

The sucrose-BSA data in Figure 2 fall between the data of others (2, 3) for urea and potassium chloride in BSA solutions. Since urea and KCl are both known definitely to bind to BSA, it could appear that sucrose binding to BSA might be the cause of the effect seen in Figure 2. However, it has been reported by Giles and McKay (7) that disaccharides could not bind with proteins. However, sucrose and BSA were studied (7) for binding along with several other sugars and proteins, but sucrose was never actually tested with BSA. Sucrose was tested with casein. Some other disaccharides were tested with BSA, but sucrose was not. In a diffusion experiment, Colton et al. (1) found a binding coefficient k_p of 0.131 for sucrose in 4% BSA solution with 4.2% other proteins present. However, the diffusion equation that Colton et al. used to calculate k_p is very sensitive to errors in diffusivity (1, 2). Their reported binding coefficient could possibly occur because of errors in the diffusivity measurements, or the presence of 4.2% of other proteins could possibly cause the binding. In view of this limited and seemingly contradictory evidence of possible binding, a sucrose-BSA binding study should probably be performed in the future.

Glossary

A	diffusing solute
B	solvent
c	concentration of A in lower chamber of diaphragm cell at time t , g-mol/m ³ of solution
c'	concentration of A in upper chamber at time t , g-mol/m ³ of solution
c_0, c_0'	concentration of A at time $t = 0$, g-mol/m ³ of solution
D_{AB}	diffusivity of A in solution with no protein present, m ² /s
D_{AP}	diffusivity of A in protein solution, m ² /s
D_{PB}	diffusivity of protein-solute complex in solution (assumed that of the protein), m ² /s
D_p	diffusivity of A in protein solution inside pore, m ² /s

D_0	free diffusivity of A in protein solution outside pore, m ² /s
k_p	protein binding coefficient (concentration dependent), [(g of bound solute)/(mL of solution)]/[(g of free solute)/(mL of protein-free solution)]
t	time, s
α	diffusivity reduction shape factor for protein (1.5 for sphere, 1.615 for BSA)
β	cell constant, m ⁻²
λ	inverse pore size ratio, solute size/pore size
τ	tortuosity, effective pore length/diaphragm thickness
ϕ_p	volume fraction of proteins in protein solution

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Vapor-Liquid Equilibria of the Formic Acid-Dimethylformamide System

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Vapor-liquid equilibria have been measured for the system formic acid-dimethylformamide at 200, 300, 400, 600, and 760 mmHg. The system presents associations in the vapor phase which have to be taken into account for a thermodynamically consistent reduction of the data. The nonideal behavior is assumed for the vapor mixture of true chemical species.

Deviations from ideal behavior in the vapor phase of systems containing components which can form intermolecular hydrogen bonds are frequently interpreted in terms of associations between like or unlike molecules (1-12). The chemical theory of vapor imperfections, in contrast to the physical theory, has been widely used in many recent works to fit vapor-liquid

equilibrium data at low or moderate pressure. The calculation of activity coefficients from x - y data, ignoring the presence of the true species in the vapor phase, can lead to values without thermodynamic meaning, i.e., inconsistent with the Gibbs-Duhem equation. In a simplified form, the chemical theory of vapor-phase nonideality assumes ideal behavior of the mixture of "true" species (monomer, dimer, etc.), whose concentrations can be evaluated by the chemical equilibrium constants of association reactions. More sophisticated formulations, however, take into account physical interactions of species present in the vapor phase (5). In the present paper the nonideal approach of Nothnagel et al. (5) is applied to the correlation of the vapor-liquid isobaric equilibria of the formic acid (FA)-dimethylformamide (DMF) system.

