid mixtures are very important for the design of industrial equipment and for the interpretation of the liquid state, particularly when polar components are involved.

In this paper, we report density ρ, viscosity η, and refractive index n_D data for pure formamide and water as well as for the binary system constituted by these two chemicals in the whole mole fraction range at $T = (293.15, 303.15, 313.15, \text{and } 323.15)$ K. Isobaric (vapor + liquid) equilibrium (VLE) data are also reported at $P = 2.5$ kPa. From these experimental results, excess molar volume V^E, viscosity $\Delta\eta$ and refractive index Δn_D deviations from the ideal behavior, and activity coefficients γ_i were calculated.

Empirical equations for the density, viscosity, and refractive index 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 to the measured data. These equations are useful for interpolation within the studied temperature range. The excess and deviation properties were fitted to a Redlich–Kister-type[1] equation using least-squares to obtain their dependencies on concentration and temperature.

Associations between formamide and water molecules at $T = 298$ K have been previously observed using proton magnetic relaxation data.[2] Also, the heat of solution, heat capacity, and density of this system at $T = 298.15$ K have been reported by Egan et al.,[3] while Sköld et al.[4] report enthalpies of solution at infinite dilution at $T = 298.15$ K. However, as far as we know, neither isobaric VLE data nor excess molar or deviation properties at temperatures other than those stated above are available in the literature for this binary system.

This work is a part of an ongoing research program in which we study thermodynamic, transport, and spectroscopic properties of binary mixtures containing formamide as one of the components.[5–8]

Experimental Section

Materials. Formamide (analytical reagent) was supplied by Riedel-de Haën. It was used as received because no impurity was detected by gas chromatography using an HP 6890 gas chromatograph with an FID detector, showing that its mole fraction was higher than 0.998. Formamide was stored over 0.3 nm molecular sieves to prevent water absorption, and its water content was periodically checked by Karl Fischer titration using an automatic Mettler DL18 Karl Fischer titrator. Degassed bidistilled water was used.

Apparatus and Procedure. For density, viscosity, and refractive index measurements, liquid mixtures were prepared by weighing each component 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 weightings were performed on a dual-range electronic balance (Mettler Toledo AG-245) accurate to 0.1/0.01 mg. The uncertainty in the mole fractions for these mixtures is estimated to be lower than $\pm 1 \cdot 10^{-4}$.

Density, refractive index for the sodium D-line, and viscosity were measured with a vibrating tube densimeter KEM DA-300 with a built-in thermostatic unit accurate to 0.01 K, which allows working over the range $T = (277 \text{ to } 363)$ K using degassed bidistilled water and dry air as calibrating substances, a Leica AR600 refractometer, and a Schott-Gerätte AVS 400 viscometer with appropriate Ubbelohde capillary viscometers calibrated by the manufacturer, respectively. The accuracies were of ± 0.1 $\text{kg}\cdot\text{m}^{-3}$ for density, ± 0.00005 for refractive index, and ± 0.001 $\text{mPa}\cdot\text{s}$ for viscosity. A Schott CT 1450 thermostatically controlled water bath, with an uncertainty of ± 0.01 K, was used for viscosity measurements.

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Table 1. Density ρ, Refractive Index n_D, and Viscosity η Values at Several Temperatures and Boiling Temperature at 2.5 kPa of the Pure Components

	$\rho/\mathrm{kg \cdot m^{-3}}$		n_D		$\eta/\mathrm{mPa \cdot s}$		
T/K	exptl	lit.	exptl	lit.	exptl	lit.	boiling temperature at 2.5 kPa$\cdot$K^{-1}
			Formamide				359.5
293.15	1133.0	1133.39[a]	1.44802	1.44754[a]	3.792	3.764[a]	
303.15	1124.6	1124.6[b]	1.44432	1.44432[b]	2.941	2.83[a]	
313.15	1116.1	1116.1[b]	1.44054	1.44054[b]	2.361	2.36[b]	
323.15	1108.0	1107.8[c]	1.43705		1.966	1.92[d]	
			Water				279.4
293.15	998.2	998.2058[a]	1.33365	1.3329880[a]	1.011	1.0019[a]	
303.15	995.7	995.6504[a]	1.33254	1.3319405[a]	0.807	0.79726[a]	
313.15	992.2	992.2191[a]	1.33055	1.3306096[a]	0.662	0.65263[a]	
323.15	988.0	988.0382[a]	1.32904	1.3290364[a]	0.556	0.54675[a]	

[a] From ref 14. [b] From ref 5. [c] From ref 6. [d] From ref 22.

