of both components of the Me_2SO-H_2O system as calculated from the usual equation

$$\phi_{V,A} = \frac{M_A}{d} - \frac{1000(d_{AB}^t - d_B^t)}{m_A d_{AB} d_B^t} \qquad (4)$$

where $\phi_{V,A}$, M_A, and m_A are the apparent molar volume, molecular weight, and molality of component A, respectively, d_B^t is the density of pure component B at t °C, and d_{AB}^t is the density of the AB mixture at temperature t.

Following the example of Kiyohara, Perron, and Desnoyers (*3*) we have used our density data to calculate the apparent molar volumes of both Me_2SO and water, and then correlate the results using polynomial equations in the concentration of each component (eq 5). The coefficients derived for calculating the apparent molar volumes of Me_2SO and H_2O at all concentrations (using a number of different units) at 25, 40, and 60 °C are listed in Tables IV and V, respectively. We have used the results of Cowie to derive similar equations for the apparent molar volume of water at 45 and 65 °C. These results are also included in Tables VI and VII.

$$\phi_{V,A} = \phi_{V,A}^0 + AC_A + BC_A^2 + ... + FC_A^6 \qquad (5)$$

Registry No. Me_2SO, 67-68-5.

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Vapor–Liquid Equilibrium for Four Mixtures Containing *N*,*N*-Dimethylformamide

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Low-pressure isothermal vapor–liquid equilibria have been measured for *N*,*N*-dimethylformamide (DMF)/benzaldehyde, *n*-butyl acetate/DMF, acetic acid/DMF, and cyclohexylamine/DMF. Activity coefficients derived from our measurements have been correlated with five thermodynamic models by using the maximum likelihood method, and used to estimate UNIFAC group contribution parameters.

Introduction

Two previous papers in this series (*1*, *2*) have reported vapor–liquid equilibrium (VLE) measurements of hydrocarbons/oxyhydrocarbon mixtures. These results were used to test activity coefficient models and to calculate parameters for the UNIFAC group contribution model (*3*). In this study we report measurements on systems containing *N*,*N*-dimethylformamide (DMF) as one component. DMF is a commonly used aprotic solvent. It is capable of separating saturated and unsaturated hydrocarbons either as a selective solvent or as a third component in extractive distillation. Because of the high dielectric constant of DMF, it is a good reaction solvent and, in some cases, it even has catalytic properties. These phenomena can be described if a model for the activity of compounds in mixtures with DMF is available. UNIFAC is an especially useful thermodynamic model because it only requires data on the interactions among individual chemical groups, such as a methylene group or an aldehyde group, and these are a relatively small number of groups compared to the number of molecules. If information is available on DMF and a relatively small number of groups, one can use these data to predict the activity of any compound in DMF, provided this compound is composed of the same chemical groups that are in the data base. This paper presents isothermal VLE values of DMF with four functional groups and makes estimates for previously unavailable group interaction parameters for DMF with each group.

Table I. Antoine Constants for Representation of Vapor Pressure of Compounds Used[a]

	A	*B*	*C*
DMF[d]	6.0459	1401.382	193.864
(lit.[b])	6.2334	1537.78	210.39
benzaldehyde[d]	6.3711	1691.620	210.02
n-butyl acetate[d]	6.0380	1294.2	195.09
(lit.[c])	6.1534	1368.50	204.00
acetic acid (lit.[b])	6.5522	1558.03	224.79
cyclohexylamine[d]	5.6851	1152.538	178.904

[a] $\log (p/p^0) = A - B/(T + C)$, where $p^0 = 1.0$ kPa, T in °C. [b] From ref 4. [c] From ref 5. [d] This work.

Experimental Section

DMF is embryotoxic to laboratory animals and should not be inhaled or allowed to contact skin; all experimental work was performed in a fume hood. Since DMF is such a good solvent, care must be exercised in the choice of materials which contact it.