Very few data of vapor-liquid equilibrium are available in the literature for the system examined. Ruhoff and Reid (13) observed a homogeneous azeotrope at 153.2 °C and atmospheric pressure with 97.4 wt % DMF. Du Pont observations (14) indicate the azeotrope position at 67 wt % DMF and a

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Table I. Refractive Index of pure Compounds

compd	<i>t</i> , °C	<i>n</i> _D measured	<i>n</i> _D lit.
formic acid	20	1.3714 ± 0.0005	1.3714
dimethylformamide	25	1.4271 ± 0.0005	1.4269

Table II. Vapor-Liquid Equilibrium Data at 200 mmHg

<i>t</i> , °C	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂
111.2	0.059	0.013	0.0839	0.9882
113.2	0.149	0.040	0.0939	0.9923
117.7	0.250	0.143	0.1650	0.8678
119.3	0.310	0.231	0.1988	0.8083
119.6	0.335	0.276	0.2151	0.7853
120.1	0.342	0.283	0.2125	0.7737
120.4	0.361	0.323	0.2255	0.7482
120.6	0.427	0.480	0.2728	0.6504
118.8	0.469	0.609	0.3245	0.5744
117.0	0.500	0.695	0.3608	0.5168
115.0	0.529	0.763	0.3922	0.4667
108.2	0.591	0.873	0.4757	0.3881
106.3	0.603	0.895	0.5013	0.3603
103.1	0.630	0.924	0.5368	0.3240
93.1	0.701	0.979	0.6554	0.1787
88.2	0.736	0.983	0.7063	0.2081
85.5	0.757	0.993	0.7402	0.1071
80.8	0.791	0.996	0.7945	0.0908
77.8	0.816	0.997	0.8278	0.0758
76.7	0.827	0.999	0.8394	0.0342
71.5	0.871	0.999	0.8992	0.0611
67.1	0.918	0.999	0.9439	0.1238

boiling point of 85 °C for a pressure of 50 mmHg. Maltese and Valentini (15) studied the entire vapor-liquid equilibrium at 100 mmHg and determined the boiling point of the azeotrope at 200 mmHg. Heats of mixing at 25 °C are reported by Carli and Di Cave (16).

Our study concerns the measurement of equilibria at 200, 300, 400, 600, and 760 mmHg and the correlation of data by a chemical theory.

Experimental Section

The products used in the experiments were analytical-grade reagents purchased from Carlo Erba. No further purification was carried out since a 99% minimum purity was guaranteed for FA and 99.5% for DMF. A comparison between measured values of refractive index and literature data (17) is reported in Table I.

The experimental runs were carried out in a vapor recirculation still already used in other works. Details of the apparatus are reported elsewhere (18).

A vacuum was maintained by a water-jet pump connected to the vapor condenser and was controlled by a Cartesian manostat which made possible the regulation of total pressure within 1 mmHg. A Hg thermometer was used to read equilibrium temperatures with an accuracy of ±0.1 °C. Samples of vapor and liquid phases were withdrawn when no noticeable changes were observed in the temperature. The analysis of samples was made at 25 °C with a Bausch and Lomb Abbe-3L precision refractometer which allowed direct readings of refractive indexes to four significant figures. The accuracy of mole fraction data was estimated to ±0.001. Each run was repeated several times with good reproducibility.

Results and Discussion

Isobaric equilibria results are reported in Tables II-VI. At each pressure a maximum boiling azeotrope can be observed. Its position moves toward the more volatile component as the pressure decreases, but it is difficult to evaluate accurately its composition because of the flatness of the equilibrium curve.

Equilibrium data can be used to determine activity coefficients in the liquid phase. A rough calculation assuming ideal behavior

Table III. Vapor-Liquid Equilibrium Data at 300 mmHg

<i>t</i> , °C	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂
124.0	0.077	0.030	0.1442	0.9668
128.5	0.212	0.115	0.1685	0.9022
129.5	0.240	0.142	0.1768	0.8812
130.0	0.258	0.171	0.1933	0.8606
130.7	0.275	0.195	0.2012	0.8389
131.2	0.299	0.228	0.2114	0.8218
131.8	0.326	0.273	0.2257	0.7938
132.0	0.347	0.302	0.2316	0.7842
132.3	0.395	0.411	0.2685	0.7168
131.9	0.426	0.487	0.2942	0.6733
130.8	0.459	0.570	0.3247	0.6281
129.0	0.490	0.665	0.3672	0.5600
125.5	0.534	0.778	0.4257	0.4687
123.2	0.560	0.818	0.4505	0.4458
116.6	0.620	0.902	0.5251	0.3640
112.5	0.652	0.933	0.5696	0.3227
103.0	0.715	0.972	0.6774	0.2492
93.0	0.785	0.992	0.7929	0.1502
87.7	0.826	0.996	0.8525	0.1201
82.7	0.870	0.998	0.9064	0.1032
79.1	0.908	0.999	0.9410	0.0884

