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Phase Equilibria and Multiple Azeotropy in the Associating System Methanol + Diethylamine

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Vapor−liquid equilibrium has been measured for the binary system of methanol (1) + diethylamine (2) at 101.3 and 300 kPa. Both equilibrium isobars show strong deviations from ideal behavior and a single maximum boiling point azeotrope of practically constant composition $x_1 \approx 0.76$, corresponding to a temperature of 339.8 K at 101.3 kPa and 370.0 K at 300 kPa. The trend of the high-pressure isobar data is consistent with the formation of a second minimum boiling azeotrope, confirming the multiple azeotropic behavior found by others at a higher temperature (398.58 K). Furthermore, the excess Gibbs energy is negative and inflects markedly with composition with increased pressure. The equilibrium behavior and polyazeotropy are discussed in terms of self-association and cross-association of hydroxyl and amino groups. The data were satisfactorily correlated using the Margules equation, the UNIQUAC model modified for association, and the Wisniak−Tamir equation.

Introduction

Binary polyazeotropy, i.e., the condition for which more than one stable azeotrope exists at a given temperature or pressure, has been reported experimentally for the four organic systems benzene + hexafluorobenzene (Gaw and Swinton, 1968; Aucejo et al., 1996), diethylamine + methanol (Srivastava and Smith, 1985), 1,2-epoxybutane + methyl ethanoate (Leu and Robinson, 1991), ethanoic acid + 2-methylpropyl ethanoate (Christensen and Olson, 1992; Burguet et al., 1996), and ammonia + 1,1,2,2,2-pentafluoroethane (Chai Kao et al., 1997). The thermodynamic aspects of the phenomena for associating and nonassociating mixtures have been analyzed by Wisniak et al. (1996) and Segura et al. (1996). Total-pressure vapor−liquid equilibrium data for the system diethylamine + methanol have been reported at (298, 348, and 398) K by Srivastava and Smith (1985); the vapor pressure values reported were smoothed by a least-squares spline fit. The system showed negative deviation from ideal behavior at 298 and 348 K and then a mixed deviation at 398 K. Maximum boiling point azeotropes rich in methanol were formed at 298 and 348 K. At 398 K double azeotropy appears clearly in the experimental data of Srivastava and Smith. Nakanishi et al. (1967) measured the vapor−liquid equilibrium of methanol + diethylamine at 97.3 kPa and found that the system showed strong negative deviations from Raoult's law, as expected from a strong hydrogen-bond interaction between hydroxyl groups and amino bases. At 97.3 kPa the system formed an azeotropic mixture at 340.35 K, with near 76.0 mol % of methanol. In addition, the $P-T$ projection of the critical line of the system diethylamine + methanol has been determined experimentally by Kay and Khera (1976); the line connects the critical points of both compounds without discontinuities, showing a sharp minimum in temperature, at about 495 K, below the critical temperatures of the pure species; no maximum or minimum boiling temperature azeotrope ends in the critical range. Excess functions of liquid mixtures consisting of an alcohol and an amine show the strongest negative values found for organic mixtures in the literature. These strikingly high values have been attributed to the formation associated amine + alcohol species caused by strong intermolecular interactions between the OH-group of the alcohol molecule and the NH-group of the amine molecules. Hydrogen-bonding energies are negative and values range from −30 to −44 kJ/mol (Reinman and Heintz, 1991). The formation of cross-associated species can be used to explain not only the exothermic enthalpy of mixing but also the negative entropy of mixing observed. It is a well-known that alcohol as well as amine molecules have a pronounced tendency to form self- and cross-associated species due to hydrogen-bonding effects. For example, Ratkovics et al. (1974) and Ratkovics and László (1977) have found that the average degree of association in mixtures of normal primary alcohols and amines is related to the viscosity of the mixtures and that in solutions of dibutylamine + methanol on the average about eight to nine molecules of alcohol are associated with one molecule of amine. Funke et al. (1989) measured the values of G^E, V^E, and H^E of mixtures of methanol + diethylamine at 298.15 K and found that the calculated values of the cross-hydrogen bonding significantly exceeded the corresponding values of self-association of alcohols and amines. In addition, they concluded that not only the NH-group was a weaker proton donator than the OH-group but also the steric hindrance may play a role in formatting the hydrogen bonding in the amine self-association because more side groups are involved than in the case of the OH···O bonding. Similarly, Nakanishi et