Table 2. Experimental Density ρ, Viscosity η, and Refractive Index n_D for $\{x_1$ Formamide + $(1-x_1)$ Water$\}$ at Several Temperatures

	$\rho/\mathrm{kg \cdot m^{-3}}$				n_D				$\eta/\mathrm{mPa \cdot s}$			
x_1[a]	T/K = 293.15	303.15	313.15	323.15	293.15	303.15	313.15	323.15	293.15	303.15	313.15	323.15
0.0000	998.2	995.7	992.2	988.0	1.33375	1.33250	1.33062	1.32905	1.011	0.807	0.662	0.556
0.0753	1024.3	1019.9	1014.9	1009.4	1.35293	1.35045	1.34864	1.34732	1.098	0.886	0.734	0.621
0.1519	1043.7	1038.1	1032.2	1026.0	1.36831	1.36573	1.36377	1.36233	1.195	0.973	0.811	0.688
0.2309	1061.5	1054.5	1048.4	1041.7	1.38233	1.37948	1.37773	1.37585	1.318	1.073	0.898	0.788
0.2959	1072.2	1065.4	1058.3	1051.3	1.39192	1.38925	1.38711	1.38480	1.446	1.182	0.988	0.840
0.3852	1083.5	1076.5	1068.9	1061.6	1.40215	1.39904	1.39620	1.39411	1.603	1.306	1.089	0.924
0.4854	1095.2	1087.6	1079.8	1072.2	1.41250	1.40943	1.40688	1.40344	1.814	1.473	1.227	1.042
0.5652	1103.1	1095.3	1087.3	1079.7	1.41967	1.41696	1.41414	1.41038	2.035	1.631	1.353	1.144
0.6138	1107.1	1100.4	1091.3	1084.0	1.42395	1.42167	1.41862	1.41455	2.162	1.743	1.441	1.220
0.6924	1114.5	1105.8	1097.1	1090.3	1.42992	1.42755	1.42415	1.42011	2.401	1.932	1.586	1.343
0.7676	1119.2	1110.9	1102.7	1094.8	1.43511	1.43233	1.42860	1.42482	2.692	2.145	1.757	1.477
0.8175	1122.6	1114.3	1105.9	1097.9	1.43806	1.43482	1.43121	1.42750	2.930	2.313	1.891	1.574
0.9254	1129.1	1120.6	1112.2	1104.1	1.44420	1.44070	1.43676	1.43334	3.418	2.661	2.155	1.784
1.0000	1133.0	1124.6	1116.1	1108.0	1.44805	1.44434	1.44050	1.43715	3.792	2.941	2.361	1.966

[a] Mole fraction of formamide.

Isobaric VLE data were obtained with commercial equipment (Labodest, model 602-S) available from Fischer Technology, Germany. 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 uncertainty of 0.02 K, whereas total pressure in the still was measured with a precision pressure transmitter (Wika, model P-10) with an uncertainty of 0.01 kPa, both connected to the Fischer VLE2+ vacuum and temperature control unit.

Samples of the condensed vapor and liquid phases were taken at stationary conditions, and their equilibrium compositions were determined by gas chromatography. A Hewlett-Packard 6890 gas chromatograph with an automatic injector (Agilent G2613A) directly connected to a ChemStation (HP G2070AA) was used, and the internal standard method was applied to obtain quantitative results. Acetone (Merck, chromatographic quality) with a mole fraction purity >0.998 (GC) was the standard compound used for this purpose. Good separation of all components was obtained on a 30 m long × 0.25 mm inner diameter × 0.5 μm film thickness cross-linked polyethylene glycol capillary column (HP-INNOWax 19091N-233). The temperature program used was as follows: initial temperature $T = 343$ K for 2 min, ramp of 50 K$\cdot$min^{-1}, and final temperature $T = 513$ K for another 5 min. The nitrogen carrier gas flow was kept constant electronically, working with a split ratio of 20:1 and with the injector maintained at $T = 503$ K. Detection was conducted by a thermal conductivity detector at $T = 523$ K. Three analyses were performed for each sample to obtain a mean mole fraction value with repeatability better than 1 %.