Table IV. Vapor-Liquid Equilibrium Data at 400 mmHg

<i>t</i> , °C	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂
131.8	0.044	0.012	0.1068	0.9945
133.5	0.095	0.034	0.1317	0.9777
135.0	0.135	0.056	0.1446	0.9578
136.8	0.190	0.097	0.1662	0.9308
137.6	0.218	0.124	0.1792	0.9155
138.3	0.240	0.147	0.1879	0.9004
139.2	0.268	0.185	0.2042	0.8730
139.5	0.272	0.195	0.2098	0.8604
139.7	0.291	0.222	0.2204	0.8508
140.5	0.331	0.286	0.2406	0.8136
141.0	0.367	0.355	0.2620	0.7714
140.6	0.397	0.431	0.2928	0.7291
139.5	0.439	0.534	0.3317	0.6725
136.6	0.501	0.692	0.3966	0.5614
135.5	0.510	0.717	0.4135	0.5465
130.7	0.565	0.824	0.4770	0.4593
123.2	0.630	0.907	0.5593	0.3805
116.7	0.676	0.952	0.6351	0.2915
107.1	0.743	0.989	0.7458	0.1265
98.1	0.807	0.998	0.8453	0.0457
90.0	0.877	0.999	0.9273	0.0526
85.1	0.930	0.999	0.9704	0.1172

of the gas phase leads to values of activity coefficients which are thermodynamically inconsistent. Therefore deviations from ideality, due to vapor-phase associations, must be taken into account, even if the pressure is low.

Self-associations of FA and DMF to form dimers are assumed. Furthermore, complexing of the type FA-DMF between unlike molecules is allowed.

In the literature (19), values are given for the dimerization constant of FA over the temperature range 50-150 °C. The data are summarized by the equation

$$\log K = -10.743 + 3083/T$$

for pressures in mmHg and *T* in Kelvin.

No experimental information has been found for the dimerization of DMF and the cross-association of DMF with FA. Therefore the equilibrium constants have been calculated by Nothnagel's equations (5) as shown in the Appendix. The adopted values of the parameters required by the method are reported in Table VII. The excluded volumes *b* have been obtained from atomic radii and bond distances as discussed by Bondi (20). The empirical parameters *d* have been determined from the values of Nothnagel (5), by arbitrarily choosing the value of a homomorphous molecule for DMF and extrapolating the values of acetic, propionic, and butanoic acids for FA. The

Table V. Vapor-Liquid Equilibrium Data at 600 mmHg

$t, ^\circ\text{C}$	x_1	y_1	γ_1	γ_2
145.8	0.045	0.014	0.1216	0.9995
146.4	0.072	0.034	0.1799	0.9922
146.8	0.075	0.035	0.1758	0.9840
147.3	0.089	0.035	0.1461	0.9862
148.1	0.110	0.046	0.1513	0.9777
148.2	0.127	0.055	0.1557	0.9849
149.6	0.157	0.082	0.1791	0.9564
150.5	0.220	0.142	0.2119	0.9465
151.2	0.240	0.177	0.2353	0.9171
151.5	0.275	0.215	0.2450	0.9123
152.5	0.305	0.269	0.2661	0.8677
152.4	0.306	0.275	0.2715	0.8644
152.0	0.327	0.311	0.2878	0.8587
151.6	0.360	0.389	0.3250	0.8159
151.3	0.367	0.397	0.3271	0.8213
150.9	0.375	0.430	0.3480	0.7979
150.7	0.402	0.508	0.3805	0.7317
149.2	0.418	0.538	0.3994	0.7385
148.5	0.426	0.560	0.4133	0.7296
148.6	0.439	0.594	0.4225	0.6911
146.0	0.482	0.695	0.4723	0.6174
145.2	0.508	0.740	0.4839	0.5730
142.7	0.532	0.781	0.5141	0.5520
141.0	0.557	0.828	0.5390	0.4887
138.5	0.576	0.862	0.5726	0.4475
134.0	0.629	0.922	0.6180	0.3418
133.0	0.630	0.917	0.6274	0.3763
129.6	0.668	0.943	0.6550	0.3270
125.0	0.702	0.967	0.7060	0.2511
124.5	0.707	0.964	0.7065	0.2834
119.0	0.748	0.985	0.7676	0.1705
116.7	0.763	0.984	0.7894	0.2112
116.6	0.767	0.983	0.7861	0.2290
109.0	0.832	0.996	0.8601	0.1277
105.2	0.865	0.997	0.8967	0.1120
104.6	0.872	0.998	0.9014	0.0808
103.0	0.883	0.998	0.9198	0.0949
99.0	0.925	0.999	0.9534	0.0887
98.4	0.927	0.999	0.9630	0.0932

