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Vapor–Liquid Equilibrium of Binary and Ternary Mixtures of Isobutyraldehyde/Ethyl Acetate/*N*,*N*-Dimethylformamide

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Low-pressure isothermal vapor–liquid equilibrium data have been measured for isobutyraldehyde/ethyl acetate/*N*,*N*-dimethylformamide (DMF) at 60 °C, and for the constituent binaries at 40 and 60 °C. It is found that DMF, a Lewis base, decreases the relative volatility of isobutyraldehyde/ethyl acetate because it is more strongly attracted to the aldehyde group in the liquid phase. The ability of several activity coefficient models to predict the ternary behavior from binary data has been studied. The use of the UNIFAC group contribution method to describe the CHO–DMF interaction in different solutions is also discussed.

Introduction

As part of an ongoing international cooperative effort, researchers at the University of Delaware and the Technical University of Berlin have been studying the behavior of aldehydes in solution (*1–3*). The dearth of data for aldehydes is due to their chemical instability at ambient conditions. In addition, recent work at the University of Delaware with *N*,*N*-dimethylformamide (DMF) has suggested that its phase behavior is influenced by its chemically basic behavior (*4*). DMF, therefore, exhibits strongly varying interactions with different functional groups and may be useful as a solvent in enhancing relative volatility and/or breaking azeotropes in mixtures of compounds with certain functionalities. DMF is already widely used in the separation of saturated and unsaturated hydrocarbons. In this communication we report vapor–liquid equilibrium data for binary and ternary mixtures of DMF, isobutyraldehyde, and ethyl acetate. The ability of several models to predict ternary behavior from binary data has also been considered, and the DMF–aldehyde interactions have been studied by using the UNIFAC model.

Table I. Vapor–Liquid Equilibrium Data for Ethyl Acetate (1)/DMF (2) at 40.00 and 60.00 °C

P, kPa	x_1	y_1	*P*, kPa	x_1	y_1
	40 °C			60 °C	
1.13	0.000	0.000	3.35	0.000	0.000
11.57	0.338	0.928	19.38	0.220	0.867
12.85	0.394	0.940	22.33	0.270	0.889
14.81	0.487	0.957	26.13	0.342	0.911
17.11	0.598	0.973	31.30	0.441	0.939
18.98	0.697	0.983	36.48	0.561	0.959
20.59	0.784	1.000	40.69	0.657	0.971
22.03	0.863	1.000	44.87	0.757	0.987
23.31	0.929	1.000	48.72	0.849	1.000
24.34	0.979	1.000	52.10	0.929	1.000
24.97	1.000	1.000	54.31	0.979	1.000
			55.69	1.000	1.000

Table II. Vapor–Liquid Equilibrium Data for Isobutyraldehyde (1)/DMF (2) at 40.00 and 60.00 °C

P, kPa	x_1	y_1	*P*, kPa	x_1	y_1
	40 °C			60 °C	
1.13	0.000	0.000	3.35	0.000	0.000
22.37	0.458	0.972	37.70	0.347	0.941
25.55	0.536	0.982	42.35	0.405	0.951
28.09	0.615	0.982	46.52	0.459	0.961
31.02	0.693	0.990	52.97	0.545	0.974
33.72	0.769	1.000	59.78	0.632	0.983
35.80	0.831	1.000	67.38	0.737	0.991
38.40	0.899	1.000	73.91	0.828	0.993
40.33	0.952	1.000	78.99	0.893	1.000
41.73	0.988	1.000	82.44	0.937	1.000
42.45	1.000	1.000	85.10	0.972	1.000
			87.05	0.993	1.000
			87.79	1.000	1.000

Table III. Vapor–Liquid Equilibrium Data for Ethyl Acetate (1)/Isobutyraldehyde (2) at 40.00 and 60.00 °C

P, kPa	x_1	y_1	*P*, kPa	x_1	y_1
	40 °C			60 °C	
25.05	0.000	0.000	55.57	0.000	0.000
25.51	0.018	0.030	56.46	0.020	0.033
26.33	0.055	0.089	57.97	0.058	0.094
27.50	0.112	0.183	60.15	0.114	0.176
28.90	0.184	0.286	62.67	0.182	0.266
30.39	0.261	0.381	65.44	0.258	0.359
31.86	0.342	0.473	68.25	0.339	0.448
33.29	0.421	0.552	71.00	0.423	0.533
34.51	0.499	0.624	73.37	0.497	0.603
34.63	0.504	0.627	73.63	0.503	0.608
35.92	0.584	0.692	76.16	0.586	0.683
37.33	0.673	0.766	78.75	0.675	0.752
38.65	0.756	0.832	81.17	0.755	0.817
39.87	0.832	0.886	83.31	0.827	0.873
40.84	0.897	0.932	85.15	0.892	0.921
41.57	0.946	0.966	86.71	0.944	0.959
42.08	0.980	0.988	87.77	0.981	0.995
42.31	1.000	1.000	88.31	1.000	1.000