The experimental equipment and operating procedures have been discussed previously (*1*, *2*). As before, a significant portion of the experimental effort was devoted to the purification and determination of the boiling points of the pure compounds. All compounds except DMF and acetic acid were purified by fractional distillation under dry nitrogen at reduced pressures. Acetic acid and DMF were acceptably pure as received; since they are very hygroscopic, they were kept under dry nitrogen at all times. Table I gives the Antoine constants we derived using the same chemicals that were used in the later VLE experiments. Note that the Antoine constants for DMF previously reported in the literature (*4*) underpredict the vapor pressure at the reported normal boiling point by about 1 kPa. We have determined the boiling points for anhydrous DMF supplied by Aldrich and by du Pont, and the results obtained with these two samples were essentially indistinguishable. We have also derived new Antoine constants which are consistent with the normal boiling point of DMF.

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Table II. Vapor-Liquid Equilibrium Data for DMF (1)/Benzaldehyde (2) at 105.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
10.12	0.0000	0.0000	17.41	0.5876	0.7692
10.36	0.0208	0.0430	17.60	0.5946	0.7763
10.96	0.0684	0.1367	18.50	0.6729	0.8278
11.71	0.1317	0.2540	19.60	0.7594	0.8828
12.76	0.2182	0.3863	20.64	0.8400	0.9319
14.05	0.3185	0.5132	21.49	0.9085	0.9618
15.35	0.4187	0.6174	22.16	0.9624	0.9878
16.65	0.5106	0.7094	22.68	1.0000	1.0000

Table III. Vapor-Liquid Equilibrium Data for DMF (1)/Benzaldehyde (2) at 125.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
20.94	0.0000	0.0000	34.89	0.5879	0.7561
21.59	0.0253	0.0534	36.92	0.6683	0.8179
22.75	0.0739	0.1440	38.96	0.7528	0.8723
24.51	0.1445	0.2617	40.92	0.8375	0.9230
26.68	0.2320	0.3946	42.53	0.9056	0.9596
29.25	0.3364	0.5190	43.72	0.9605	0.9912
31.80	0.4385	0.6235	44.74	1.0000	1.0000
34.37	0.5418	0.7183			

Table IV. Vapor-Liquid Equilibrium Data for *n*-Butyl Acetate (1)/DMF (2) at 90.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
12.90	0.0000	0.0000	25.84	0.4720	0.6991
13.47	0.0103	0.0473	27.13	0.5601	0.7481
14.35	0.0291	0.1206	28.24	0.6536	0.7947
15.88	0.0629	0.2309	29.33	0.7491	0.8399
17.65	0.1105	0.3410	30.16	0.8287	0.8790
19.62	0.1733	0.4414	30.69	0.8899	0.9217
20.93	0.2222	0.5074	31.10	0.9409	0.9556
21.48	0.2450	0.5339	31.30	0.9771	0.9811
23.05	0.3143	0.5956	31.47	1.0000	1.0000
24.46	0.3906	0.6497			

Benzaldehyde was the most reactive component used. It oxidizes easily to form benzoic acid, which freezes at room temperature. It also undergoes a rapid condensation reaction at room temperature when exposed to air; when fractionated, this is apparent as significant amounts of water are found in the distillate. At room temperatures cyclohexylamine reacts with carbonic acid to form a salt, and therefore also must not be exposed to air.

Consequently, the components used here were exposed only to dry nitrogen. Whereas our previous work used a Porapak Q gas chromatography column, we found that the amine adsorbed significantly, causing excessive peak broadening. Therefore, the column used for the gas chromatographic analysis of the cyclohexylamine/DMF mixture was Carbopack B/4% Carbowax 20M/0.8% KOH.

Our measured butyl acetate gave boiling points consistent with the published Antoine constants (*5*), but we calculated our own coefficients to optimize the fit for the range of pressures studied. Acetic acid is hygroscopic, and it is very difficult to remove the last traces of water. Commercial glacial acetic acid generally contains about 0.3% water; we were unable to remove this amount even when the acid was distilled over phosphorous pentoxide, a strong desiccant (*6*). However, the effect of this very small amount of water should be insignificant.