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Table 1. Properties of the Pure Compounds

	d(298.15 K)/g·cm^{-3}		n(D, 298.15 K)		T_b(101.3 kPa)/K	
components	exptl[a]	lit.	exptl[a]	lit.	exptl[a]	lit.
methanol	0.787 32	0.787 30[b]	1.3270	1.3267[b]	337.7	337.65[b]
diethylamine	0.699 71	0.698 91[c]	1.3826	1.3825[c]	328.4	328.6[c]

[a] Measured. [b] TRC Tables, a-5030. [c] TRC Tables, a-9090.

al. (1970) measured the enthalpies of mixing of solutions of methanol + diethylamine at 298 and 318 K and found that the system exhibits large negative enthalpies of mixing, which become less negative as the temperature is increased. These results were explained as being the consequence of a positive heat effect caused by the breaking of hydrogen bonds between alcohol molecules and a large asymmetrical negative heat effect due to formation of hydrogen bonds between the free alcohol and amine molecules. The fact that the enthalpy of mixing decreased as the temperature was increased was explained by assuming that the hydrogen bonding OH···N is somewhat more stronger than the OH−H bonding in alcohols or NH···N in amines and that moderately stable complexes between alcohol and amines are formed.

It is the purpose of this work to determine the vapor−liquid equilibrium of the system diethylamine + methanol at different pressure levels and study the effect of the azeotropic composition on this variable.

Experimental Section

Chemicals. Methanol (99.9+%, HPLC grade) was purchased from Aldrich. Diethylamine was a high-purity grade (>99.5%) Fluka reactive. The purity of the chemicals, as checked by gas chromatography (GC), was methanol, 99.85 mass %, and diethylamine, 99.83 mass %. They were used without further purification. The experimental densities, refractive indexes, and normal boiling points are listed in Table 1 and shown to be in good agreement with the corresponding values reported in the literature.

Apparatus and Procedure. The equilibrium vessel was an all-glass, dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa and temperature up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature-sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low-pressure zone with an accuracy of 0.01 kPa and another one for the high-pressure range with an accuracy of 0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of high-purity water (100 mass %). The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. At this moment, samples of liquid and condensate were taken for analysis. Samples extractions were carried out with special syringes (Hamilton, RSN 1001), which allowed one to withdraw small volume samples (0.2 mL) in a system under partial vacuum or under overpressure conditions.

Analysis. Compositions of the sampled liquid and condensed vapor phases were analyzed with a Varian Star 3400 CX gas chromatograph using a thermal conductivity detector, the response was treated with a Star Chromatography Station. The chromatographic column (2 m × $^1/_8$ in.) was packed with Porapak P. The gas carrier was helium flowing at 50 cm^3/min, and the column and detector temperatures were 473 and 503 K, respectively. The calibration was carefully carried out with gravimetrically prepared standard solutions. The accuracy of measured liquid and vapor compositions was usually less than 0.001 mole fraction.

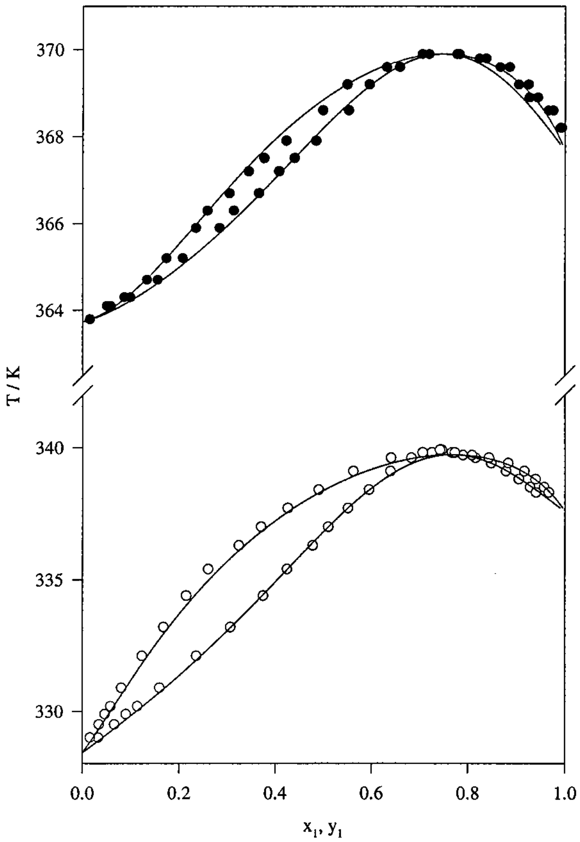


Figure 1. Experimental data for the system methanol (1) + diethylamine (2) at 101.3 and 300 kPa: experimental data at 101.3 kPa (○); experimental data at 300 kPa (●); smoothed data using the Margules equation (—).

