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Vapor−Liquid Equilibrium of Binary Mixtures Containing Diethylamine + Diisopropylamine, Diethylamine + Dipropylamine, and Chloroform + Diisopropylamine at 101.3 kPa, and Vapor Pressures of Dipropylamine

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Isobaric vapor−liquid equilibria have been measured with a dynamic still for the systems diethylamine + diisopropylamine, diethylamine + dipropylamine, and chloroform + diisopropylamine. The chloroform + diisopropylamine system shows an azeotrope in the range 0−0.040 mole fraction of chloroform. The thermodynamic consistency of the experimental data was checked by means of modified Dechema test. The activity coefficients were correlated by means of the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. UNIFAC and ASOG predictions have been also used. Experimental vapor pressures of dipropylamine are also included and the Antoine constants were determined.

Introduction

Vapor−liquid equilibria are required both for practical use such as in the design and operation of distillation equipment and for theoretical use to determine the thermodynamic properties of binary mixtures. The development and extension of prediction methods such as UNIFAC or ASOG 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 measurements for systems including these groups. Ninov et al.[2] have published a paper of vapor−liquid equilibria at 101.3 kPa for diethylamine + chloroform. This system shows a maximum boiling point azeotrope at 341.55 K at 0.415 mole fraction of diethylamine.

We have measured the vapor−liquid equilibria at 101.3 kPa of diethylamine + diisopropylamine, diethylamine + dipropylamine, and chloroform + diisopropylamine systems. Data for the three systems were not found in the literature. The vapor−liquid equilibrium of chloroform + dipropylamine system could not be measured because of the formation of crystals of a chlorhydrate when heating in the ebulliometer. Nevertheless, we have measured the densities and refractive indexes of the mixtures.

Experimental Section

Diethylamine (99.5 mol %) and chloroform (99.5 mol %) were supplied by Fluka and were used without further purification. Diisopropylamine (>99.0 mol %) and dipropylamine (>99.0 mol %) were purified by distillation in a laboratory column. The purity of the materials was checked by gas−liquid chromatography (GLC) and was better than 99.7 mol %. All products were degassed using ultrasound and dried on molecular sieves (type pore diameter 3 Å from Fluka) before use. Densities, refractive indexes, and boiling points of the pure substances are given in Table 1 and compared with literature values of Riddick et al.[3]

Measurements were made in an all-glass vapor recirculating type equilibrium still, similar to the apparatus proposed by Gillespie.[4] In this work we have used an apparatus manufactured by Fritz GmbH (Normag, Germany). The details of the still and its operations were described in a previous paper.[5] The equilibrium temperature was measured with a platinum 100Ω resistance thermometer with an accuracy of ±0.1 K. The pressure was maintained constant with a digital manometer regulator with an accuracy of ±0.1 kPa.

Vapor condensate and liquid-phase compositions of three binary systems were determined by densimetry and refractometry. Densities were measured using an Anton Paar vibrating tube densimeter, with an accuracy of ±0.000 01 g cm^{-3}, that was previously calibrated at atmospheric pressure with doubly distilled water and nonane. The temperature of the densimeter was mantained at $T =$ 298.15 K by means of a semiconductor Peltier element with a precision of cell sensor of ±0.01 K. Refractive indexes were measured with a Mettler RE50 refractometer, accuracy ±0.000 01, and temperature control was measured by Peltier effect (as the densimeter), temperature precision ±0.01 K. Pattern curves density and refractive index vs mole fraction were used to calculate the compositions of the vapor and liquid phases. All samples were prepared by weighing with a Salter electronic balance (Model ER-182A, accuracy ±0.0001 g). The uncertainty of comparison measurements was estimated to be ±0.001 mole fraction. Table 2 shows the density and refractive index−composition values.

Results and Discussion

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = \frac{y_i \phi_i P}{x_i P_i^\circ} \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, ϕ_i is the fugacity cofficient, P is the total pressure, and P_i° is the vapor pressure of pure component i. These vapor pressures were calculated from the Antoine equation

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Table 1. Physical Properties of Pure Compounds: Densities ρ and Refractive Indexes n_D at 298.15 K, and Normal Boiling Points T_b

	ρ (kg·m^{-3})		n_D		T_b (K)	
	obsd	lit.[a]	obsd	lit.[a]	obsd	lit.
diethylamine	698.99	701.6	1.381 70	1.382 5	328.5	328.70
diisopropylamine	710.95	710.0	1.388 93	not available	357.1	356.72
dipropylamine	733.26	732.9	1.401 32	1.401 8	382.3	382.4
chloroform	1471.56	1479.70	1.441 91	1.442 93	334.1	334.328