Experimental Results and Discussion

Isothermal vapor-liquid equilibrium measurements were made for DMF/benzaldehyde at 105 and 125 °C, *n*-butyl acetate/DMF at 90 and 115 °C, acetic acid/DMF at 95 and 110 °C, and cyclohexylamine/DMF at 100 and 120 °C. The results are presented in Figures 1-5 and Tables II-IX. The calculated azeotropic compositions and pressures for acetic acid/DMF and cyclohexylamine/DMF are given in Table X.

Table V. Vapor-Liquid Equilibrium Data for *n*-Butyl Acetate (1)/DMF (2) at 115.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
32.27	0.0000	0.0000	60.70	0.4760	0.6833
33.55	0.0118	0.0440	63.35	0.5578	0.7325
35.34	0.0299	0.1138	66.17	0.6572	0.7832
38.55	0.0641	0.2187	68.55	0.7504	0.8360
42.20	0.1095	0.3196	70.35	0.8327	0.8826
45.81	0.1610	0.4120	71.84	0.9020	0.9260
50.31	0.2363	0.5054	72.66	0.9531	0.9622
54.14	0.3119	0.5754	73.07	0.9852	0.9871
57.75	0.3957	0.6391	73.14	1.0000	1.0000

Table VI. Vapor-Liquid Equilibrium Data for Acetic Acid (1)/DMF (2) at 95.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
12.71	0.0000	0.0000	15.39	0.5872	0.8415
15.51	0.0156	0.0046	19.65	0.6619	0.9231
15.16	0.0413	0.0095	22.17	0.6959	0.9465
14.58	0.0834	0.0221	28.70	0.7750	0.9792
13.70	0.1475	0.0520	36.21	0.8583	0.9928
12.51	0.2345	0.1212	41.86	0.9228	0.9977
11.54	0.3223	0.2483	45.66	0.9681	0.9999
11.34	0.4248	0.4732	47.48	0.9901	0.9999
12.80	0.5153	0.7008	48.18	1.0000	1.0000

Table VII. Vapor-Liquid Equilibrium Data for Acetic Acid (1)/DMF (2) at 110.00 °C

P, KPa	x_1	y_1	P, KPa	x_1	y_1
27.11	0.0000	0.0000	35.71	0.6728	0.9273
26.68	0.0173	0.0039	44.70	0.7477	0.9677
25.82	0.0579	0.0157	53.55	0.8119	0.9841
24.86	0.1000	0.0303	62.06	0.8718	0.9930
23.35	0.1713	0.0750	68.45	0.9176	0.9965
21.65	0.2617	0.1637	73.35	0.9532	0.9999
20.47	0.3512	0.3200	76.54	0.9780	0.9999
21.01	0.4423	0.5299	78.70	0.9944	0.9999
23.98	0.5304	0.7343	79.36	1.0000	1.0000
30.08	0.6173	0.8685			

Table VIII. Vapor-Liquid Equilibrium Data for Cyclohexylamine (1)/DMF (2) at 100.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
18.87	0.0000	0.0000	32.91	0.4297	0.6262
19.40	0.0102	0.0414	34.15	0.5204	0.6751
20.51	0.0297	0.1098	35.23	0.6173	0.7245
22.51	0.0691	0.2166	36.08	0.7221	0.7824
24.75	0.1220	0.3224	36.49	0.8195	0.8381
27.14	0.1920	0.4228	36.58	0.8972	0.8944
29.32	0.2678	0.5038	36.30	0.9541	0.9450
31.34	0.3479	0.5708	35.97	0.9781	0.9749
31.29	0.3527	0.5704	35.70	1.0000	1.0000

Table IX. Vapor-Liquid Equilibrium Data for Cyclohexylamine (1)/DMF (2) at 120.00 °C

P, kPa	x_1	y_1	P, kPa	x_1	y_1
38.03	0.0000	0.0000	61.93	0.4216	0.6055
38.64	0.0062	0.0212	66.46	0.6149	0.7131
40.03	0.0186	0.0650	68.05	0.7342	0.7762
42.58	0.0467	0.1424	68.87	0.8330	0.8397
45.64	0.0831	0.2301	68.78	0.8921	0.8857
49.59	0.1379	0.3272	68.46	0.9458	0.9349
53.55	0.2037	0.4199	67.87	0.9785	0.9747
57.39	0.2789	0.4949	67.40	1.0000	1.0000
61.05	0.3651	0.5648			