Experimental Section

The experimental procedure and equipment used by both research groups have been discussed previously (*1*, *2*). High-purity DMF was purchased from Aldrich in the USA and Merck in Berlin. DMF is embryotoxic to laboratory animals and should not be inhaled or allowed to contact skin. Since DMF is such a good solvent, care must be exercised in the choice of materials which contact it. Also, it is very hydroscopic, and care must be taken to avoid exposure to air. Isobutyraldehyde readily oxidizes and undergoes a condensation reaction at ambient conditions. It was, therefore, used immediately after purification by distillation. Purification and measurements with isobutyraldehyde were completed within 12 h; there were not measurable reaction products over this period of time. Ethyl

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Table IV. Data for 60 °C Isobutyraldehyde (1)/Ethyl Acetate (2)/DMF (3) with Approximately 25 mol % DMF

P, kPa	x_1	x_2	y_1	y_2
		25 mol % DMF		
44.84	0.000	0.752	0.000	0.971
46.88	0.045	0.715	0.088	0.887
48.63	0.092	0.671	0.173	0.803
50.49	0.153	0.603	0.274	0.703
52.45	0.207	0.555	0.355	0.624
54.19	0.256	0.507	0.425	0.555
55.79	0.311	0.449	0.499	0.481
58.65	0.355	0.439	0.538	0.449
61.11	0.446	0.344	0.644	0.340
63.86	0.541	0.244	0.748	0.236
65.79	0.627	0.145	0.846	0.138
66.94	0.692	0.066	0.920	0.063
67.73	0.731	0.023	0.961	0.022
68.29	0.723	0.000	0.980	0.000
		50 mol % DMF		
33.36	0.000	0.480	0.000	0.946
33.38	0.041	0.409	0.122	0.817
34.42	0.060	0.390	0.176	0.770
36.87	0.104	0.364	0.283	0.668
39.34	0.140	0.356	0.350	0.606
40.80	0.172	0.326	0.417	0.541
41.82	0.199	0.304	0.464	0.495
42.88	0.229	0.273	0.523	0.438
43.79	0.256	0.246	0.574	0.388
43.20	0.277	0.192	0.647	0.312
43.72	0.308	0.151	0.716	0.244
44.65	0.349	0.107	0.789	0.171
45.61	0.392	0.062	0.861	0.100
44.15	0.394	0.032	0.907	0.053
47.27	0.467	0.000	0.959	0.000

Table V. Virial Coefficients (cm^3/mol)

	T, °C	
	40	60
isobutyraldehyde, B_1	-1535	-1283
ethyl acetate, B_2	-1660	-1407
DMF, B_3	-3500	-2850
isobutyraldehyde/DMF, B_{13}	-1894	-1555
ethyl acetate/DMF, B_{23}	-1775	-1476
isobutyraldehyde/ethyl acetate, B_{12}	-1201	-1010

acetate is stable and required no purification or special handling.

The ternary solutions contained approximately constant mole fractions of DMF—either 25 or 50%. The ternary data were measured in a manner analogous to the measurement of the binary data. Initially only ethyl acetate was mixed with DMF, and pressure and phase compositions were measured. Incremental amounts of isobutyraldehyde were added before the measurement of each data point until the mole fractions of isobutyraldehyde and ethyl acetate were equal. The still was then cleaned and charged with isobutyraldehyde and DMF, and incremental amounts of ethyl acetate were added for each data point. To maintain the liquid-phase mole fraction of DMF as constant as possible during this procedure, the liquid-phase compositions were measured and an appropriate amount of DMF was added before the measurement of the next data point.