[a] Riddick et al.[3]

Table 2. Densities and Refractive Indexes of Diethylamine (1) + Diisopropylamine (2), Diethylamine + Dipropylamine (2), Chloroform (1) + Diisopropylamine (2), and Chloroform (1) + Dipropylamine (2) Mixtures as a Function of the Mole Fraction (x_1) of Compound 1 at 298.15 K

x_1	ρ/kg·m^{-3}	n_D	x_1	ρ/kg·m^{-3}	n_D	x_1	ρ/kg·m^{-3}	n_D
			Diethylamine (1) + Diisopropylamine (2)					
0.000	710.95	1.388 93	0.351	707.72	1.386 87	0.698	703.72	1.384 48
0.051	710.51	1.388 58	0.399	707.20	1.386 54	0.750	703.01	1.384 05
0.100	710.16	1.388 31	0.449	706.56	1.386 25	0.801	702.23	1.383 66
0.146	709.67	1.388 13	0.499	706.05	1.385 95	0.850	701.52	1.383 33
0.203	709.15	1.387 73	0.551	705.47	1.385 62	0.899	700.73	1.382 78
0.252	708.64	1.387 48	0.602	704.94	1.385 14	0.951	699.91	1.382 36
0.300	708.19	1.387 11	0.652	704.36	1.384 71	1.000	698.99	1.381 70
			Diethylamine (1) + Dipropylamine (2)					
0.000	733.26	1.401 32	0.356	723.23	1.397 46	0.697	711.36	1.390 16
0.047	732.01	1.401 15	0.399	721.71	1.396 25	0.751	709.35	1.388 68
0.099	730.62	1.400 14	0.449	720.61	1.395 38	0.800	707.42	1.387 64
0.152	729.15	1.399 47	0.501	718.42	1.393 63	0.851	705.33	1.386 21
0.195	727.93	1.398 66	0.552	716.66	1.393 10	0.897	703.47	1.385 52
0.255	726.15	1.398 82	0.603	714.91	1.391 98	0.949	701.28	1.384 13
0.299	724.80	1.397 81	0.654	712.96	1.390 54	1.000	698.99	1.381 70
			Chloroform (1) + Diisopropylamine (2)					
0.000	710.95	1.388 93	0.357	908.34	1.408 35	0.701	1164.10	1.426 05
0.037	728.45	1.390 82	0.409	943.00	1.411 31	0.755	1212.49	1.428 69
0.105	762.38	1.394 34	0.468	983.79	1.414 51	0.803	1256.33	1.430 80
0.157	790.23	1.397 23	0.514	1016.48	1.416 84	0.852	1305.57	1.433 40
0.208	818.05	1.400 04	0.547	1040.23	1.418 37	0.901	1357.49	1.436 04
0.241	837.29	1.401 92	0.598	1079.69	1.420 90	0.948	1409.83	1.438 90
0.304	875.06	1.405 39	0.659	1128.65	1.424 00	1.000	1471.56	1.441 91
			Chloroform (1) + Dipropylamine (2)					
0.000	733.26	1.401 32	0.355	921.15	1.414 72	0.695	1164.89	1.428 10
0.054	758.29	1.403 21	0.398	947.96	1.416 43	0.743	1206.53	1.430 02
0.097	779.28	1.404 81	0.454	984.65	1.418 67	0.808	1265.46	1.432 59
0.146	803.71	1.406 64	0.518	1028.28	1.421 12	0.861	1317.35	1.434 70
0.208	836.76	1.409 06	0.552	1053.24	1.422 49	0.900	1357.56	1.436 77
0.263	867.18	1.411 23	0.608	1095.28	1.424 78	0.944	1405.22	1.439 03
0.291	883.09	1.412 23	0.661	1136.94	1.426 38	1.000	1471.56	1.441 91

$$\log(P/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \tag{2}$$

where the constants A_i, B_i, and C_i are reported in Table 3. The values of the Antoine constants for diethylamine, diisopropylamine, and chloroform were obtained from Riddick et al.[3] The corresponding values of dipropylamine were determined from experimental vapor pressures using the same still used in this work, because there are no values for this compound in the literature. Table 4 shows experimental pressures as function of temperature. The standard deviation resulted $\sigma = 0.25$, and was computed using eq 3, where n is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n} (P^\circ_{\text{exptl}} - P^\circ_{\text{calcd}})^2}{n} \right)^{1/2} \tag{3}$$