Table X. Estimated Azeotropic Point

system	T, °C	x_1^{az}	p^{az}, kPa
acetic acid/DMF	95.00	0.3886	11.25
acetic acid/DMF	110.00	0.3759	20.43
cyclohexylamine/DMF	100.00	0.8620	36.56
cyclohexylamine/DMF	120.00	0.8620	68.85

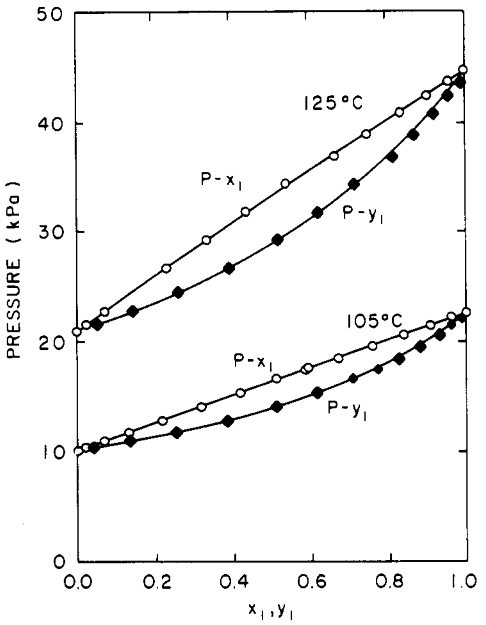

Figure 1. *P*-*x*-*y* phase equilibrium diagram for DMF (1) and benzaldehyde (2) at 105 and 125 °C. The points ○ and ◆ are the liquid and vapor compositions, respectively, and the lines result from the Wilson equation fit of the data.

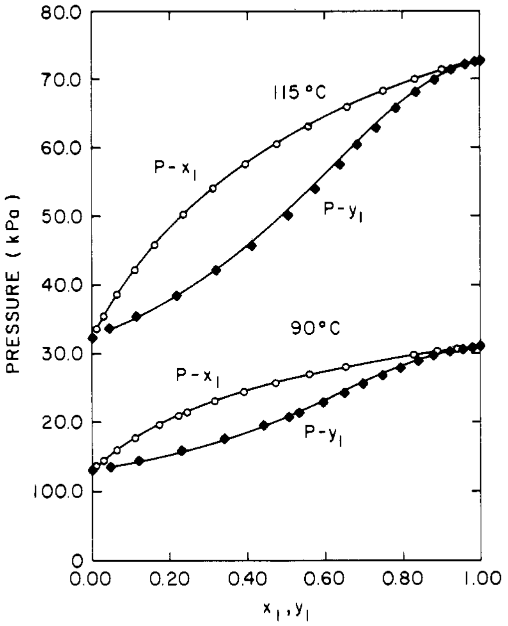

Figure 2. *P*-*x*-*y* phase equilibrium diagram for *n*-butyl acetate (1) and DMF (2) at 90 and 115 °C. Legend as in Figure 1.

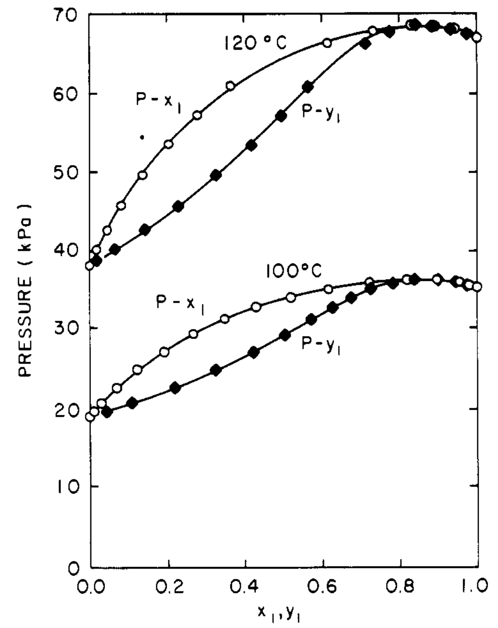

Figure 3. *P*-*x*-*y* phase equilibrium diagram for cyclohexylamine (1) and DMF (2) at 100 and 120 °C. Legend as in Figure 1.

