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Vapor−Liquid Equilibria at 101.3 kPa for Diethylamine + Chloroform

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Vapor−liquid equilibria for diethylamine (1) + chloroform (2) were measured at 101.3 kPa. This system shows negative deviation from ideal behavior and presents a maximum boiling point azeotrope at 341.55 K at $x_1 = 0.4145$. The experimental data were well correlated with the Wilson, UNIQUAC, and NRTL equations.

Introduction

The development and extension of prediction methods such as ASOG or UNIFAC require experimental data on some representative binary systems. As can be seen after the last revision by Hansen et al. (*1*), the UNIFAC-group interaction parameters between CNH (main group 15) and CCl_3 (main group 23) are not available. This is because of the lack of vapor−liquid equilibria measurements for systems including these groups.

In this paper isobaric vapor−liquid equilibrium measurements on diethylamine (1) + chloroform (2) are reported. The results are correlated by the Wilson, UNIQUAC, and NRTL equations.

Experimental Section

Purity of Materials. Diethylamine was supplied by Fluka Chemical Corp., and chloroform was supplied by Merck. The reagents were of analytical grade and diethylamine (99.5+%) was used without further purification. Chloroform (99.0−99.4%) was purified from ethanol (about 0.5%) with sulfuric acid, washed, dried with $CaCl_2$, and distilled twice. The purity of both reagents was checked by refractive indices, densities at 293.15 K, and boiling points at 101.3 kPa (see Table 1); results were confirmed by gas chromatography analysis.

Apparatus. Measurements were made using an isobaric stage still consisting of a vapor−liquid equilibrium apparatus 0601 with vacuum constant holder VKH-100 and digital thermometer DT4 (all from Fischer Co.). When a constant boiling temperature was established, samples of the liquid and the condensate were taken for analysis. Pressure and temperature were determined at an accuracy of $\Delta P = \pm 0.067$ kPa and $\Delta T = \pm 0.05$ K.

Analysis. The composition of equilibrium samples was obtained by measuring their refractive index at 293.0 ± 0.1 K with an Abbe precision refractometer (with an accuracy of ±0.0002). Analysis was made by means of a calibration curve, fitted by the equation

$$x_1 = 2788.028[n_D^{20}]^3 - 11867.899[n_D^{20}]^2 + 16820.228[n_D^{20}] - 7936.780 \quad (1)$$

with a correlation coefficient of 0.9987 and maximum error in the composition measurements of 0.0077. Table 2 shows the refractive index composition values.

Table 1. Physical Properties of Pure Compounds

	ϱ (kg·m^{-3}/293.15 K)		T_b/K (1 atm)		n_D^{20}	
	obsd	ref 2	obsd	ref 2	obsd	ref 2
diethylamine	704.80	705.60	329.25	329.45	1.3863	1.3864
chloroform	1480.3	1483.2	334.45	334.85	1.4459	1.4459

Table 2. Refractive Index Composition for Diethylamine (1) + Chloroform (2) at 293.15 K

x_1	n_D^{20}	x_1	n_D^{20}	x_1	n_D^{20}
0.0000	1.4459	0.3545	1.4243	0.7170	1.4056
0.0744	1.4405	0.4339	1.4203	0.8034	1.3996
0.1617	1.4349	0.4833	1.4181	0.8778	1.3949
0.2235	1.4315	0.5557	1.4146	0.9339	1.3915
0.2994	1.4272	0.6005	1.4119	1.0000	1.3863

Results

The vapor−liquid equilibrium results at 101.3 kPa for diethylamine (1) + chloroform (2) are presented in Table 3 and in Figures 1 and 2. The system presents maximum boiling point azeotrope at 341.55 K with $x_1 = 0.4145$.

The activity coefficient at each data point was calculated by using

$$\gamma_i = y_i \phi_i P/(x_i P_i^0) \quad (2)$$

where x_i and y_i are the liquid and vapor mole fractions, P is the pressure, ϕ_i is the fugacity coefficient, and P_i^0 is the vapor pressure of the pure component. Fugacity coefficients were calculated by means of a virial equation

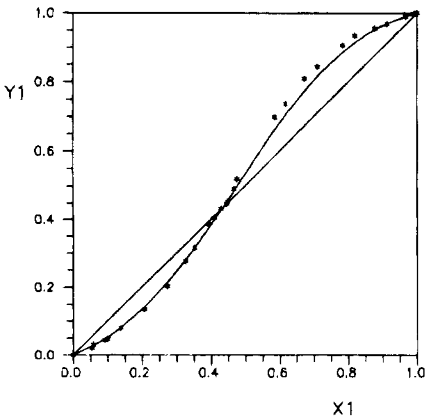

Figure 1. $y-x$ phase equilibrium diagram for diethylamine (1) + chloroform (2) at 101.3 kPa: *, experimental; −, Wilson.