The fugacity coefficients for the binary mixture ϕ_1 and ϕ_2 were calculated by the expressions

$$\ln \phi_1 = \frac{P}{RT}(B_{11} + y_2^{\,2}\delta_{12}) \tag{4}$$

$$\ln \phi_2 = \frac{P}{RT}(B_{22} + y_1^{\,2}\delta_{12}) \tag{5}$$

where P is the total pressure and T is the experimental temperature of each point, y_1 and y_2 are the vapor mole fractions of compounds 1 and 2, B_{11} and B_{22} represent the virial coefficient for pure compounds, and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$, where B_{12} is the cross section virial coefficient.

Pitzer's correlation for the second virial coefficient was extended by Reid et al.[6] for mixtures to calculate B_{12} by

$$B_{12} = \frac{RT_{c12}}{P_{c12}}(B^\circ + w_{12}B^1) \tag{6}$$

where B° and B^1 are functions which depend exclusively on reduced temperature. They can be represented satisfactorily by

$$B^\circ = 0.083 - 0.422/T_r^{\,1.6} \tag{7}$$

$$B^1 = 0.139 - 0.172/T_r^{\,4.2} \tag{8}$$

The mixing rules of mixing proposed by Prausnitz et al.[7] for the calculation of w_{12}, T_{c12}, and P_{c12} are

Table 3. Antoine Coefficients, Eq 2

compound	A_i	B_i	C_i
diethylamine	4.926 49	583.297	−129.005
diisopropylamine	5.698 125	1038.183	−75.550
dipropylamine	5.398 46	909.505	−114.24
chloroform	5.962 88	1106.94	−54.598

Table 4. Experimental Vapor Pressures of Dipropylamine as a Function of Temperature

T/K	$P°_{\mathrm{exptl}}$/kPa	$P°_{\mathrm{calcd}}$/kPa	$P°_{\mathrm{exptl}} - P°_{\mathrm{calcd}}$/kPa
382.3	101.3	101.1	0.2
380.4	95.5	95.6	−0.1
378.4	89.8	90.1	−0.3
375.9	84.1	83.6	0.5
374.1	78.4	79.0	−0.6
371.3	72.7	72.4	0.3
368.9	67.0	67.0	0.0
366.3	61.3	61.6	−0.3
363.1	55.6	55.3	0.3
360.0	49.9	49.8	0.1
356.6	44.2	44.2	0.0
352.8	38.5	38.5	0.0
348.6	32.8	32.9	−0.1
343.8	27.1	27.3	−0.2
337.8	21.4	21.3	0.1
330.7	15.7	15.7	0.0
321.3	10.0	10.1	−0.1

$$w_{12} = \frac{w_1 + w_2}{2} \tag{9}$$

where w_1 and w_2 are the acentric factors

$$T_{c12} = (T_{c1}T_{c2})^{0.5} \tag{10}$$

where T_{c1} and T_{c2} are the critical temperatures.

$$P_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} \tag{11}$$

where Z_{c12} is calculated by

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} \tag{12}$$

Z_{c1} and Z_{c2} are the critical compressibility factors, and V_{c12} is defined by the expression

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2}\right)^3 \tag{13}$$

where V_{c1} and V_{c2} are the critical volumes of compounds 1 and 2. Values of critical volumes have been obtained from literature values.[8]

The vapor−liquid equilibrium data for the three systems were measured at 101.3 kPa and are presented in Table 4 with an accuracy in the mole fractions of ± 0.001. The T−x_1−y_1 diagrams are shown in Figures 1−3.

The activity coefficients were correlated with Margules,[9] van Laar,[10] Wilson,[11] NRTL (Renon and Prausnitz[12]), and UNIQUAC (Abrams and Prausnitz[13]) equations. To determine the constants of each model, the "VLE calc" method suggested by Gess et al.[14] has been used. Parameters for the equation were estimated by an iterative solution, using the maximum likelihood regression of the objective function Q_i [15] with the activity coefficients obtained from the consistency test as experimental values,