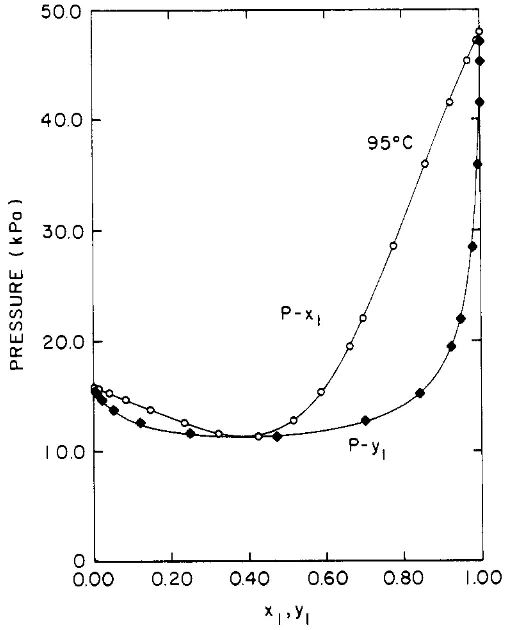

Figure 4. *P*-*x*-*y* phase equilibrium diagram for acetic acid (1) and DMF (2) at 95 °C. The points ○ and ◆ are the liquid and vapor compositions, respectively.

Acetic acid is a weak acid and does not dissociate in water or DMF. If it did, due to dissociation, Henry's law would not hold for the dilute acid, and its partial pressure would vary as the square of its concentration (*7*). Negative deviations from Raoult's law, as seen in acetic acid/DMF, result from weak chemical interactions between the compounds; DMF is a Lewis base which hydrogen bonds with acetic acid. A stronger Lewis base would give even more negative deviations. DMF and benzaldehyde form an essentially ideal mixture; presumably this is because the repulsion between DMF and the aromatic portion of benzaldehyde balances the attraction between DMF (a strong Lewis base) and the electron-poor carbon of the carbonyl group.

The point-to-point consistency test reviewed by Fredenslund et al. (*3*), which models G^E with a third-order Legendre polynomial, shows that each data set has average deviations less than 0.006 in vapor-phase mole fraction and less than 0.11 kPa in pressure.

Activity Coefficients and Models

The data were fit with a variety of activity coefficient models in an effort to determine the relative accuracy of each. The objective function was discussed in a previous paper (*1*). Vapor-phase nonidealities were accounted for by estimating the second virial coefficients (see Table XI) from the correlation of Hayden and O'Connell (*8*). Acetic acid vapor-phase nonidealities cannot be described by a second virial coefficient due to the formation of dimers. The calculation of the fugacity of the monomers in the gas phase requires a quantitative description of the monomer-dimer equilibrium, assuming they form an ideal gas mixture. Tables XII-XIII give the fugacity coefficients of monomeric, gaseous acetic acid and DMF as

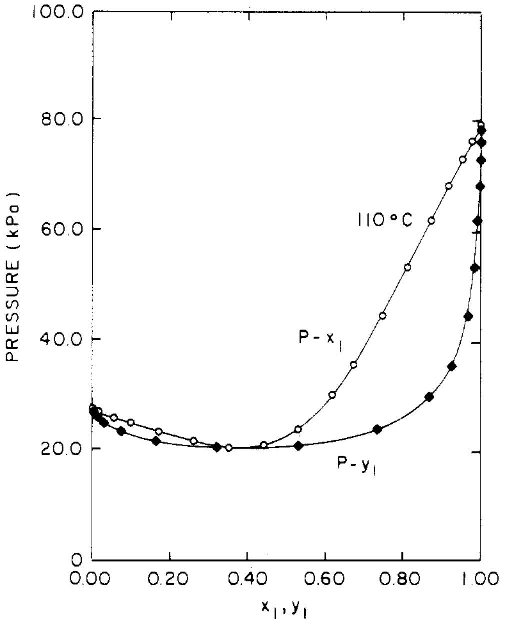

Figure 5. P-x-y phase equilibrium diagram for acetic acid (1) and DMF (2) at 110 °C. Legend as in Figure 4.