Table VI. Vapor-Liquid Equilibrium Data at 760 mmHg

$t, ^\circ\text{C}$	x_1	y_1	γ_1	γ_2
155.0	0.047	0.017	0.1395	0.9940
155.9	0.078	0.030	0.1441	0.9919
156.4	0.102	0.042	0.1515	0.9938
156.7	0.105	0.051	0.1767	0.9801
157.4	0.141	0.067	0.1689	0.9881
158.1	0.158	0.088	0.1931	0.9694
158.2	0.179	0.107	0.2054	0.9718
159.4	0.222	0.153	0.2268	0.9470
159.0	0.235	0.167	0.2352	0.9571
159.5	0.269	0.222	0.2659	0.9275
159.3	0.298	0.275	0.2950	0.9082
158.5	0.346	0.376	0.3465	0.8643
157.3	0.385	0.470	0.3934	0.8142
157.5	0.394	0.492	0.3993	0.7905
155.4	0.439	0.602	0.4525	0.7191
155.7	0.442	0.617	0.4567	0.6922
153.5	0.470	0.684	0.4961	0.6462
153.6	0.483	0.694	0.4882	0.6411
149.4	0.530	0.789	0.5497	0.5592
148.1	0.558	0.824	0.5594	0.5200
141.5	0.627	0.910	0.6306	0.3957
140.9	0.629	0.916	0.6408	0.3792
139.2	0.658	0.924	0.6405	0.3941
136.9	0.669	0.944	0.6754	0.3260
134.3	0.694	0.952	0.6935	0.3307
132.8	0.706	0.963	0.7115	0.2806
125.6	0.755	0.981	0.7872	0.2249
125.3	0.765	0.982	0.7825	0.2247
122.4	0.788	0.989	0.8120	0.1701
117.9	0.822	0.992	0.8557	0.1751
113.6	0.860	0.996	0.8955	0.1321
110.3	0.893	0.998	0.9229	0.0987
106.5	0.927	0.999	0.9594	0.0853

Table VII. Pure Fluid Parameters

	formic acid	dimethylformamide
$b, \text{cm}^3/\text{mol}$	88.36	187.16
d	2.08	0.41
p	0.75	0.15
T_c, K	579.0	654.2
$v, \text{cm}^3/\text{mol}$	49.50	13.19
$v', \text{cm}^3/(\text{mol K})$	-0.09	0.02
$v'', \text{cm}^3/(\text{mol K}^2)$	1.73×10^{-4}	
A	7.3779	6.0480
B	1563.28	900.62
C	247.06	130.86
$\log P_s = A - B/(t + C)$		

polarity factor p of FA has been assumed to have the same value as acetic, propionic, and butanoic acids ($p = 0.75$), whereas for DMF a value of 0.15 has been arbitrarily chosen.

From chemical equilibrium constants, K_1 , K_2 , and $K_{1,2}$, and material balances, it is possible to calculate the mole fractions of the "true" species for each composition of the binary mixture as well as the "true" mole fractions of monomers and dimers for pure components at each temperature. From these data we can evaluate the fugacity coefficients of FA and DMF in the mixture and the values for pure components at saturation conditions. The procedure and the pertinent equations are reported in the Appendix. Activity coefficients then can be obtained by the classical vapor-liquid equilibrium conditions:

$$\varphi_1 y_1 P = x_1 P_{s,1} \varphi_{s,1} \nu_{L,1} \gamma_1$$

$$\varphi_2 y_2 P = x_2 P_{s,2} \varphi_{s,2} \nu_{L,2} \gamma_2$$

where ν_L takes into account the Poynting effect and φ and φ_s are the fugacity coefficients in the binary mixture and for pure components at saturation conditions, respectively. Liquid volumes required to calculate the Poynting effect at each temperature have been expressed by the following equation:

$$\nu_L = v + v'T + v''T^2$$

The values of v , v' , and v'' for each component have been obtained by fitting experimental data of ν_L and are reported in Table VII.