The response of the gas chromatograph used for component analysis was calibrated by using gravimetrically prepared binary solutions. The data so obtained were fit with the equation

$$x_1 - a_1 = a_1 a_2[\alpha_{12} + \beta_{12}(a_1 - a_2) + \delta_{12}(a_1 - a_2)^2] \qquad (1)$$

where x_i and a_i are the mole fraction and area fraction, respectively, and α_{12}, β_{12}, and δ_{12} parameters fit to the calibration data. For ternary solutions, we used the equation

$$x_1 - a_1 = a_1 a_j[\alpha_{1j} + \beta_{1j}(a_1 - a_j) + \delta_{1j}(a_1 - a_j)^2] + a_1 a_k[\alpha_{1k} + \beta_{1k}(a_1 - a_k) + \delta_{1k}(a_1 - a_k)^2] \qquad (2)$$

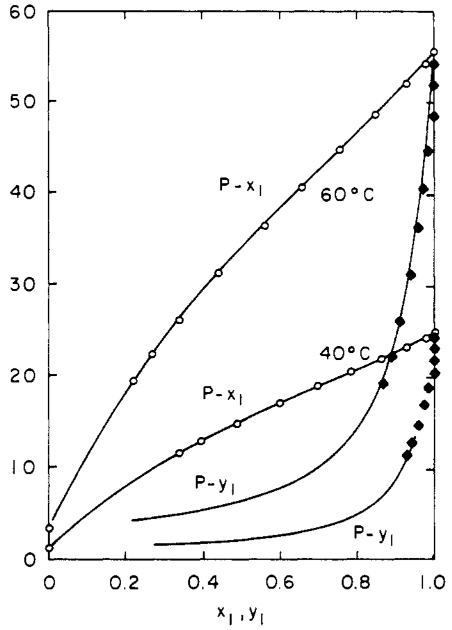

Figure 1. P-x-y phase equilibrium diagram for ethyl acetate (1) and DMF (2) at 40 and 60 °C. The points ○ and ◆ are the liquid and vapor compositions, respectively, and the lines result from the Wilson equation fit of the data.

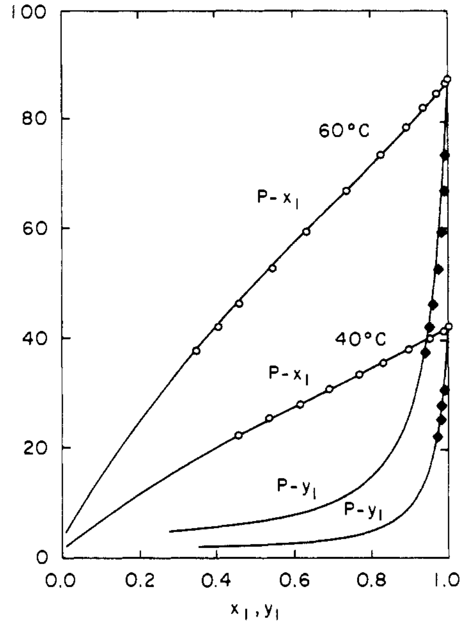

Figure 2. P-x-y phase equilibrium diagram for isobutyraldehyde (1) and DMF (2) at 40 and 60 °C. Legend as in Figure 1.

with similar equations for species 2 and 3, with all parameters determined from the binary data. The use of eq 2 was checked by using gravimetrically prepared ternary solutions, and it was found that the solution composition was predicted with an average error of less than 0.004.

Experimental Results and Discussion

The isothermal VLE data we obtained are presented in Table I–IV and the binary data are shown in Figures 1–3. Note that the vapor–liquid equilibrium for the isobutyraldehyde/DMF and ethyl acetate/DMF mixtures data were not measured for liquid phase mole fractions of DMF greater than 0.70. Higher liquid-phase mole fractions could not be studied in our equipment because DMF (bp = 153 °C) is so much less volatile than

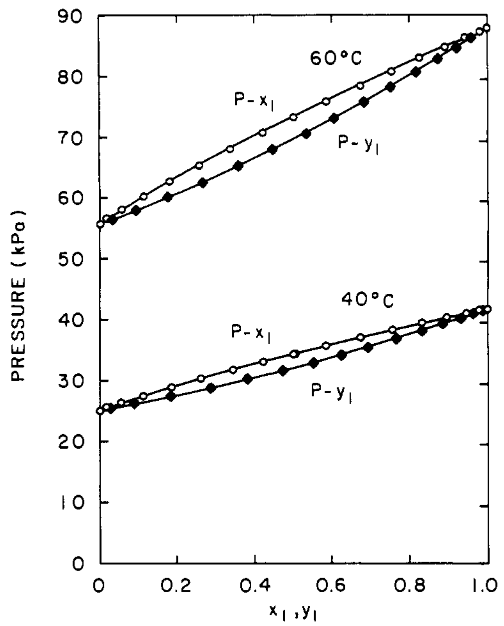

Figure 3. P-x-y phase equilibrium diagram for isobutyraldehyde (1) and ethyl acetate (2) at 40 and 60 °C. Legend as in Figure 1.