Table XI. Second Virial Coefficients ($cm^3 \cdot mol^{-1}$)

	T, °C	
	105	125
DMF	-1906	-1634
benzylaldehyde	-1714	-1477
DMF/benzaldehyde	-1522	-1302
	T, °C	
	90	115
n-butyl acetate	-1916	-1592
DMF	-2157	-1762
n-butyl acetate/DMF	-1427	-1186
	T, °C	
	100	120
cyclohexylamine	-2116	-1848
DMF	-1985	-1696
cyclohexylamine/DMF	-1361	-1191

Table XII. Fugacity Coefficients for Acetic Acid (1)/DMF (2) at 95.00 °C

y_1	P, kPa	ϕ_1	ϕ_2
0.0000	15.71	1.0000	0.9976
0.0046	15.51	0.9914	0.9977
0.0095	15.16	0.9752	0.9978
0.0221	14.58	0.9435	0.9983
0.0520	13.70	0.8832	1.0008
0.1212	12.51	0.7881	1.0124
0.2483	11.54	0.6975	1.0457
0.4732	11.34	0.6189	1.1299
0.7008	12.80	0.5656	1.2443
0.8415	15.39	0.5249	1.3444
0.9231	19.65	0.4810	1.4393
0.9465	22.17	0.4609	1.4770
0.9792	28.70	0.4197	1.5459
0.9928	36.21	0.3847	1.5955
0.9977	41.86	0.3638	1.6217
0.9999	45.66	0.3516	1.6357
0.9999	47.48	0.3463	1.6415
1.0000	48.18	0.3443	1.6437

calculated by the procedure and programs discussed by Fredenslund et al. (3). The liquid phase of acetic acid is assumed to be entirely monomers, with association being described by the activity coefficient.

Table XIII. Fugacity Coefficients for Acetic Acid (1)/DMF (2) at 110.00 °C

y_1	P, kPa	ϕ_1	ϕ_2
0.0000	27.11	1.0000	0.9967
0.0039	26.68	0.9905	0.9968
0.0157	25.82	0.9645	0.9971
0.0303	24.86	0.9319	0.9980
0.0750	23.35	0.8659	1.0024
0.1637	21.65	0.7744	1.0197
0.3200	20.47	0.6964	1.0619
0.5299	21.01	0.6359	1.1403
0.7343	23.98	0.5884	1.2433
0.8685	30.08	0.5413	1.3512
0.9273	35.71	0.5106	1.4134
0.9677	44.70	0.4726	1.4813
0.9841	53.55	0.4434	1.5261
0.9930	62.06	0.4203	1.5576
0.9965	68.45	0.4053	1.5763
0.9999	73.35	0.3950	1.5884
0.9999	76.54	0.3886	1.5955
0.9999	78.69	0.3846	1.5999
1.0000	79.36	0.3833	1.6013