The analytical balance described above was used in the range accurate to ± 0.01 mg both for the calibration curves and for the analysis of the unknown samples, and 10 mixtures were prepared to obtain the calibration curves for each component. To validate the reported mole fraction values, three samples of well-known compositions (determined by mass) were analyzed. These analyses show that the reported mole fraction values have an uncertainty of ± 0.001.

Results and Discussion

Experimental results for refractive index, density, and viscosity of pure compounds at several temperatures are summarized in Table 1. For comparison, existing values found in the literature are also included.

Experimental results for the density, viscosity, and refractive index corresponding to temperatures over the range $T = (293.15$ to $323.15)$ K for the system $\{x_1$ formamide + $(1-x_1)$ water$\}$ are listed in Table 2.

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

$$\rho/\mathrm{kg \cdot m^{-3}} = a_1 + b_1 \cdot (T/\mathrm{K}) \tag{1}$$

$$n_D = a_2 + b_2 \cdot (T/\mathrm{K}) \tag{2}$$

$$\eta/\mathrm{mPa \cdot s} = a_3 \cdot \exp[b_3/(T/\mathrm{K})] \tag{3}$$

where a_i and b_i are constants given in Table 3 together with the standard deviations. 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 above-reported experimental errors for density, viscosity, refractive index, and temperature. Calculated values from these equations compare

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

	ρ/kg·m^{-3}			n_D			η/mPa·s		
compound	a_1	b_1	σ	a_2	$10^4 b_2$	$10^4 \sigma$	$10^3 a_3$	b_3	σ
formamide	1377.6	−0.835	0.1	1.5555	−3.67	1	2.8	2111	0.04
water	1098.6	−0.341	0.6	1.3802	−1.58	3	1.5	1907	0.006

well with experimental data within the standard deviations reported in Table 3.

Polynomial equations were used to correlate the same properties for $\{x_1$ formamide $+ (1-x_1)$ water$\}$, as follows

$$\rho/\text{kg}\cdot\text{m}^{-3}(x_1, (T/\text{K})) = \sum_{i=0}^{m}\sum_{j=0}^{n} a_{ij}\cdot(T/\text{K})^i\cdot x_1^j \tag{4}$$

$$n_D(x_1, (T/\text{K})) = \sum_{i=0}^{m}\sum_{j=0}^{n} b_{ij}(T/\text{K})^i\cdot x_1^j \tag{5}$$

$$\eta/\text{mPa}\cdot\text{s}(x_1, (T/\text{K})) = \sum_{j=0}^{m} c_j\cdot x_1^j\cdot\exp[d_j\cdot x_1^j/(T/\text{K})] \tag{6}$$

where a_{ij}, b_{ij}, c_j, and d_j are parameters given in Table 4 together with their standard deviations.

Equations 4, 5, and 6 were fitted using a nonlinear regression method based on the Levenberg–Marquardt algorithm.[9] These fits show linear behaviors for density and refractive index with temperature, while for viscosity, this dependence is exponential. To obtain the respective dependencies on composition and temperature, we adopt the same procedure that was previously described.[5,6,8,10] The appropriate number of significant digits was selected taking into account the experimental errors for density, refractive index, viscosity, and temperature reported above.

Equations 4, 5, and 6 make it possible to predict the density, refractive index, and viscosity of the binary system at any concentration and over the temperature range $T = (293.15$ to $323.15)$ K, respectively, using the parameters reported in Table 4 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.[5,6,10]

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

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

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

$$\Delta n_D = n_D - (\varphi_1\cdot n_{D_1} + \varphi_2\cdot n_{D_2}) \tag{9}$$

where x_1 is the mole fraction of formamide; M_1 and M_2 are the molar masses of formamide and water, respectively; ρ, n_D, and η are the density, refractive index, and viscosity of the mixture; ρ_1, ρ_2, n_{D1}, n_{D2}, η_1, and η_2 are the densities, refractive indices, and viscosities of the pure components; and φ_1 and φ_2 are the mole volume fractions of the pure components. The activity coefficients of formamide γ_1 and water γ_2, in the liquid phase, are related to VLE by

$$\gamma_i = y_i P/x_i P_i^o \tag{10}$$

where x_i and y_i are the equilibrium mole fractions in the liquid and vapor phases of component i, and P and P_i^o 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 work pressure is low, which makes this simplification reasonable.