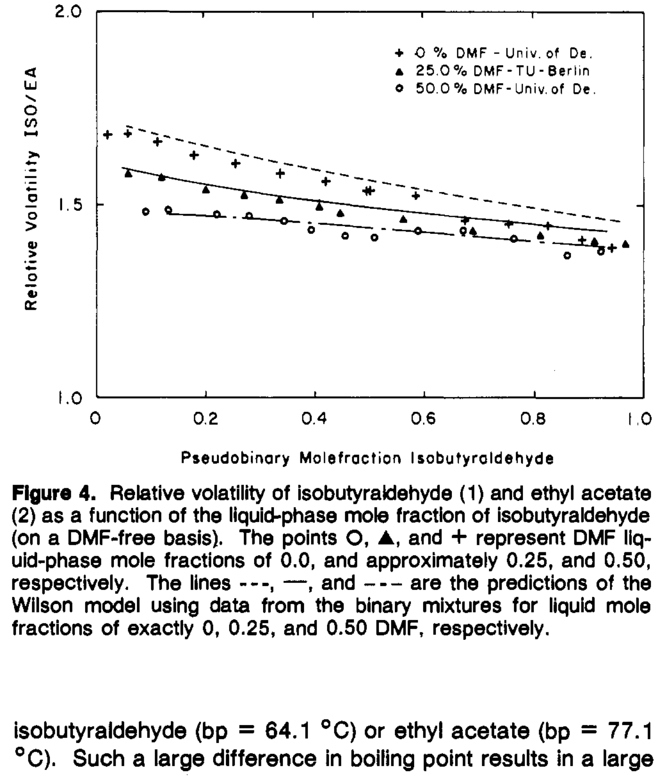

Figure 4. Relative volatility of isobutyraldehyde (1) and ethyl acetate (2) as a function of the liquid-phase mole fraction of isobutyraldehyde (on a DMF-free basis). The points O, ▲, and + represent DMF liquid-phase mole fractions of 0.0, and approximately 0.25, and 0.50, respectively. The lines - - -, —, and — — — are the predictions of the Wilson model using data from the binary mixtures for liquid mole fractions of exactly 0, 0.25, and 0.50 DMF, respectively.

isobutyraldehyde (bp = 64.1 °C) or ethyl acetate (bp = 77.1 °C). Such a large difference in boiling point results in a large temperature variation in the recirculating equilibrium still so that it is difficult to completely condense the vapor phase. Consequently, the Gibbs–Duhem consistency text could not be used on these data. However, the point-to-point test of Fredenslund et al. (*5*) judges binary data to be thermodynamically consistent if the difference between the experimental vapor-phase composition (y^{exptl}) and that calculated (y^{calcd}) by using a polynomial expansion in the Gibbs free energy is sufficiently small. With only one exception, each of our binary data points met the criterion that $|y^{\text{calcd}} - y^{\text{exptl}}| < 0.01$. Therefore, we consider our binary data sets to be consistent, even though mixtures containing high concentrations of DMF could not be measured. Further, each set of data was obtained with at least two refillings and restarts of our equipment with data obtained in overlapping composition ranges.

There is no accepted consistency test for ternary data. Note that the ternary system containing approximately 25% DMF was measured, using a different experimental setup and calibration data, at the Technical University of Berlin, while all other data were measured at the University of Delaware. Nonetheless, the data sets are in good agreement. The slight difference in the binary data in Tables I and II measured in Delaware and the binary points in Table IV measured in Berlin is of little consequence, especially when one considers the very dilute vapor-phase composition of DMF.

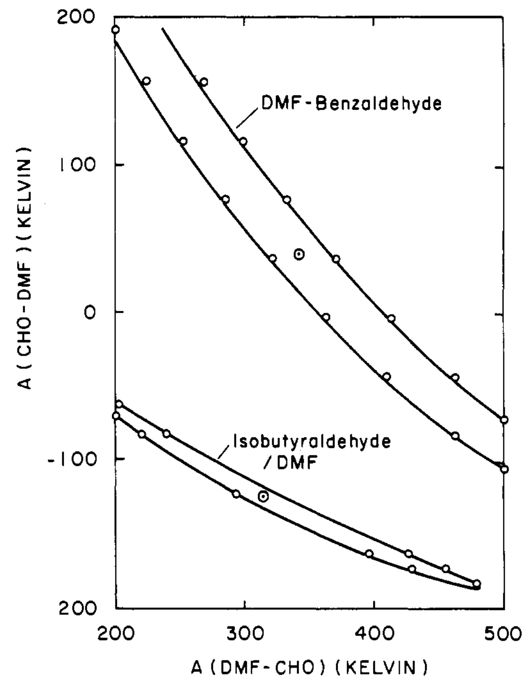

Figure 5. Parameter intercorrelation diagram for the UNIFAC parameters describing VLE of isobutyraldehyde/DMF (lower ellipse) and DMF/benzaldehyde (upper ellipse). These ellipses, which are not quite closed because of the range of parameters considered, represent constant values of the objective function, average absolute deviation in pressure, equal to 0.30 kPa. Inside these open ellipses are the range of best fit parameters.