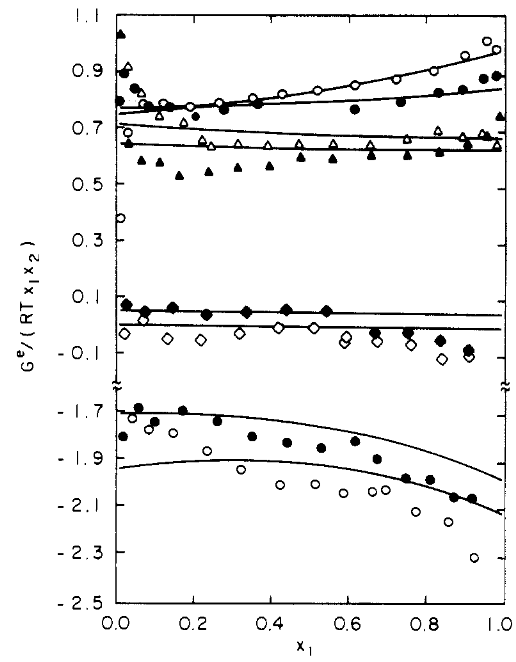

Figure 6. Measured and fitted values of dimensionless excess Gibbs free energy. The lines result from the Wilson equation fit of the data. Acetic acid/DMF at 95 and 110 °C (○ and ●, values less than 0), DMF/benzaldehyde at 105 and 110 °C °C (◇ and ◆), n-butyl acetate/DMF at 90 and 115 °C (△ and ▲), cyclohexylamine/DMF at 100 and 120 °C (○ and ●, values greater than 0).

The nature of the liquid-phase nonidealities is most easily observed when the data are presented in the form of G^e/RTx_1x_2. Figure 6 shows the data of each experiment presented in this form. The curves shown were calculated by using the Wilson parameters obtained from the fit of the P-x-y data in Figures 1-5. Since G^e/RTx_1x_2 is nearly constant, the data are well represented by a two-constant Margules expression and all the two-parameter models fit the data equally well. Table XIV contains the fitted constants for each of the models and deviations from these models. The negative deviations for acetic acid/DMF are about twice as great as those for acetone/chloroform (9). The temperature dependence of G^e for DMF/benzaldehyde and acetic acid/DMF indicate they mix exothermically.

The estimated UNIFAC group interaction parameters are given in Table XV. The parameters for the acetate group and the DMF group interaction are much smaller than the other group interaction parameters. Indeed, when considering the (small) scatter in the experimental data, and the uncertainty in the group contribution method, they can be set equal to zero.

Table XIV. Estimated Parameters[a] from Data Correlation

T, °C	model	A_{12}	A_{21}	AAD (Δy)	AAD (ΔP), kPa
		DMF/Benzaldehyde			
105	Margules	−0.0045	0.0129	0.0053	0.04
	Van Laar	0.2415	−0.0022	0.0060	0.04
	Wilson	0.9986	1.001	0.0057	0.04
	NRTL	97.11	−99.93	0.0052	0.04
	UNIQUAC	86.69	−393.4	0.0054	0.04
125	Margules	0.0500	0.0047	0.0058	0.08
	Van Laar	0.0473	0.0531	0.0058	0.08
	Wilson	0.9247	1.026	0.0059	0.08
	NRTL	590.5	−401.0	0.0059	0.08
	UNIQUAC	627.0	−820.9	0.0059	0.08
		n-Butyl Acetate/DMF			
90	Margules	0.6883	−0.014	0.0043	0.05
	Van Laar	0.7085	0.6681	0.0044	0.05
	Wilson	0.6478	0.7210	0.0044	0.04
	NRTL	878.0	1324.9	0.0043	0.05
	UNIQUAC	1485.9	−588.2	0.0043	0.05
115	Margules	0.6350	−0.001	0.0076	0.10
	Van Laar	0.6359	0.6342	0.0076	0.10
	Wilson	0.6997	0.7132	0.0076	0.09
	NRTL	1051.2	1106.2	0.0076	0.10
	UNIQUAC	1641.8	−712.0	0.0076	0.10
		Cyclohexylamine/DMF			
100	Margules	0.837	0.120	0.0040	0.07
	Van Laar	0.732	0.972	0.0034	0.06
	Wilson	0.829	0.440	0.0030	0.05
	NRTL	3040	−3.9	0.0036	0.06
	UNIQUAC	2273	−992	0.0034	0.06
120	Margules	0.800	0.044	0.0026	0.11
	Van Laar	0.757	0.846	0.0027	0.11
	Wilson	0.713	0.567	0.0028	0.11
	NRTL	1994	831.5	0.0027	0.11
	UNIQUAC	1793	−703	0.0027	0.11
		Acetic Acid/DMF			
95	Margules	−1.943	−0.1077	0.0050	0.21
	Van Laar	−1.8532	−2.0462	0.0050	0.21
	Wilson	2.3953	2.0705	0.0072	0.29
	NRTL	−2143	3092	0.0058	0.24
	UNIQUAC	−1609	−595	0.0056	0.23
110	Margules	−1.7708	−0.1455	0.0051	0.34
	Van Laar	−1.6473	−1.9093	0.0054	0.34
	Wilson	2.3637	1.8515	0.0066	0.44
	NRTL	−1994	−3031	0.0060	0.33
	UNIQUAC	−1444	−674	0.0056	0.36