Results

The temperature T and the liquid-phase x_i and vapor-phase y_i mole fractions at P = 101.3 and 300 kPa are reported in Figure 1 and Tables 2 and 3. Figure 2 shows the activity coefficients γ_i that were calculated from the following equation (Van Ness and Abbott, 1982)

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^{L} is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, P_i^0 is the vapor pressure, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor

Table 2. Experimental Vapor−Liquid Equilibrium Data for Methanol (1) + Diethylamine (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ cm^3 mol^{-1}	$-B_{22}$/ cm^3 mol^{-1}	$-B_{12}$/ cm^3 mol^{-1}	G^E/J mol^{-1}
329.0	0.032	0.016	0.726	0.999	1433	1132	559	−30.6
329.5	0.066	0.034	0.748	0.999	1420	1128	557	−53.9
329.9	0.090	0.046	0.729	1.000	1409	1125	556	−78.4
330.2	0.114	0.058	0.716	1.004	1400	1122	555	−94.4
330.9	0.159	0.080	0.685	1.011	1382	1117	552	−141.6
332.1	0.236	0.123	0.673	1.020	1350	1107	548	−215.8
333.2	0.307	0.168	0.672	1.031	1322	1098	544	−279.2
334.4	0.375	0.215	0.668	1.039	1293	1089	540	−352.9
335.4	0.424	0.261	0.686	1.031	1269	1081	537	−397.1
336.3	0.478	0.324	0.729	1.012	1248	1075	534	−406.1
337.0	0.510	0.371	0.757	0.985	1232	1069	532	−419.9
337.7	0.551	0.426	0.782	0.960	1216	1064	530	−432.4
338.4	0.595	0.490	0.809	0.926	1201	1059	527	−441.2
339.1	0.639	0.562	0.838	0.878	1186	1054	525	−451.1
339.6	0.682	0.640	0.875	0.810	1175	1050	524	−446.5
339.8	0.725	0.706	0.900	0.762	1171	1049	523	−427.3
339.9	0.746	0.742	0.915	0.724	1169	1048	523	−420.2
339.8	0.766	0.773	0.930	0.697	1171	1049	523	−395.4
339.7	0.789	0.808	0.947	0.656	1173	1050	523	−371.3
339.6	0.815	0.843	0.960	0.615	1175	1050	524	−347.4
339.4	0.848	0.883	0.974	0.562	1179	1052	524	−311.2
339.1	0.879	0.916	0.986	0.511	1186	1054	525	−265.5
338.8	0.905	0.939	0.992	0.478	1192	1056	526	−217.4
338.5	0.928	0.957	0.997	0.452	1199	1058	527	−168.6
338.3	0.940	0.967	1.001	0.426	1203	1060	528	−139.2

Table 3. Experimental Vapor−Liquid Equilibrium Data for Methanol (1) + Diethylamine (2) at 300 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ cm^3 mol^{-1}	$-B_{22}$/ cm^3 mol^{-1}	$-B_{12}$/ cm^3 mol^{-1}	G^E/J mol^{-1}
363.8	0.015	0.015	1.213	1.000	789	897	455	7.5
364.1	0.058	0.050	1.030	1.001	785	895	455	7.2
364.3	0.099	0.086	1.026	1.002	783	894	454	13.1
364.7	0.155	0.133	0.995	1.004	778	892	453	8.0
365.2	0.207	0.173	0.949	1.009	773	889	452	−11.7
365.9	0.283	0.234	0.912	1.018	765	885	450	−41.5
366.3	0.313	0.258	0.895	1.019	760	883	449	−65.1
366.7	0.365	0.304	0.889	1.026	756	881	448	−80.3
367.2	0.407	0.344	0.885	1.025	750	878	447	−106.8
367.5	0.439	0.376	0.886	1.025	747	876	446	−120.2
367.9	0.484	0.422	0.888	1.024	742	874	445	−138.2
368.6	0.552	0.498	0.894	1.012	735	871	444	−172.7
369.2	0.595	0.549	0.895	0.995	728	867	442	−209.1
369.6	0.658	0.631	0.915	0.961	724	865	441	−222.0
369.9	0.719	0.705	0.924	0.934	721	864	440	−233.7
369.9	0.777	0.782	0.946	0.877	721	864	440	−223.3
369.8	0.823	0.837	0.957	0.833	722	864	441	−210.0
369.6	0.866	0.885	0.967	0.785	724	865	441	−189.9
369.2	0.904	0.924	0.978	0.735	728	867	442	−152.5
368.9	0.926	0.943	0.983	0.722	732	869	443	−122.6
368.6	0.966	0.975	0.983	0.697	735	871	444	−88.6
368.2	0.990	0.993	0.989	0.672	739	873	445	−47.1

phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The pure component vapor pressures P_i^0 were determined experimentally as a function of the temperature using the same equipment as that for obtaining the VLE data; the pertinent results appear in Table 4. The measured vapor pressures were correlated using the Antoine equation

$$\log(P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \tag{3}$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 5. In addition, the vapor pressure data measured in this work show good agreement when compared with other experimental references, as can be seen in Figures 3 and 4. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) using the molecular parameters suggested by Prausnitz et al. (1980), and the pure component liquid volume was estimated according to the Rackett equation (Smith and Van Ness, 1987). Critical properties of both components

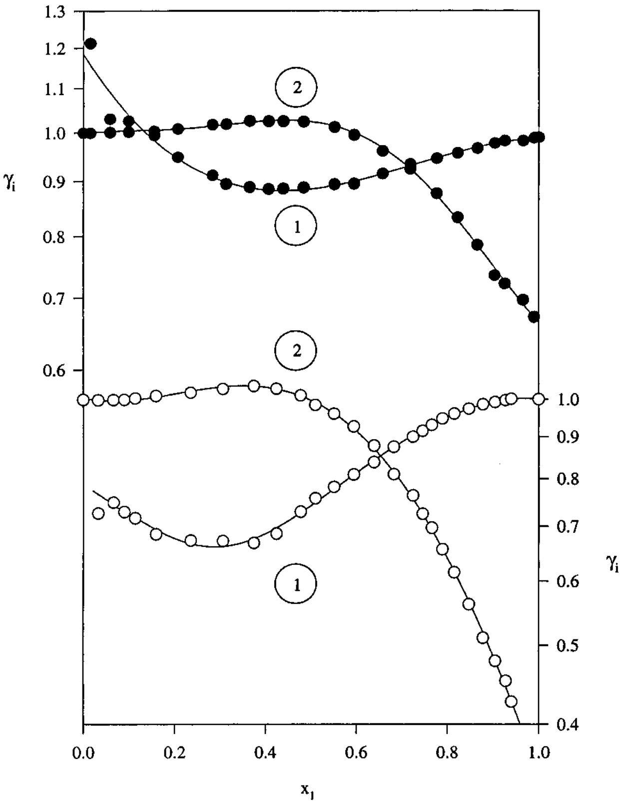


Figure 2. Activity coefficients of the system methanol (1) + diethylamine (2) at 101.3 and 300 kPa, calculated from experimental data: experimental data at 101.3 kPa (○); experimental data at 300 kPa (●); smoothed data (—).

Table 4. Experimental Data of Vapor Pressure of Pure Components

T/K	P°/kPa	T/K	P°/kPa	T/K	P°/kPa
		Methanol			
325.3	60.83	340.3	112.43	357.1	209.89
327.2	65.88	341.1	115.86	358.4	219.93
329.0	71.22	342.1	120.39	359.8	230.08
330.7	76.45	343.0	125.62	361.0	240.23
332.4	81.94	344.1	130.70	362.1	249.48
333.7	86.46	346.0	140.65	363.4	259.93
334.9	90.71	347.9	150.49	364.5	269.97
336.2	95.55	349.6	160.44	365.6	280.32
337.3	99.85	351.3	170.69	366.6	289.27
337.7	101.29	352.8	180.14	367.7	299.72
338.5	104.84	354.3	190.09	368.7	309.47
339.4	108.65	355.8	200.24		
		Diethylamine			
303.8	40.08	333.5	120.07	354.3	229.40
306.6	45.10	335.4	128.11	355.7	239.00
309.2	50.16	335.4	128.20	357.2	249.50
311.5	55.00	338.1	140.00	357.2	249.60
313.8	60.16	338.2	139.80	358.6	259.70
315.9	65.12	340.4	150.10	359.8	269.30
317.8	69.88	342.3	159.70	361.2	280.00
319.8	74.98	344.2	169.50	362.4	289.70
320.0	75.06	346.1	180.00	363.6	299.90
321.7	80.06	346.1	179.80	364.8	309.50
323.4	85.08	347.9	189.80	366.0	319.90
325.0	90.06	349.6	199.90	367.1	329.30
326.6	95.02	351.1	209.40	368.4	339.10
328.4	101.26	352.8	219.70	369.5	349.70
330.8	109.73				