It should be emphasized that the choice of vapor pressures is fundamental for a correct evaluation of activity coefficients. Use of inappropriate values introduces nonrandom bias into the γ calculated from the experimental data. This effect is thoroughly discussed by Van Ness et al. (22), who suggest the use of values of P_s as determined from a least-squares spline fit of the boiling-point data of the binary system rather than directly measured or literature values. This choice ensures that the pure-component vapor pressures are at least in reasonable accord with the rest of the data. Indeed the P_s values of DMF obtained by the Antoine equation with the constants reported by Hala (23) give results inconsistent with our data in the region of the pure component. Besides, the vapor-pressure equation of Hala does not fully agree, in the range of temperatures of this work, with the measurements of P_s by other authors (15, 24). Therefore, boiling points of DMF at each one of the pressures analyzed have been determined from a least-squares fit of $T-x$ data. The results are in good agreement with the data of the literature (15, 24), as shown in Figure 1. Vapor pressures so obtained have been correlated by the Antoine equation. The constants are reported in Table VII together with the constants of FA taken from the literature (25). Activity coefficients deduced by the above procedure are reported in Tables II-VI.

Thermodynamic consistency was verified at each pressure by the semiempirical method of Herington (26). The factor J was 26.4, 25.1, 25.9, 24.2, and 20.5, respectively, for the five

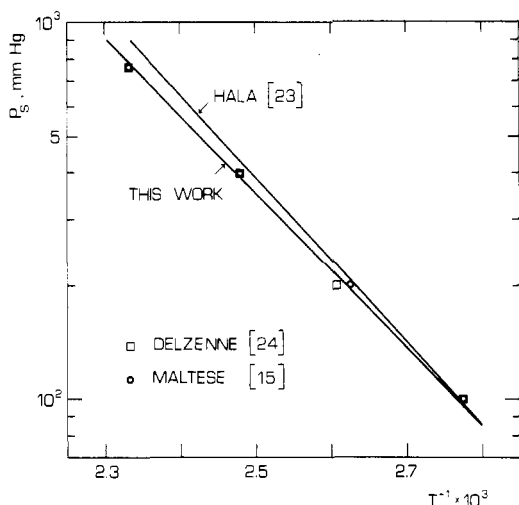


Figure 1. Vapor pressure of dimethylformamide.

Table VIII. NRTL Parameters and Value of Objective Function

n	3
A_1	-7.31×10^2
A_2	-1.40×10^3
B_1	1.32×10^{-4}
B_2	-2.34×10^{-5}
Φ	4.70×10^{-3}

sets of data. The factor D was 6.5, 7.7, 2.8, 1.1, and 3.5, all of which satisfy Herington's criteria for consistency, $D < J$.

Correlation of Activity Coefficients

The activity-coefficient data have been correlated by means of the NRTL equation. The nonrandomness parameter α_{12} has been set equal to 0.3. Small variations around this value give negligible effects on the quality of the correlation. The parameters $g_{12} - g_{22}$ and $g_{21} - g_{11}$ have been assumed to be functions of temperature according to the following expressions:

$$g_{12} - g_{22} = A_1 + B_1 T^n$$

$$g_{21} - g_{11} = A_2 + B_2 T^n$$

The four constants A_1 , A_2 , B_1 , and B_2 have been obtained by minimizing the following objective function:

$$\Phi = \frac{\sum_i (\gamma_{1,e} - \gamma_{1,c})^2}{\sum_i (\gamma_{1,e} - 1)^2} + \frac{\sum_i (\gamma_{2,e} - \gamma_{2,c})^2}{\sum_i (\gamma_{2,e} - 1)^2}$$

Another objective function has been also used without appreciable differences.