[a] Margules: $\ln \gamma_1 = x_2^2(A_{12} + A_{21}(3 - 4x_2))$; $\ln \gamma_2 = x_1^2(A_{12} - A_{21}(3 - 4x_1))$. Wilson:

$$A_{12} = \frac{V_2^{\mathrm{L}}}{V_1^{\mathrm{L}}} \exp\left[-\left(\frac{\lambda_{12} - \lambda_{11}}{RT}\right)\right]$$

$$A_{21} = \frac{V_1^{\mathrm{L}}}{V_2^{\mathrm{L}}} \exp\left[-\left(\frac{\lambda_{21} - \lambda_{22}}{RT}\right)\right]$$

NRTL: $A_{12} = g_{12} - g_{22}$, $A_{21} = g_{21} - g_{11}/\mathrm{J{\cdot}mol^{-1}}$, $\alpha = 0.3$. UNIQUAC: $A_{12} = u_{12} - u_{22}$, $A_{21} = u_{21} - u_{22}/\mathrm{J{\cdot}mol^{-1}}$.

Table XV. Fitted UNIFAC Interaction Energies, K^{-1}

	T, °C	
	105	125
	Benzaldehyde	
CHO–DMF[a]	44.6	42.7
DMF–CHO	311.9	341.7
	T, °C	
	90	115
	n-Butyl Acetate/DMF	
COOC–DMF	−52.8	−21.1
DMF–COOC	76.9	25.3
	T, °C	
	95	110
	Acetic Acid/DMF	
COOH–DMF	−384.2	−398.2
DMF–COOH	229.3	276.3
	T, °C	
	100	120
	Cyclohexylamine/DMF	
CNH_2–DMF	−306.5	−269.7
DMF–CNH_2	391.3	249.0

[a] Calculation of these parameters required the use of unpublished values of the ACH–CHO and CHO–ACH interaction parameters (*10*). The values used were ACH–CHO = 1182.9; CHO–ACH = 172.1.

The DMF–CNH_2 and CNH_2–DMF interaction parameters appear to be a strong function of temperature, but these parameters are highly correlated, and the data at both temperatures can be fit with parameters intermediate in value. Calculation of the CHO–DMF and DMF–CHO interaction parameters required the use of unpublished values of the ACH–CHO and CHO–ACH interaction parameters (*10*); see Table XV for the values used.

Conclusions

Low-pressure vapor–liquid equilibrium measurements have been reported for binary mixtures of *N*,*N*-dimethylformamide with benzaldehyde, acetic acid, *n*-butyl acetate, and cyclohexylamine. The acetic acid/DMF system showed a negative deviation azeotrope at 95 and 110 °C, the cyclohexylamine/DMF system had a positive deviation azeotrope at both 100 and 120 °C, while the DMF/benzaldehyde and *n*-butyl acetate/DMF systems exhibited no azeotrope. Since data for these systems were not previously available, the information provided herein should be of interest in engineering design and, as here, to estimate interaction parameters in the UNIFAC and other functional group methods.

Glossary

A, *B*, *C*	Antoine constants
G^{e}	excess Gibbs free energy
P	pressure, kPa
R	gas constant
T	temperature, °C
x	liquid-phase mole fraction
y	vapor-phase mole fraction
ϕ	fugacity coefficient
AAD	absolute average deviation

Registry No. DMF, 68-12-2; benzaldehyde, 100-52-7; *n*-butyl acetate, 123-86-4; acetic acid, 64-19-7; cyclohexylamine, 108-91-8.

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