Table 5. Antoine Coefficients, Eq 3[a]

compound	A_i	B_i	C_i
methanol	6.767 72	1304.592	63.608
diethylamine	6.481 47	1342.957	28.358

[a] Determined from experimental information using the equilibrium cell and the components used in this work.

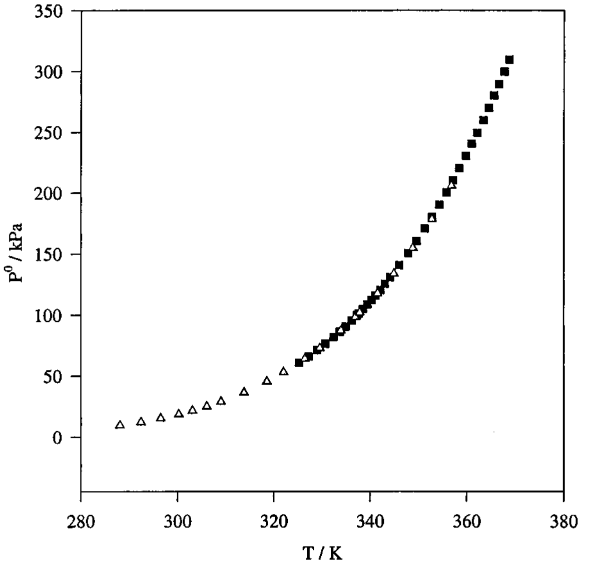


Figure 3. Vapor pressures of methanol: (■) this work; (△) data of Ambrose and Sprake (1970).

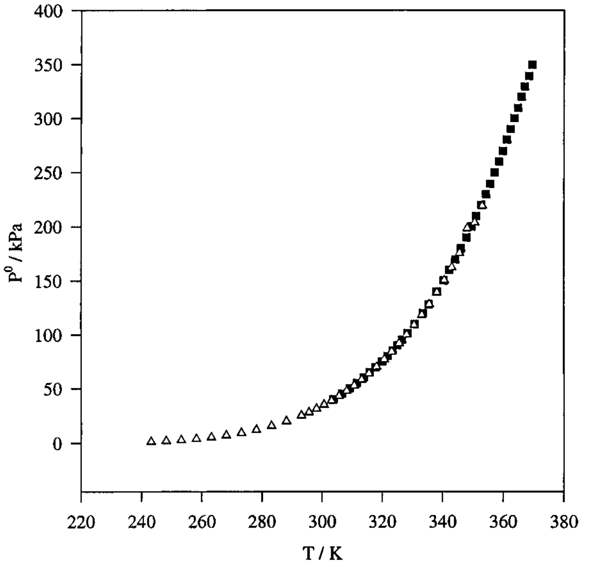


Figure 4. Vapor pressures of diethylamine: (■) this work; (△) data of Wolff and Schiller (1985).

were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 5% to the activity coefficients in the binary of methanol with diethyamine at 101.3 kPa and less than 7% at 300 kPa; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Tables 2 and 3 and are estimated accurate to within ±3%. The results reported in these tables indicate that the system exhibits combined negative and positive deviations from ideal behavior, depending on the concentration of methanol, and sharp maximum boiling point azeotropes are present in the range of concentrated methanol.

Table 6. Consistency Statistics of the VLE Data for the System Methanol (1) + Diethylamine (2) at 101.3 and 300 kPa

P/kPa	$100 \times \overline{\delta y}$[a]	$\overline{\delta P}$/kPa[b]
101.3	0.941	0.321
300.0	0.737	1.387

[a] $\overline{\delta y} = 1/N\ \Sigma|\delta y|$ (where $\delta y = y_{\text{exptl}} - y_{\text{calcd}}$, N = number of data points). [b] $\overline{\delta P} = 1/N\ \Sigma|\delta P|$(where $\delta P = P_{\text{exptl}} - P_{\text{calcd}}$).