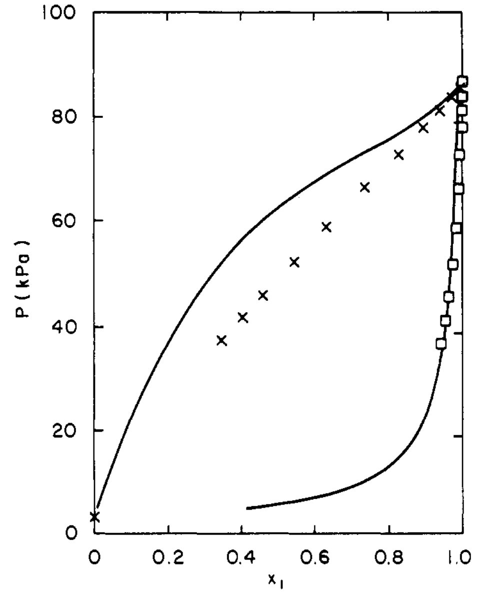

Figure 6. UNIFAC predictions for isobutyraldehyde/DMF at 60 °C using CHO–DMF interaction parameters derived from DMF/benzaldehyde at 125 °C compared to experimental data (□ and ×).

Figure 4 shows the effect of DMF on the relative volatility of the isobutyraldehyde/ethyl acetate mixture. There it is found

Table VI. Parameters in the Thermodynamic Models

	T = 40 °C		T = 60 °C	
	A_{12}	A_{21}	A_{12}	A_{21}
Margules				
ethyl acetate/DMF	0.5344	0.0947	0.5390	0.0681
isobutyraldehyde/DMF	0.3860	0.0519	0.3890	0.0340
ethyl acetate/isobutyraldehyde	-0.0109	0.1206	-0.0115	0.1068
Van Laar				
ethyl acetate/DMF	0.4712	0.6401	0.4842	0.6138
isobutyraldehyde/DMF	0.3579	0.4428	0.3573	0.4262
ethyl acetate/isobutyraldehyde	0.1097	0.1339	0.0965	0.1191
Wilson				
ethyl acetate/DMF	0.8753	0.6041	0.9378	0.5738
isobutyraldehyde/DMF	0.9880	0.6490	0.9640	0.6757
ethyl acetate/isobutyraldehyde	1.1300	0.7681	1.1455	0.7675
NRTL				
ethyl acetate/DMF	1720	-37.45	1910	-211.1
isobutyraldehyde/DMF	1513	-347	1401	-216.6
ethyl acetate/isobutyraldehyde	946	-562	1065	-683
UNIQUAC				
ethyl acetate/DMF	1383	-673.8	1295	-598.5
isobutyraldehyde/DMF	877	-418.8	820.5	-363.2
ethyl acetate/isobutyraldehyde	673.5	-500.5	729.6	-554.6

	UNIFAC parameters, K^{-1}			
	T = 105 °C		T = 125 °C	
	CHO-DMF	DMF-CHO	CHO-DMF	DMF-CHO
DMF/benzaldehyde	44.6	311.9	42.7	341.7

	UNIFAC parameters, K^{-1}			
	T = 40 °C		T = 60 °C	
	CHO-DMF	DMF-CHO	CHO-DMF	DMF-CHO
DMF/isobutyraldehyde	-110.4	290	-122.5	314

that DMF slightly decreases the isobutyraldehyde/ethyl acetate relative volatility because of a chemical interaction with the more volatile component, isobutyraldehyde. This is because DMF, an electron-rich Lewis base, interacts strongly with the aldehyde carbon atom which is electron-poor (and consequently so reactive).

The excess Gibbs free energy for the binary mixtures we have studied can be calculated from

$$\frac{G^{ex}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (3)$$

where each activity coefficient was computed from

$$\gamma_i = \frac{y_i \phi_i P}{x_i P_i^{vap}} \qquad (4)$$

Here P_i^{vap} is the vapor pressure of species i and ϕ_i is the vapor-phase fugacity coefficient calculated from the virial equation truncated after the second term which gives

$$\ln \phi_i = \frac{P}{RT}\sum_j\sum_k y_j y_k (2B_{ji} - B_{jk}) \qquad (5)$$

The second virial coefficients, B, were obtained by the method of Hayden and O'Connell (*6*) and appear in Table V.