Vapor pressures of pure formamide over the range $P = (0.280$ to $26.700)$ kPa were determined experimentally as a function of temperature, using the same equipment as for the VLE measurements. The pertinent results appear in Table 5 together with literature values reported by Stull.[11] As can be seen, our values do not agree with those of Stull, which are always significantly lower. On the other hand, vapor pressures of pure water were calculated over the whole range of temperatures listed in Table 6 applying the Antoine equation, with the constants reported in the literature:[14]

$$\log(P_i^o/\text{Pa}) = A_i - B_i/[(T/{}^\circ\text{C}) + C_i] \tag{11}$$

Fitting our experimental vapor pressure values for formamide, listed in Table 5, and using least-squares with all points equally weighted, the Antoine constants A_i, B_i, and C_i were calculated using eq 11. The values so obtained are also reported in Table 5. The significant digits of each constant were established taking into account their standard deviations. Using these constants, the vapor pressure of formamide can be calculated with a standard deviation of 0.08 kPa.

The VLE data reported in Table 6 for $\{x_1$ formamide $+ (1-x_1)$ water$\}$ were plotted in Figure 1, which shows that this binary system presents negative deviations from the ideal behavior and no azeotrope. These VLE data were found to be thermodynamically consistent according to the point-to-point test of Van Ness et al.,[12] as modified by Fredenslund et al.[13] Consistency criteria were met using a one-parameter Legendre polynomial. The average absolute deviations in vapor-phase mole fractions and pressure are $\Delta y = 0.02$ and $\Delta P = 0.60$ Pa, respectively.

The excess molar volume and viscosity and refractive index deviations were fitted to the experimental results by means of a Redlich–Kister-type equation[1] with the same fitting procedure as indicated above:

$$Y^E = x_1(1 - x_1)\sum_{j=0}^{n} e_j(1 - 2x_1)^j \tag{12}$$

where Y^E represents either V^E, $\Delta\eta$, or Δn_D.

Since the coefficients e_j are functions of the temperature, they were plotted against this variable to obtain equations that represent each property over the studied temperature range. We propose the following dependence with temperature for these coefficients, as previously[6,8,10]

$$e_j = \sum_{i=0}^{m} e_{ji}\cdot(T/\text{K})^i \tag{13}$$

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

$$Y^E = x_1(1 - x_1)\sum_{j=0}^{n}\sum_{i=0}^{m} e_{ji}\cdot(T/\text{K})^i\cdot(1 - 2x_1)^j \tag{14}$$

where the e_{ji} parameters are also given in Table 4 together with their standard deviations σ, defined as

$$\sigma = \left[\sum (Y^E_{\text{exptl}} - Y^E_{\text{calcd}})^2/(N - p)\right]^{1/2} \tag{15}$$

where N and p are the numbers of experimental points and parameters, respectively. The choice of the appropriate number

Table 4. Coefficients and Standard Deviations of Equations 4, 5, 6, and 14

property	$i-j$	a_{ij}	property	$i-j$	b_{ij}
ρ/kg·m^{-3}(x_1, T/K)			n_D(x_1, T/K)		
	0–0	1106.0		0–0	1.39766
	0–1	833		0–1	0.2820
	0–2	−1016		0–2	−0.127
	0–3	459.3		1–0	$-1.59157 \cdot 10^{-4}$
	1–0	−0.3608		1–1	$-4.4528 \cdot 10^{-4}$
	1–1	−1.72		1–2	$2.5008 \cdot 10^{-4}$
	1–2	2.31	σ	0.007	
	1–3	−1.08			
σ	1/kg·m^{-3}				
η/mPa·s(x_1, T/K)			V^E/m^3·mol^{-1}(x^1, T/K)		
j	c_j	d_j		$j-i$	e_{ji}
0	0.0015	1857.9		0–0	$-1.575 \cdot 10^{-5}$
1	0.011	−695		0–1	$8.96 \cdot 10^{-8}$
2	0.01	1000		0–2	$-1.297 \cdot 10^{-10}$
σ		0.06/mPa·s		1–0	$1.075 \cdot 10^{-5}$
				1–1	$-8.02 \cdot 10^{-8}$
				1–2	$1.416 \cdot 10^{-10}$
				2–0	$-1.467 \cdot 10^{-5}$
				2–1	$8.74 \cdot 10^{-8}$
				2–2	$-1.322 \cdot 10^{-10}$
			σ	$9 \cdot 10^{9}$/m^3·mol^{-1}	
$\Delta\eta$/mPa·s(x_1, T/K)			Δn_D(x_1, T/K)		
	$j-i$	e_{ji}		$j-i$	e_{ji}
	0–0	−125		0–0	0.42
	0–1	0.759		0–1	$-2.5 \cdot 10^{-3}$
	0–2	$-1.16 \cdot 10^{-3}$		0–2	$3.9 \cdot 10^{-6}$
	1–0	45.2		1–0	0.4
	1–1	−0.28		1–1	$-2.4 \cdot 10^{-3}$
	1–2	$4.37 \cdot 10^{-4}$		1–2	$3.7 \cdot 10^{-6}$
σ	0.02/mPa·s			2–0	0.26
				2–1	$-1.7 \cdot 10^{-3}$
				2–2	$2.7 \cdot 10^{-6}$
			σ	$3 \cdot 10^{-3}$	