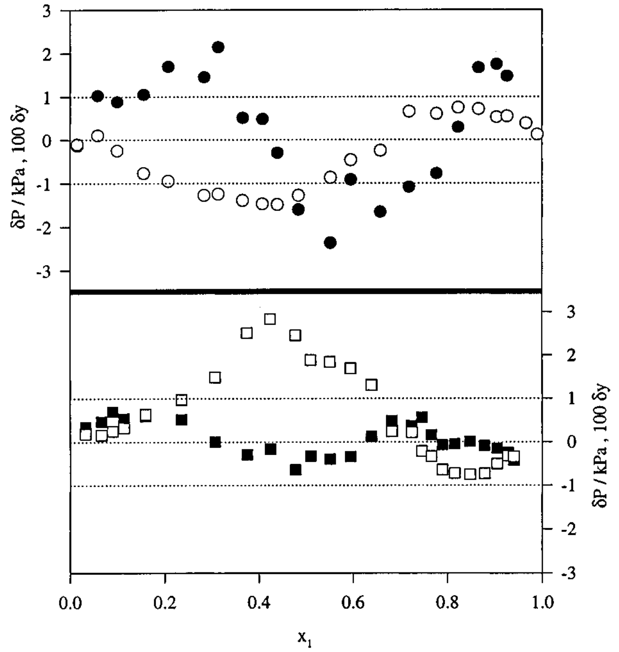


Figure 5. Consistency residuals plot: 100 × δy at 300 kPa (○); δP/kPa at 300 kPa (●); 100 × δy at 101.3 kPa (□); δP/kPa at 101.3 kPa (■).

The VLE data reported in Tables 2 and 3 were found to be thermodynamically consistent according to the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977), using a two-parameter Legendre polynomial. Consistency statistics are reported in Table 6. However, as can be seen in Figure 5, for both binaries the residuals of the Fredenslund test were not randomly distributed, probably as a consequence of the large heat of mixing not considered in the consistency analysis.

The variation of the excess energy (G^E) with the composition appears in Tables 2 and 3 and in Figure 6. From the indicated tables, it is concluded that the value of $G^E(x_1{=}0.5)$ at 101.3 kPa is almost three times lower than that of the system at 300 kPa, illustrating the strong dependency of the excess energy on temperature due to the negative heat of mixing. Figure 6 shows the clear inflectant behavior of the excess energy as pressure increases. Such an inflectant behavior of G^E is confirmed by the singular double intersection of activity coefficients observed in the high-pressure range of Figure 2; each intersection corresponds to a stationary point of the excess energy. It is interesting to note that the deviation from ideal behavior of the activity coefficient of methanol changes from negative to positive as pressure (as well the temperature) increases. According to the chemical theory, as discussed by Prausnitz et al. (1986), positive deviations should be expected when the components of the mixture tend to associate, while negative deviations from ideality are usual in cross-association. Mixed deviations in the system methanol + diethylamine can be explained in terms of a competitive self-association between pure species (fundamentally induced by OH···H bonding in the alcohol) and the cross-

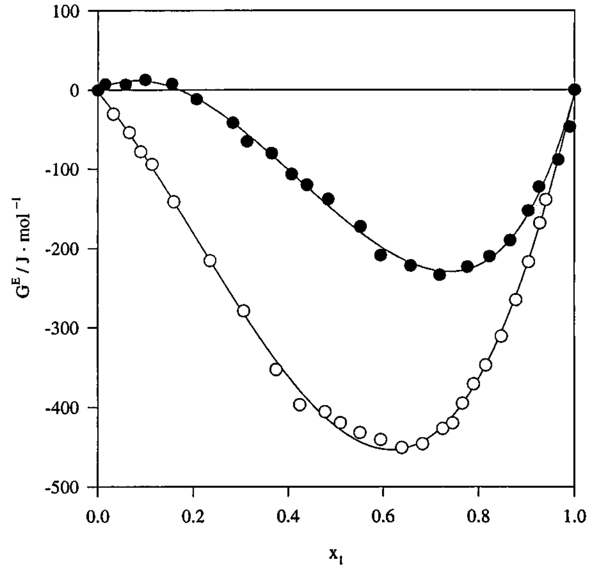


Figure 6. Excess Gibbs energy of the system methanol (1) + diethylamine (2) at 101.3 and 300 kPa: experimental data at 101.3 kPa (○), calculated from experimental data; experimental data at 300 kPa (●); smoothed data (—).

association between constituents (which gives place to the hydrogen bonding OH···N).