The quantity $G^{EX}/(RTx_1x_2)$ for both binary systems containing DMF as one component at T = 60 °C is approximately constant (indicating that the data could almost be fit with a one-constant Margules equation) and similar in magnitude (equal to approximately 0.40 over the whole concentration range for the isobutyraldehyde/DMF system, and approximately 0.55 for the ethyl acetate/DMF system). Consequently, it is not surprising that, since the interaction of DMF with isobutyraldehyde and ethyl acetate is so similar, the addition of DMF to the ethyl acetate/isobutyraldehyde mixture changes their relative volatility little.

Thermodynamic Model Parameters

The binary data were used to fit the adjustable constants in the Margules, van Laar, Wilson, UNIQUAC, and NRTL activity coefficient models. The maximum likelihood method was used with the objective function discussed in a previous paper (*2*). Vapor-phase nonidealities were described as discussed earlier using second virial coefficients. The model parameters so obtained appear in Table VI.

The DMF-aldehyde UNIFAC group interaction parameters have been determined by using the DMF/benzaldehyde mixture (*4*) and again here by using the DMF/isobutyraldehyde data. These parameters are also given in Table VI. Figure 5 shows constant values of the absolute average deviation in pressure residual function, AADP, for the isobutyraldehyde/DMF and DMF/benzaldehyde mixtures. It is clear that the parameters for each mixture are highly intercorrelated, and that the best-fit parameters for each mixture do not agree. This is further evident from Figure 6 which shows UNIFAC predictions for the isobutyraldehyde/DMF mixture using DMF-aldehyde group interaction parameters determined from the DMF/benzaldehyde mixture. This disagreement is a result of the group contribution assumption not being valid since the DMF-CHO interaction is different depending on whether the aldehyde group is part of isobutyraldehyde or benzaldehyde. As discussed above, the isobutyraldehyde/DMF mixture exhibits a strong chemical interaction between the electron-rich DMF and the electron-poor carbon atom of the aldehyde group. This effect is not as strong in the DMF/benzaldehyde mixture because in this case the aldehyde carbon atom is resonance-stabilized with electrons from the aromatic ring being supplied to the carbon atom in the aldehyde group. Therefore, the aldehyde group in isobutyraldehyde has a stronger chemical interaction with DMF than does the aldehyde group in benzaldehyde. This is why the data in Figure 6 give less positive deviations from Raoult's law than do the predictions based on the DMF/benzaldehyde solution parameters.

Table VII. Multicomponent Activity Coefficient Models

Van Laar

$$\ln \gamma_1 = \frac{\sum_{j=1}^{M} x_j A_{ij}}{1 - x_1}\left[1 - \frac{\sum_{i=1}^{M} x_j A_{ij}^2}{x_i \sum_{j=1}^{M} (x_i A_{ij}) + (1 - x_1) \sum_{j=1}^{M} (x_j A_{ji})}\right]$$

$$A_{ii} = A_{jj} = 0$$

Wilson

$$\ln \gamma_k = 1 - \ln \sum_{j=1}^{M} x_i \Lambda_{kj} - \frac{\sum_{i=1}^{M} x_i \Lambda_{ik}}{\sum_{j=1}^{M} x_j \Lambda_{ij}}$$

$$\Lambda_{ij} \equiv \frac{V_j}{V_i \exp\left[\frac{-(\lambda_{ij} - \lambda_{ii})}{RT}\right]}, \quad \lambda_{ji} = \lambda_{ij}; \Lambda_{ji} \neq \Lambda_{ij}$$

Redlich-Kister (2-Constant Margules)

$$\ln \gamma_i = Q - \sum_{k \neq i} x_k \left(\frac{\partial Q}{\partial x_k}\right)_{x_{j \neq i,k}}$$

$$Q = \frac{G^{\mathrm{EX}}}{RT} = \sum_i \sum_j x_i x_j [A_{ij} + A_{ji}(x_i - x_j)], \quad i < j,\ A_{ii} = 0$$