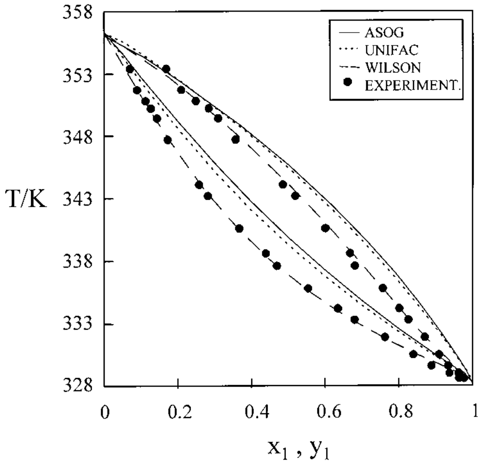

Figure 1. T−x_1−y_1 diagram for diethylamine (1) + diisopropylamine (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; ···, UNIFAC prediction; —, ASOG prediction.

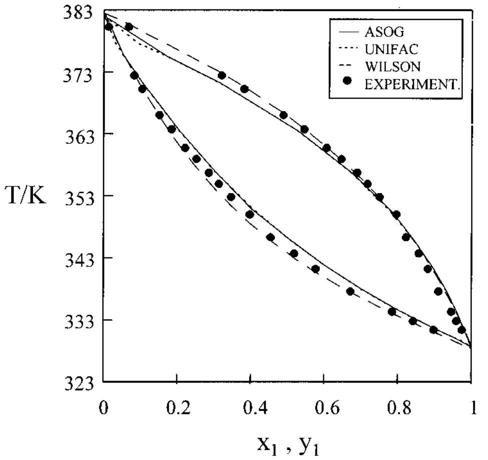

Figure 2. T−x_1−y_1 diagram for diethylamine (1) + dipropylamine (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; ···, UNIFAC prediction; —, ASOG prediction.

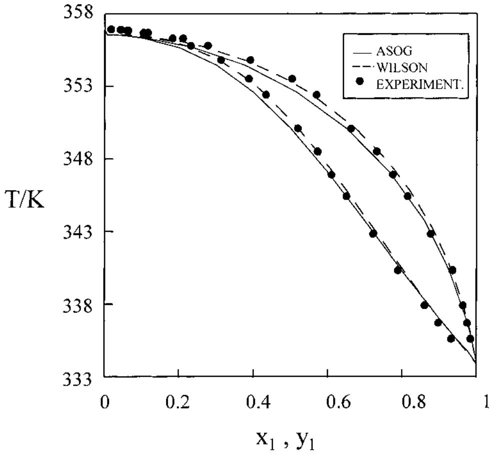

Figure 3. T−x_1−y_1 diagram for chloroform (1) + diisopropylamine (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; —, ASOG prediction.

$$Q_i = \sum_{i=1}^{n}\left(\frac{\gamma_{\mathrm{exptl}} - \gamma_{\mathrm{calcd}}}{\gamma_{\mathrm{exptl}}}\right)^2 \tag{14}$$

where γ_{exptl} are the activity coefficients calculated from experimental data and γ_{calcd} are the coefficients calculated with the y and T of correlations. The parameters along with

Table 5. Vapor−Liquid Equilibrium Data for the Diethylamine (1) + Diisopropylamine (2), Diethylamine (1) + Dipropylamine (2), and Chloroform (1) + Diisopropylamine (2) Systems. Liquid-Phase Mole Fraction (x_1); Vapor-Phase Mole Fraction (y_1); Boiling Temperature (T), Activity Coefficients (γ_1 and γ_2), and Fugacity Coefficients (ϕ_1 and ϕ_2) at 101.3 kPa