As pointed by Wisniak et al. (1996), when fugacity coefficients of the vapor phase depend weakly on the vapor phase concentration, a necessary condition of polyazeotropy in associated systems is the inflection of the liquid phase excess energy on composition. In addition, when organic systems are taken under consideration, all the experimental evidence of polyazeotropy shows that multiple azeotropes are observed in the neighborhood of a Bancroft point (where the vapor pressure of the pure constituents becomes equal). Some of the previous conditions are found in our data of the system methanol + diethylamine, for which Srivastava and Smith (1985) have found experimentally two azeotropes at 398.58 K. As indicated before, the excess Gibbs energy of the system inflects with composition for increasing pressure, inducing compositional inflections in the dew and in the bubble point pressure curves as can be seen in the side rich in amine in Figure 1. In the concentration range under consideration, a second minimum boiling azeotrope appears when the equilibrium pressure tends to the Bancroft point pressure. The Bancroft point of the system methanol (1) + diethylamine (2) is estimated in the range 380−390 K, corresponding to a pressure of the order of 500 kPa; these conditions were not attainable in this work due to operational limitations of the equipment. Nevertheless, by judging the available information, the polyazeotropic behavior of the system under consideration may be characterized as follows:

(1) At low pressures, cross-association between diethylamine and methanol is favored, and the system shows single maximum boiling point azeotropy.

(2) As pressure increases, the increasing equilibrium temperature increases the importance of association of the pure species in the range of diluted methanol. Mixed deviations from ideal behavior induce clear inflections on the excess energy. Under such conditions the system achieves its Bancroft point, allowing polyazeotropic behavior. The second azeotrope, rich in amine, corresponds to a minimum boiling point azeotrope, as can be confirmed by inspection of the data of Srivastava and Smith (1985).

(3) In the classification of Wisniak et al. (1996), the system seems to correspond to a case of convergent azeotropy, where the composition of neighboring azeotropes becomes closer as pressure (or temperature) increases, yielding a common point of tangent azeotropy. Above the point of tangent azeotropy, no azeotropic behavior can be observed. These facts are confirmed by the critical equilibrium line of the system, measured by Kay and Khera (1976), because no azeotropic composition ends in the critical range.

Table 7. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models

A. Statistics

	bubble-point temperature		dew-point temperature	
P/kPa	δT^a/K	$\delta y_1{}^b \times 100$	δT/K	$\delta x_1{}^c \times 100$
		A.1. Margules		
101.3	0.1	0.73	0.1	0.69
300.0	0.1	0.83	0.1	0.88
		A.2. UNIQUAC-A		
101.3	0.3	0.42	0.3	0.41
300.0	0.1	0.30	0.1	0.34

B. Parameters

B.1. Margules

i/j	A_{ij}^0	A_{ij}^1
1/2	−3.237	9.240×10^{-3}
2/1	−5.327	1.280×10^{-2}

B.2. UNIQUAC-A

P/kPa	$U_{12}{}^d$	$U_{21}{}^d$	$\alpha^{B_2C_2}$
101.3	−237.40	−2.5966	0.1495
300.0	−114.48	−21.556	0.4031

[a] $\delta T = \Sigma|T_{exptl} - T_{calcd}|/N$ (N = number of data points). [b] $\delta y = \Sigma|y_{exptl} - y_{calcd}|/N$. [c] $\delta x = \Sigma|x_{exptl} - x_{calcd}|/N$. [d] Parameters in K.