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Table 3. Vapor–Liquid Equilibrium Data and Deviations for Diethylamine (1) + Chloroform (2) at 101.3 kPa

measured values			residuals NRTL		residuals UNIQUAC		residuals Wilson	
T/K	x_1	y_1	ΔT/K	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1
334.45	0.0000	0.0000		0.0		0.0		0.0
334.55	0.0546	0.0211	−0.99	−0.0005	−0.23	0.0008	−0.98	−0.0009
335.45	0.0591	0.0311	−0.56	0.0051	0.27	0.0094	−0.55	0.0048
336.15	0.0917	0.0442	−0.52	−0.0009	0.31	0.0120	−0.51	−0.0012
336.25	0.1005	0.0472	−0.56	−0.0033	0.25	0.0115	−0.54	−0.0036
337.35	0.1391	0.0799	−0.38	0.0004	0.21	0.0218	−0.35	0.0004
338.75	0.2066	0.1358	−0.28	−0.0037	−0.14	0.0210	−0.26	−0.0031
340.05	0.2738	0.2031	−0.12	−0.0099	−0.33	0.0060	−0.11	−0.0087
340.85	0.3262	0.2776	−0.02	−0.0030	−0.34	−0.0004	−0.02	−0.0016
341.05	0.3518	0.3149	−0.03	−0.0006	−0.36	−0.0050	−0.04	0.0006
341.45	0.3939	0.3852	0.06	0.0079	−0.20	−0.0072	0.05	0.0088
341.45	0.4111	0.4044	0.04	0.0032	−0.19	−0.0152	0.02	0.0040
341.55	0.4294	0.4333	0.08	0.0047	−0.09	−0.0170	0.06	0.0053
341.55	0.4468	0.4487	0.09	−0.0037	−0.03	−0.0275	0.07	−0.0033
341.55	0.4487	0.4545	0.09	−0.0013	−0.02	−0.0255	0.07	−0.0010
341.55	0.4680	0.4911	0.18	0.0050	0.14	−0.0213	0.16	0.0050
341.45	0.4757	0.5199	0.08	0.0186	0.08	−0.0092	0.06	0.0185
340.25	0.5866	0.6973	0.03	0.0309	0.42	0.0053	0.02	0.0296
339.75	0.6167	0.7361	0.02	0.0292	0.49	0.0069	0.02	0.0278
338.75	0.6720	0.8084	0.07	0.0323	0.63	0.0175	0.08	0.0310
337.85	0.7098	0.8483	0.03	0.0253	0.61	0.0155	0.06	0.0241
335.85	0.7821	0.9058	−0.05	0.0186	0.47	0.0177	−0.02	0.0180
334.55	0.8180	0.9336	−0.21	0.0170	0.23	0.0194	−0.18	0.0167
333.15	0.8761	0.9546	−0.11	0.0024	0.20	0.0073	−0.08	0.0025
331.75	0.9126	0.9686	−0.31	−0.0028	−0.12	0.0022	−0.29	−0.0026
330.15	0.9652	0.9892	−0.42	−0.0023	−0.37	0.0004	−0.42	−0.0022
329.25	0.9882	0.9973	−0.60	−0.0012	−0.60	−0.0004	−0.60	−0.0011
329.25	1.000	1.000		0.0		0.0		0.0
RMSD[a]			0.33	0.0136	0.33	0.0142	0.32	0.0131
AAD[b]				0.0090		0.0112		0.0087

[a] RMSD = $\sum_i \mathrm{dev}_i^2/N$. [b] AAD = $\sum_i |\mathrm{dev}_i|/N$, where $\mathrm{dev}_i = \Delta T_i$ or Δy_{1_i} and N is the number of data points.