x_1	y_1	T/K	γ_1	ϕ_1	γ_2	ϕ_2
Diethylamine (1) + Diisopropylamine (2)						
0.000	0.000	357.1		0.971		0.956
0.070	0.168	353.6	1.106	0.970	0.941	0.954
0.089	0.209	351.9	1.132	0.969	0.962	0.954
0.112	0.249	351.0	1.098	0.969	0.963	0.953
0.126	0.284	350.4	1.132	0.969	0.951	0.953
0.143	0.310	349.6	1.112	0.969	0.958	0.953
0.172	0.357	347.9	1.116	0.968	0.975	0.952
0.258	0.485	344.3	1.118	0.967	0.978	0.950
0.282	0.519	343.4	1.123	0.966	0.972	0.950
0.367	0.601	340.8	1.078	0.965	0.997	0.948
0.439	0.668	338.8	1.063	0.964	1.002	0.947
0.469	0.681	337.8	1.046	0.964	1.052	0.947
0.554	0.757	336.0	1.040	0.963	1.015	0.946
0.635	0.802	334.4	1.011	0.962	1.069	0.945
0.680	0.827	333.5	1.001	0.962	1.100	0.945
0.763	0.871	332.1	0.983	0.962	1.164	0.944
0.840	0.910	330.7	0.976	0.961	1.265	0.943
0.889	0.935	329.8	0.976	0.961	1.360	0.943
0.938	0.962	329.2	0.970	0.960	1.455	0.942
0.964	0.978	328.8	0.973	0.960	1.473	0.942
1.000	1.000	328.5		0.960		0.942
Diethylamine (1) + Dipropylamine (2)						
0.000	0.000	382.3		0.979		0.960
0.013	0.067	380.45	1.264	0.978	0.958	0.959
0.082	0.320	372.6	1.135	0.976	0.952	0.956
0.104	0.381	370.4	1.119	0.975	0.951	0.955
0.151	0.488	366.2	1.088	0.973	0.949	0.954
0.184	0.545	363.9	1.053	0.973	0.947	0.953
0.221	0.606	360.9	1.049	0.972	0.949	0.952
0.252	0.646	359.1	1.025	0.971	0.945	0.951
0.286	0.688	356.9	1.017	0.970	0.942	0.950
0.313	0.717	355.1	1.015	0.970	0.946	0.950
0.346	0.750	353.0	1.014	0.969	0.947	0.949
0.397	0.796	350.2	1.011	0.968	0.929	0.948
0.454	0.822	346.5	1.010	0.966	1.028	0.947
0.518	0.857	343.9	0.994	0.965	1.034	0.943
0.577	0.882	341.4	0.988	0.964	1.074	0.942
0.671	0.911	337.8	0.977	0.962	1.204	0.941
0.785	0.946	334.5	0.961	0.962	1.286	0.938
0.842	0.960	333.0	0.953	0.961	1.382	0.937
0.898	0.975	331.6	0.949	0.960	1.208	0.936
1.000	1.000	328.5		0.960		0.934
Chloroform (1) + Diisopropylamine (2)						
0.000	0.000	357.1		0.977		0.956
0.007	0.007	357.1	0.491	0.977	0.945	0.956
0.017	0.017	357.1	0.492	0.977	0.945	0.956
0.042	0.044	357.1	0.516	0.977	0.944	0.956
0.059	0.063	357.0	0.527	0.977	0.944	0.956
0.104	0.116	356.9	0.552	0.977	0.939	0.956
0.182	0.210	356.5	0.578	0.976	0.930	0.956
0.231	0.277	356.0	0.609	0.976	0.919	0.956
0.312	0.391	355.0	0.654	0.976	0.892	0.955
0.387	0.503	353.7	0.703	0.975	0.850	0.955
0.433	0.569	352.6	0.734	0.975	0.824	0.954
0.519	0.667	350.3	0.766	0.974	0.806	0.954
0.572	0.732	348.7	0.799	0.973	0.767	0.953
0.610	0.775	347.1	0.832	0.973	0.744	0.952
0.650	0.815	345.6	0.858	0.973	0.715	0.952
0.722	0.877	343.0	0.899	0.972	0.651	0.951
0.789	0.936	340.5	0.948	0.971	0.485	0.949
0.861	0.965	338.1	0.965	0.970	0.437	0.948
0.898	0.976	336.9	0.972	0.970	0.426	0.948
0.933	0.985	335.8	0.978	0.970	0.421	0.947
1.000	1.000	334.1		0.969		0.946

the average deviation in T (ΔT) and the average deviation in y (Δy) are listed in Table 6.

Table 6. Correlation Parameters for Activity Coefficients, and Average Deviation for Studied Systems

equation	A_{12}	A_{21}	ΔT/K	Δy_1
Diethylamine (1) + Diisopropylamine (2)				
Margules[a]	0.1634	0.4183	0.18	0.0022
van Laar[a]	0.1962	0.5055	0.19	0.0023
Wilson[b]	−390.92	2068.74	0.19	0.0022
NRTL[c] (a_{12} = 0.40)	3128.70	−1492.56	0.19	0.0021
UNIQUAC[d]	1908.67	−1204.40	0.21	0.0030
Diethylamine (1) + Dipropylamine (2)				
Margules[a]	0.1169	0.2763	0.33	0.0082
van Laar[a]	0.1356	0.3418	0.29	0.0077
Wilson[b]	−513.13	1789.92	0.29	0.0077
NRTL[c] (a_{12} = 0.30)	3493.76	−2083.95	0.29	0.0080
UNIQUAC[d]	1472.36	−1007.16	0.29	0.0079
Chloroform (1) + Diisopropylamine (2)				
Margules[a]	−0.6872	−0.9876	0.07	0.0038
van Laar[a]	−0.7101	−1.0087	0.09	0.0037
Wilson[b]	−257.42	−1870.63	0.11	0.0030
NRTL[c] (a_{12} = 0.18)	1556.02	−3539.41	0.10	0.0029
UNIQUAC[d]	−2173.07	2448.46	0.11	0.0033