The value of n has been determined by a parametric analysis of its effect on the minimum value of Φ . In Table VIII the parameters obtained are reported together with the corresponding value of the objective function.

By means of the NRTL equation, vapor-liquid equilibria have been evaluated at each pressure. Results at 200 and 760 mmHg are compared with experimental data in Figures 2 and 3. Furthermore, a test of the temperature dependence of activity coefficients has been carried out by calculating the heat of mixing at 25 °C. The comparison with the experimental data (16) shows a maximum deviation of $\sim 25\%$, which can be considered satisfactory if one accounts for the procedure used.

Appendix

The equilibrium constant K of the dimerization reaction of DMF can be calculated by

$$-\ln(RTK) = \Delta H/RT - \Delta S/R \quad (1)$$

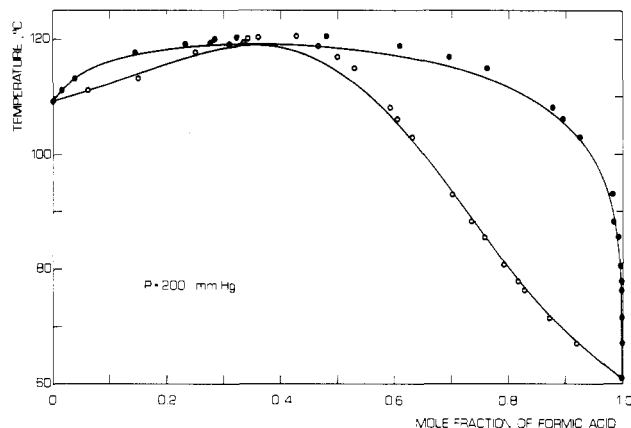


Figure 2. Vapor-liquid equilibrium at the lowest pressure.

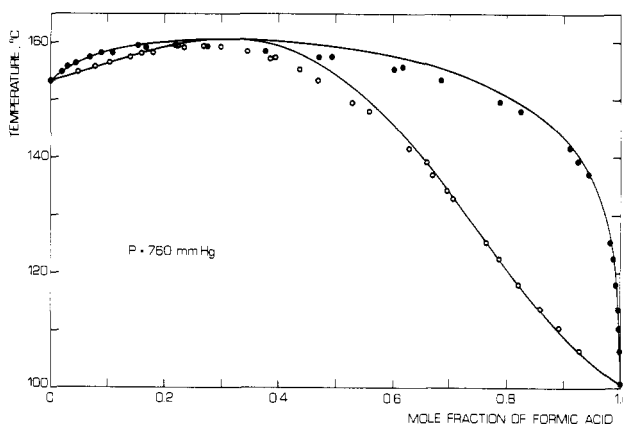


Figure 3. Vapor-liquid equilibrium at the highest pressure.

where ΔH and ΔS are respectively the enthalpy and the entropy of dimerization in the standard state. In eq 1 the value of R on the left-hand side is $82.06 \text{ (cm}^3 \text{ atm)/(mol K)}$ and on the right-hand side is $1.987 \text{ cal/(mol K)}$. According to Nothnagel, ΔH and ΔS are given by

$$-\Delta H = dT_b(8.75 + 4.576 \log T_b) - RT_b \quad (2)$$

$$\Delta S/R = 1.1[\Delta H/(RT_c)] + \ln(3.06b) \quad (3)$$

where T_b and T_c are the normal boiling point (K) and the critical temperature (K), respectively, b is the excluded volume, and d is an empirical constant.

The equilibrium constant $K_{1,2}$ for the complexing reaction $\text{DMF} + \text{FA} = \text{DMF} \cdot \text{FA}$ can be evaluated with eq 1 by using cross-terms $\Delta S_{1,2}$ and $\Delta H_{1,2}$ given by

$$\Delta S_{1,2}/R = 1.1[\Delta H_{1,2}/(RT_{c1,2})] + \ln(3.06b_{1,2}) + \ln 2 \quad (4)$$

$$\Delta H_{1,2} =$$

$$\frac{1}{2}[(1 - p_1)\Delta H_1 + (1 - p_2)\Delta H_2] - [p_1\Delta H_1 p_2\Delta H_2]^{1/2} \quad (5)$$

The last equation holds when components 1 and 2 are both polar and requires the use of polarity factors p_1 and p_2 .