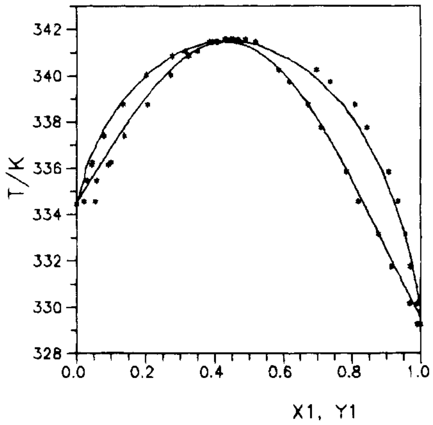

Figure 2. T–y–x diagram for diethylamine (1) + chloroform (2) at 101.3 kPa: *, experimental; —, Wilson.

Table 4. Correlation Constants (J/mol)

NRTL	$\tau_{12} = -0.3882706$	$\tau_{21} = -0.5016800$
UNIQUAC	$\tau_{12} = 3.7641684$	$\tau_{21} = 0.0349858$
Wilson	$\Lambda_{12} = 1.8145746$	$\Lambda_{21} = 1.4525650$

truncated after the second term

$$\ln \phi_i = P(2\sum_{j=1}^{2} y_j B_{ij} - B)/(RT) \qquad (3)$$

where B is the second virial coefficient, calculated by

$$B = \sum_{i=1}^{2} \sum_{i=1}^{2} y_i y_j B_{ij} \qquad (4)$$

where B_{ij} represents interactions between molecules i and j. To predict the virial coefficients from available data, we used the Hayden and O'Connell (*3*) method.

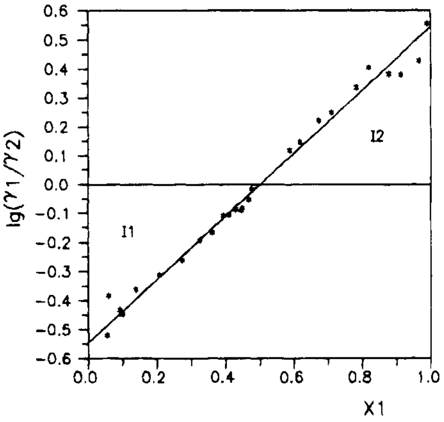

Figure 3. Area test for diethylamine (1) + chloroform (2).

Pure components vapor pressures, P_i^0, were calculated according to Antoine's equation:

$$\log_{10}(P_i^0)(\mathrm{Torr}) = A_i - \frac{B_i}{T/\mathrm{K} + C_i} \qquad (5)$$

The following values for A_i, B_i, and C_i were used:

	A_i	B_i	C_i
diethylamine (*4*)	16.0545	2595.01	−53.15
chloroform (*4*)	15.9732	2696.79	−46.16

The activity coefficient data were fitted into the NRTL (*5*), UNIQUAC (*6*), and Wilson (*7*) correlations. The NRTL and Wilson equations correlated the composition data properly—their average absolute deviations (AAD) for vapor phase compositions are less than 0.01, and root-mean-square deviations (RMSD) are smaller. The parameters obtained are given in Table 4. The experimental values regarding composition and their fit to the Wilson equation are plotted in Figure 1.

Thermodynamic consistency was examined by using several tests. An iterative nonlinear least-squares minimization procedure described in detail by Fredenslund et al. (*8*) was carried out to calculate the AADs between the experimental and calculated y_1 values. According to this test, the data set is considered to be consistent if the AAD (see Table 3) in y is less than 0.01. The estimated standard deviations for the vapor phase compositions and temperature for the three equations are reported in Table 3.

The results were also assessed for thermodynamic consistency by applying the Herington (*9*) and Redlich and Kister (*10*) tests. A plot of the tests is presented on Figure 3. Both areas are $I_1 = 0.132059$ and $I_2 = 0.133414$, respectively. Using the Herington test we have

$$I = \int_0^1 \lg(\gamma_1/\gamma_2)\mathrm{d}x = I_1 + I_2 = 0.00135$$

$$\Sigma = |I_1| + |I_2| = 0.265473$$

$$D = (100I)/\Sigma = 0.5104$$

$$J = 150(T_{\max} - T_{\min})/T_{\min} = 5.604$$

Since D is less than J, the results are thermodynamically consistent. The Redlich and Kister test yielded the ratio $R = |I_1|/|I_2| = 0.9898$, which is close to unity.

As the results conform entirely to the above different tests, it may be concluded that they are thermodynamically consistent.

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