[a] Margules and van Laar constants (dimensionless). [b] Wilson's interaction parameters (J·mol^{-1}). [c] NRTL's interaction parameters (J·mol^{-1}). [d] UNIQUAC's interaction parameters (J·mol^{-1}).

The UNIFAC[16] and ASOG[17] methods were also used for the obtained predictions; see Figures 1−3.

The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test[18] where the fugacity coefficients were calculated by the method of Hayden and O'Connell,[19] and activity coefficients were calculated using the four-suffix Margules equation

$$g^{E}/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \tag{15}$$

with the corresponding activity coefficients

$$\ln \gamma_1 = x_2^{2}[A + 2(B - A - D)x_1 + 3Dx_1^{2}] \tag{16}$$

$$\ln \gamma_2 = x_1^{2}[B + 2(A - B - D)x_2 + 3Dx_2^{2}] \tag{17}$$

Estimated parameters A, B, and D were obtaining using the error-in-variables regression maximum likelihood technique. The constraint equation for the regression was

$$F = P - \left(\frac{x_1\gamma_1{}^{*}f_1{}^{\circ}}{\phi_1} + \frac{x_2\gamma_2{}^{*}f_2{}^{\circ}}{\phi_2}\right) \tag{18}$$

Here the asterisk (*) denotes a calculated or predicted value. The experimental value has no asterik; $f_1°$ and $f_2°$ are the standard state fugacities. The errors in the prediction of y_1 were calculated. Predicted y_1* values were obtained using the equation

$$y_1{}^{*} = \frac{x_1\gamma_1{}^{*}f_1{}^{\circ}}{\phi_1P^{*}} \tag{19}$$

An average deviation was calculated as

$$\text{average deviation} = \frac{\sum_{i=1}^{n}|\Delta y|}{n} \tag{20}$$

Table 7. Results of the Thermodynamic Consistency Test

system	Δy	A	B	D
diethylamine (1) + diisopropylamine (2)	0.0021	0.2049	0.4614	0.1875
diethylamine (1) + dipropylamine (2)	0.0047	0.2568	0.3821	0.4830
chloroform (1) + diisopropylamine (2)	0.0042	−0.6419	−0.9411	0.2090

Table 8. Results of the Constants of the Margules Test

system	Margules constant
diethylamine (1) + diisopropylamine (2)	0.3274
diethylamine (1) + dipropylamine (2)	0.3398
chloroform (1) + diisopropylamine (2)	−0.8544

Here $\Delta y = y_1 - y_1{}^*$ and n = number of experimental data points. A system must have an average deviation less than 0.01 to satisfy the consistency test. The three systems included in this work have passed the consistency test. The values for A, B, and D of eqs 16 and 17 are listed in Table 7.

We also carried out the Margules constant test using the program of Gess et al.[14] The Margules constant test can be used to indicate the ideality of a system. Systems which yield a Margules constant whose absolute value is less than 0.60 can be considered ideal, while those which yield an absolute value grater than 0.60 can be considered nonideal. This criterion for classification, however, is not rigorous. Table 8 shows the values of this constant.

New vapor−liquid equilibria data not previously reported in the literature have been measured. Binary systems formed by the two amines show a nearly ideal behavior corroborated by the Margules constant value and by the activity coefficients very close to the unity. By contrast, the system formed by a secondary aliphatic amine and chloroform is not ideal. The Margules constant value is higher than 0.6 and the activity coefficients of the halogenated compound are very far from the unity. The system chloroform + diisopropylamine shows an azeotrope that persists over a range of composition (x = 0.007−0.04). The azeotrope is also predicted by the ASOG method as can be observed in Figure 3. Both UNIFAC and ASOG prediction methods show good agreement with experimental data for amine−amine systems. For the chloroform + diisopropylamine system, ASOG method shows values more similar to the obtained ones.

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