Table 5. Experimental and Literature Vapor Pressure Data for Formamide at Several Temperatures and Antoine Coefficients for Equation 11

	P/Pa			P/Pa	
T/K	exptl	lit.[a]	T/K	exptl	lit.[a]
348.4	280	182	401.8	5330	3569
359.3	650	359	411.9	8000	5744
371.7	1300	741	425.3	13330	10430
386.3	2670	1638	444.5	26700	23028

antoine equation[b]	A_i	B_i	C_i
formamide	8.24669	1098.42418	114.96308

[a] Interpolated from ref 11. [b] Eq 11.

Table 6. Experimental Results for the Mole Fraction of Formamide in the Liquid x_1 and Vapor y_1 Equilibrium Phases, Temperature T, and Calculated Activity Coefficients γ_i for {x_1 Formamide + (1−x_1) Water} at P = 2.5 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	279.4		2.628
0.232	0.004	293.55	31.93	1.353
0.391	0.004	302.05	6.280	1.027
0.466	0.005	305.97	4.131	0.935
0.545	0.002	310.05	0.892	0.878
0.589	0.002	314.82	0.497	0.753
0.748	0.004	320.45	0.447	0.917
0.806	0.025	330.75	1.022	0.705
0.879	0.076	339.05	1.453	0.733
0.937	0.364	352.75	2.438	0.541
1.000	1.000	359.5	4.058	

of constants in eq 14 was based on the variation with n and m of the standard error of the estimated value. The significant digits of each coefficient were established taking into account their standard deviation.

Figures 2, 3, and 4 show the excess molar volumes, viscosity, and refractive index deviations, plotted against the mole fraction of formamide for the binary system at several temperatures, respectively. These plots show that the excess molar volumes and viscosity deviations are always negative, while the refractive index deviations are always positive over the whole studied concentration and temperature ranges. Furthermore, and for any composition, when temperature is increased, the excess molar volume and viscosity deviation values become less negative while refractive index deviation values become less positive.

Usually, the excess molar volume and the viscosity deviation have opposite signs. However, for {x_1 formamide + (1−x_1) water}, this does not happen, as can be seen in Figures 2 and 3. This behavior is also observed for other binary systems.[15–18]

As can be seen in Figure 3, the viscosity deviations are negative for all the studied temperatures and over the whole composition range, which would correspond to binary systems

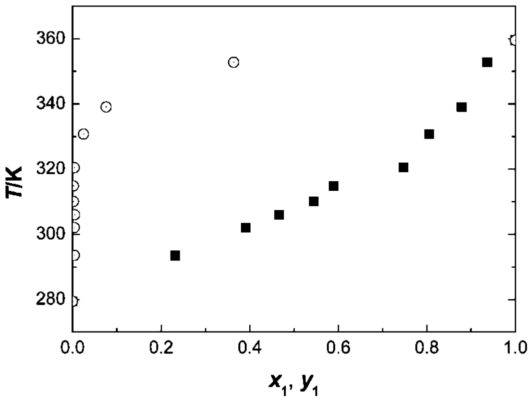

Figure 1. Plot of temperature T/K against ■, liquid-phase mole fractions x_1; and ○, vapor-phase mole fractions y_1 for {x_1 formamide + (1−x_1) water} at P = 2.5 kPa. Error bars have the same size of the symbols.