NRTL

$$\ln \gamma_i = \frac{\sum_{j=1}^{M} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{M} G_{li} x_l} + \sum_{j=1}^{M} \frac{x_j G_{ij}}{\sum_{l=1}^{M} G_{ij} x_l}\left[\tau_{ij} - \frac{\sum_{r=1}^{M} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{M} G_{lj} x_l}\right]$$

$$\tau_{ji} \equiv \frac{g_{ji} - g_{ii}}{RT}, \quad g_{ji} = g_{ij},\ \tau_{ji} \neq \tau_{ij},$$

$$G_{ji} \equiv \exp(-\alpha_{ji}\tau_{ji}),\ (\alpha_{ji} = \alpha_{ij})$$

UNIQUAC

$$\ln \gamma_k = \ln \gamma_k^{\mathrm{COMB}} + \ln \gamma_k^{\mathrm{RES}}$$

$$\ln \gamma_k^{\mathrm{COMB}} = \ln \frac{\phi_k}{x_k} + \frac{z}{2} q_k \ln \frac{\theta_k}{\phi_k} + l_k - \frac{\phi_k}{x_k} \sum_{j=1}^{M} x_j l_j$$

$$\ln \gamma_k^{\mathrm{R}} = q_k \left[1 - \ln\left(\sum_{j=1}^{M} \theta_j \tau_{jk}\right) - \sum_{j=1}^{M}\left(\frac{\theta_i \tau_{kj}}{\sum_{i=1}^{M} \theta_i \tau_{ij}}\right)\right]$$

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right), u_{ji} = u_{ij},\ \tau_{ji} \neq \tau_{ij}$$

$$l_k = \frac{z}{2}(r_k - q_k) - (r_k - 1), \quad z = 10,$$

$$\theta_k = \frac{q_k x_k}{\sum_{j=1}^{M} q_j x_j}, \ \phi_k = \frac{r_k x_k}{\sum_{j=1}^{M} r_j x_j}$$

UNIFAC

$$\ln \gamma_k = \ln \gamma_k^{\mathrm{COMB}} + \ln \gamma_k^{\mathrm{RES}}$$

$$\ln \gamma_k^{\mathrm{COMB}} = \ln \frac{\phi_k}{x_k} + \frac{z}{2} q_k \ln \frac{\theta_k}{\phi_k} + l_k - \frac{\phi_k}{x_k} \sum_{j=1}^{M} x_j l_j$$

$$\ln \gamma_i^{\mathrm{RES}} = \sum_{k=1}^{N} \nu_k{}^i [\ln \Gamma_k - \ln \Gamma_k{}^i]$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{j=1}^{M} \Theta_j \psi_{jk}\right) - \sum_{j=1}^{M}\left(\frac{\Theta_j \psi_{kj}}{\sum_{i=1}^{N} \Theta_i \psi_{ij}}\right)\right]$$

$$\psi_{ji} = \exp\left(-\frac{\mu_{ji}}{T}\right), \quad \psi_{ji} \neq \psi_{ij},$$

$$l_k = \frac{z}{2}(r_k - q_k) - (r_k - 1),\ z = 10$$

$$\theta_k = \frac{q_k x_k}{\sum_{j=1}^{M} q_j x_j}, \ \phi_k = \frac{r_k x_k}{\sum_{j=1}^{M} r_j x_j}, \ r_i = \sum_{k=1}^{N} \nu_k{}^i R_k, \ q_i = \sum_{k=1}^{N} \nu_k{}^i Q_k$$

$$\Theta_k = \frac{Q_k \chi_k}{\sum_{j=1}^{N} Q_j \chi_j}, \ \chi_k = \frac{\sum_{i=1}^{M} \nu_k{}^i x_i}{\sum_{k=1}^{N} \sum_{i=1}^{M} \nu_k{}^i x_i}$$

Table VIII. Multicomponent Predictions from Binary Data for 25% and 50% DMF

model	AADP, kPa	AADY
	25% DMF	
Margules	0.17	0.0020
Van Laar	1.71	0.0055
Wilson	0.18	0.0020
UNIQUAC	0.17	0.0020
NRTL	0.18	0.0020
UNIFAC	0.22	0.0020
	50% DMF	
Margules	0.90	0.0040
Van Laar	0.58	0.0068
Wilson	0.80	0.0039
UNIQUAC	0.83	0.0039
NRTL	0.80	0.0039
UNIFAC	0.66	0.0040

Predictions of Ternary Behavior from Binary Data

Table VII shows the multicomponent form of each model which was used for prediction of ternary behavior. The ability of each model to predict ternary behavior is summarized in Table VIII. As was observed by Holmes and van Winkle (7), the van Laar model is least capable of predicing ternary mixture behavior from binary data. Also, the multicomponent form of the van Laar equation requires that

$$\frac{A_{12}}{A_{21}}\frac{A_{23}}{A_{32}}\frac{A_{31}}{A_{13}} = 1.0$$

and our individually determined binary van Laar parameters do not meet this criterion. Further, adjustment of any one parameter to satisfy this criterion does not improve the accuracy of the ternary predictions. The Wilson, UNIQUAC, Margules, NRTL, and Wilson models are all approximately equal in their predictions of ternary vapor-liquid equilibrium from binary data.