The cross-terms $p_{1,2}$, $T_{c1,2}$, and $b_{1,2}$ are calculated by the following relationships:

$$p_{1,2} = (p_1 p_2)^{1/2} + [(1 - p_1)(1 - p_2)]^{1/2} \quad (6)$$

$$T_{c1,2} = p_{1,2}[(T_{c1} T_{c2})]^{1/2} \quad (7)$$

$$b_{1,2} = \frac{1}{8}(b_1^{1/3} + b_2^{1/3})^3 \quad (8)$$

In eq 5, the enthalpy of dimerization of pure DMF has been calculated by eq 2, whereas that of FA has been deduced from the empirical equation relating K_{FA} to temperature, by differentiating $\ln K$ with respect to T . Once the equilibrium constants

are known, we can evaluate, at each condition, the fugacity coefficients of components 1 and 2 in the vapor phase by the following equations:

$$\varphi_1 = (Z_A/y_1) \exp(b_1P/RT) \quad (9)$$

$$\varphi_2 = (Z_B/y_2) \exp(b_2P/RT) \quad (10)$$

where y_1 and y_2 are the measured mole fractions and Z_A and Z_B are the mole fractions of the monomers of each compound in the mixture of "true" chemical species. They can be obtained by solving the following set of equations:

$$PK_1 = \frac{Z_{A_2}}{Z_A^2} \exp\left(-\frac{b_1P}{RT}\right) \quad (11)$$

$$PK_2 = \frac{Z_{B_2}}{Z_B^2} \exp\left(-\frac{b_2P}{RT}\right) \quad (12)$$

$$PK_{1,2} = \frac{Z_{AB}}{Z_A Z_B} \exp\left[\frac{(b_{1,2} - b_1 - b_2)P}{RT}\right] \quad (13)$$

$$y_1 = \frac{Z_A + 2Z_{A_2} + Z_{AB}}{1 + Z_{A_2} + Z_{B_2} + Z_{AB}} \quad (14)$$

$$y_2 = \frac{Z_B + 2Z_{B_2} + Z_{AB}}{1 + Z_{A_2} + Z_{B_2} + Z_{AB}} \quad (15)$$

where eq 14 and 15 derive from material balances. In the same way fugacity coefficients of pure components at saturation conditions can be found by the relationships

$$\varphi_{s,1} = Z_A \exp(b_1P_{s,1}/RT) \quad (16)$$

$$\varphi_{s,2} = Z_B \exp(b_2P_{s,2}/RT) \quad (17)$$

In this case Z_A and Z_B represent the monomer mole fractions in the vapor of pure component 1 or 2, respectively, and can be obtained from the fraction α of molecules dimerized by

$$Z = (1 - \alpha)/(1 - \alpha/2) \quad (18)$$

The value of α of each component is given, at temperature T , by

$$P_s K \exp\left(\frac{bP_s}{RT}\right) = \frac{\alpha}{2} \frac{(1 - \alpha/2)}{(1 - \alpha)^2} \quad (19)$$

Glossary

A, B, C	Antoine equation constants
$A_1, A_2,$ $B_1,$ B_2	NRTL parameters
b	size parameter, cm^3/mol
d	empirical constant
H	enthalpy
K	chemical equilibrium constant
n	temperature exponent in NRTL equation
n_D	refractive index
p	polarity factor

P	pressure, mmHg
P_s	vapor pressure, mmHg
R	gas constant
S	entropy
t, T	temperature, $^{\circ}\text{C}$, K
T_b	normal boiling point, K
T_c	critical temperature, K
v_L	liquid volume, cm^3/mol
x	liquid-phase mole fraction
y	apparent vapor-phase mole fraction
Z	true vapor-phase mole fraction

Greek Letters

α	fraction of molecules dimerized
γ	activity coefficient
φ_s, φ	apparent fugacity coefficient
ν	Poynting effect
Φ	objective function

Subscripts

1, 2	apparent components
A, $A_2,$ B, $B_2,$ AB	true components
c	calculated
e	experimental

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