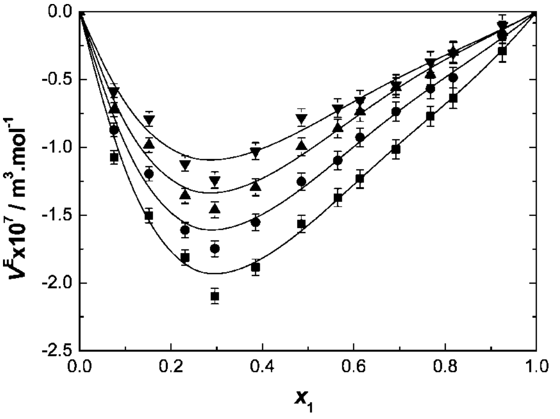

Figure 2. Plot of excess molar volume V^E against mole fraction x_1 for $\{x_1$ formamide + $(1-x_1)$ water$\}$: T = ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K. Solid lines correspond to the least-squares fit using eq 14. ψ, error bars.

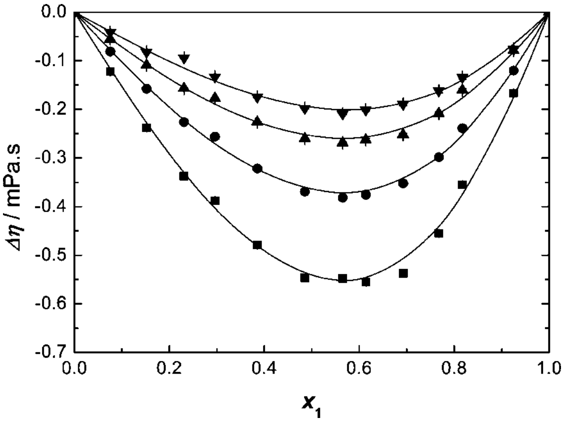

Figure 3. Plot of viscosity deviation $\Delta\eta$ against mole fraction x_1 for $\{x_1$ formamide + $(1-x_1)$ water$\}$: T = ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K. Solid lines correspond to the least-squares fit using eq 14. ψ, error bars.

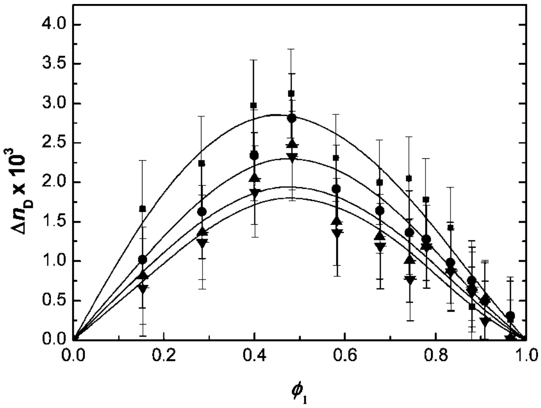

Figure 4. Plot of refractive index deviation Δn_D against mole volume fraction φ_1 for $\{x_1$ formamide + $(1-x_1)$ water$\}$: T = ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K. Solid lines correspond to the least-squares fit using eq 14. ψ, error bars.

that exhibit negative deviations from Raoult's law. The sign of $\Delta\eta$ is also in agreement with the conclusion reported by Fort and Moore[19] and with the endothermic behavior of this binary system.[3] As can be observed in Figure 3, increasing the temperature leads to less negative $\Delta\eta$ values, due to an increase of the thermal energy.

Intermolecular complexes have also been investigated by Voronkov et al.[20,21] using methods based upon the refractive index deviation from ideal behavior. For many binary systems, in which spectroscopic or other methods indicate that molecular interactions occur, Δn_D was found to be greater than 0.004. Therefore, these authors conclude that $\Delta n_D > 0.004$ is an indication of complex formation. Although several types of intermolecular complexes between formamide and water in the solution were previously reported by Sukhno et al.,[2] the Δn_D values for $\{x_1$ formamide + $(1-x_1)$ water$\}$ are always lower than 0.004 (see Figure 4), probably due to the high self-association of formamide and water.

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