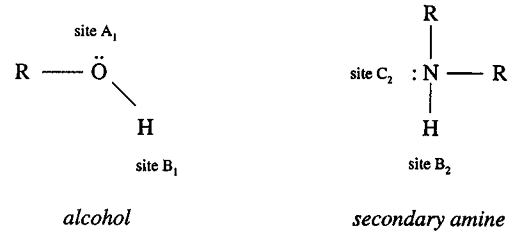
The activity coefficients were correlated with the Margules equation and the UNIQUAC model (Abrams and Prausnitz, 1975), as modified by Fu et al. (1995) for the treatment of association in the liquid phase. The predicted values appear in Figure 1. To include the strong dependency of the excess energy on temperature, the parameters of the Margules equation (A_{12}, A_{21}) were considered to be a linear function of the temperature

$$A_{ij} = A_{ij}^0 + A_{ij}^1 T \tag{4}$$

Parameters and pertinent statistics for the Margules model are shown in Table 7, from which it is concluded that the assumed model gives an excellent representation of the system. The Margules equation can be qualified as adequate for this system, due to its flexibility for representing inflections of the excess energy (Wisniak et al., 1996). However, it should be recognized that the Margules model is unable to explain possible molecular interactions in associating systems.

In the model proposed by Fu et al. (1995) [UNIQUAC-A model], the association can be treated as strong interactions between specific sites of associating molecules rather than a chemical reaction. This approach avoids the direct use of the chemical theory (Prausnitz et al., 1986), which may yield complex chemical equilibrium relations for the calculation of activity coefficients. In the UNIQUAC-A model, the excess Gibbs energy is considered an additive contribution of weak physical interactions, given by the UNIQUAC model (Abrams and Prausnitz, 1975), and the chemical contribution is based on an approximation of the association theory of Wertheim (1984a,b, 1986a,b). For describing the chemical contribution, a set of adjustable association parameters between association sites type A in the mol-

Table 8. Description of Association and Cross-Association Sites Used for the Correlation of the System Methanol (1) + Diethylamine (2) by Means of the UNIQUAC-A Excess Model (Fu et al., 1995)



Association type

$$\alpha^{A_1A_1} = \alpha^{B_1B_1} = \alpha^{C_2C_2} = \alpha^{B_2B_2} = \alpha^{B_1B_2} = 0$$

$$\alpha^{A_1B_1} \neq \alpha^{B_2C_2} \neq \alpha^{A_1B_2} = \alpha^{B_1C_2} \neq 0$$

Cross association

$$\alpha^{A_1B_2} = \alpha^{B_1C_2} = \sqrt{\alpha^{A_1B_1}\,\alpha^{B_2C_2}}$$

Table 9. Coefficients in Correlation of Boiling Points, Eq 5, for the System Methanol (1) + Diethylamine (2); Average Deviation and Root Mean Square Deviations in Temperature, rmsd

P/kPa	C_0	C_1	C_2	C_3	max dev[a]/K	avg dev[b]/K	rmsd[c]/K
101.3	15.72	19.85	0.50	−14.80	0.19	0.06	0.02
300.0	8.24	16.22	12.14	0.00	0.63	0.32	0.08

[a] Maximum deviation. [b] Average deviation. [c] Root mean square deviation.

ecule i and association sites type B in a molecule j ($\alpha^{A_iB_j} = \alpha^{B_jA_i}$) are needed. Considering the experimental evidence regarding association in the system methanol (1) + diethylamine (2), specifically, self-association of pure species and cross-association between the constituents, the sites have been selected as shown in Table 8. To reduce parameters, it has been assumed that the association parameter of methanol ($\alpha^{A_1B_1}$) is equivalent to that of ethanol (which is given in the work of Fu et al., 1995). Furthermore, it has been assumed that the cross-bondings N···H and H···O can be represented by numerically equivalent $\alpha^{A_1B_2}$, $\alpha^{B_1C_2}$ association parameters, which, in turn, are given by the geometric mean of the association parameters of pure species. These previous simplifications yield a reasonable total of three adjustable parameters per equilibrium isobar, the current UNIQUAC energy parameters (denoted by U_{12} and U_{21}), and the self-association parameter for diethylamine $\alpha^{B_2C_2}$. Pertinent parameters and fit statistics are shown in Table 7, from which it is concluded again that the assumed model gives a good representation of the system.

The boiling point of the solution at both pressure levels was correlated with its composition by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1T_1^0 + x_2T_2^0 + x_1x_2\sum_{k=0}^{m} C_k(x_1 - x_2)^k \qquad (5)$$

In this equation T_i^0/K is the boiling point of the pure component i and m is the number of terms in the series expansion of ($x_1 - x_2$). The various constants of eq 5 are reported in Table 9, which also contains information indicating the degree of goodness of the correlation.

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