In Figure 4 we also show the predictions of the Wilson model for the relative volatility of isobutyraldehyde/ethyl acetate in liquid mixtures containing exactly 0, 25, and 50 mol% DMF, using parameters obtained from binary mixtures. There we see that the predictions are quite good, especially when one realizes that the experimental data are for slightly varying DMF concentrations.

Conclusion

Accurate low-pressure VLE of isobutyraldehyde/ethyl acetate/DMF and the constituent binaries have been obtained. The lowering of the relative volatility of isobutyraldehyde/ethyl acetate by DMF in their ternary mixture can be understood in terms of the chemical interaction between DMF and the aldehyde group. All models considered, except the van Laar model, predict the behavior of the isobutyraldehyde/ethyl acetate/DMF ternary mixture accurately with only binary information. The DMF-aldehyde group interaction in the isobutyraldehyde/DMF and DMF/benzaldehyde mixtures are significantly different as discussed above, and the UNIFAC group contribution model cannot describe both mixtures accurately with one set of DMF-aldehyde parameters.

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Registry No. DMF, 68-12-2; isobutyraldehyde, 78-84-2; ethyl acetate, 141-78-6.

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Thermodynamic Properties of Dichloromethane Gas

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Virial coefficients, derived from an analysis of precise *P-V-T* data, form a basis for the determination of thermodynamic properties and the force constants of appropriate intermolecular potential models. An earlier work reports experimental *P-V-T* measurements for dichloromethane gas from about 350 to 510 K along with compression factors and second virial coefficients. This study presents revised values of second virial coefficients and the following other derived quantities (the figure in parentheses indicates the estimated percent uncertainty): (i) third virial coefficients (2-20); (ii) Stockmayer (12-6-3) force constants; (iii) thermodynamic properties (0.2-0.5 up to 10 atm, increasing to 5 at 30 atm and above); and (iv) fugacity coefficients. Stockmayer force constants of this work, evaluated from the revised second virial coefficients, are in close agreement with literature values. The experimental third virial coefficients are reported for the first time here. Though the uncertainty in these values is large, the usefulness of the values is considerable as is evident from the excellent agreement of the present entropy values with those available in the literature.

Introduction

The present investigation is a part of an extensive research program for evaluating the chemical thermodynamic properties of selected halogenated alkanes over a wide range of temperatures and pressures. The volumetric properties of dichloromethane gas from about 350 to 510 K at pressures below the saturation pressure at each temperature were determined by using a Kay-type apparatus which was fabricated in a previous investigation (*1*). The compression factors and second virial coefficients computed from the measured P,V,T values, with the estimated percent uncertainties of 0.02-0.5 and 0.5, respectively, have been reported elswhere (*1*).

Virial coefficients, derived from an analysis of precise $P-V-T$ data, form a basis for the determination of thermodynamic properties and the force constants of suitable potential models. No experimental values are available for the third and higher virial coefficients of dichloromethane. Using the second virial coefficient data of Perez Masia and Diaz Pena (*2*) in the range 349.53-510.0 K and those of Fogg et al. (*3*) in the range 319.4-382.6 K as compiled by Dymond and Smith (*4*), Polak and Lu (*5*) evaluated the parameters of the Stockmayer (12-6-3) potential function. Rätzsch and Freydank (*6*) report the parameters of the Stockmayer (18-6-3) potential. Dzung (*7*) calculated the thermodynamic properties of dichloromethane up to a temperature of 423 K and a pressure of about 2.6 atm, using published values of the specific heat capacity of the saturated liquid and other pertinent data. Seshadri et al. (*8*) extended the range of Dzung's work by computing the thermodynamic properties of dichloromethane up to a temperature of 750 K and a pressure of 200 atm by using the 11-constant Martin-Hou equation of state (*9*).

This work reports revised values of second virial coefficients and the following other quantities derived from the experimental $P-V-T$ data (*1*) (the figure in parentheses indicates the estimated percent uncertainty): (i) third virial coefficients (2-20); (ii) Stockmayer (12-6-3) force constants; (iii) thermodynamic properties (0.2-0.5 up to 10 atm, increasing to 5 at 30 atm and above); and (iv) fugacity coefficients. The experimental third virial coefficients are reported for the first time in the present investigation. The revised second virial coefficients are of a higher precision than those reported earlier (*1*), these values and the present third virial coefficients being very nearly consistent with each other.

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