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Vapor–Liquid Equilibrium Measurements on the *N*,*N*-Dimethylformamide/1-Butanol System at 65 and 125 °C

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Vapor–liquid equilibrium measurements have been performed by the total-pressure method on the *N*,*N*-dimethylformamide (DMF)/1-butanol system at 65 and 125 °C. The data were reduced to equilibrium phase compositions by using the Wilson activity coefficient equation to model the liquid phase and the Soave equation of state to model the vapor phase.

Introduction

The total-pressure (*PTx*) method is a fast and accurate method for obtaining vapor–liquid equilibrium data. The required measurements are total pressure as a function of charge composition at constant temperature and known cell volume. With accurate models to represent the liquid and vapor phases, these measurements are used to give reliable phase compositions, as well as activity and fugacity coefficients.

Experimental Apparatus and Procedure

The measurements on the *N*,*N*-dimethylformamide/1-butanol binary system were performed at two temperatures, 65 and 125 °C. The entire composition range was covered at both temperatures.

Each isotherm was traversed in two runs. To initiate a run, the cell was charged with a known amount of one component. The cell contents were then degassed by removing vapor into a weighed evacuated sample cylinder. The cell contents were allowed to equilibrate and the pressure was measured. This procedure was repeated until a reliable and repeatable pure component vapor pressure was measured. Increments of the second component were then charged to the cell. After each increment the cell contents were degassed and allowed to equilibrate before the pressure was measured. The amount of material removed from the cell as degas was accounted for in the data reduction procedure. Additions of each component to the cell were made by using weighed syringes. The weights were measured to ±0.002 g.

The second run was similar to the first except that the second component was charged to the cell before adding increments of the first component. The ranges of compositions covered in the runs were designed to overlap to check for consistency between the runs.

The *PTx* runs were made in the glass apparatus shown in Figure 1. This apparatus consisted of a glass cell and manometer suspended in a constant-temperature bath. The contents of the flask were magnetically stirred to promote thermal and phase equilibrium. The heights of the mercury columns in the manometer were read with a cathetometer. The cell volume was 1000 mL for the 65 °C run and 320 mL for the 125 °C run. The pressure on the reference side of the manometer was measured with a McLeod gauge for the 65 °C run. For the 125 °C run the reference side of the manometer was opened to the atmosphere, and atmospheric pressure was measured with a barometer. Pressures were measured to an accuracy of ±0.3 mmHg. Temperatures were measured by a calibrated platinum resistance thermometer to an accuracy of ±0.05 °C. The temperature probe was calibrated against the ice and steam points of water. The DMF and 1-butanol used for the measurements were obtained from Aldrich Chemical Co. and had purities of 99+ and 99.9%, respectively.

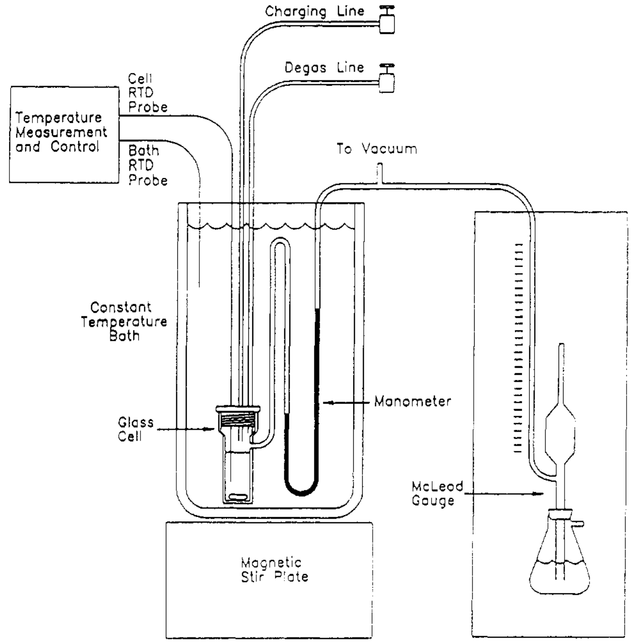

Figure 1. *PTx* experimental apparatus.

Data Reduction Procedure

The *PTx* measurement results, which are total pressure as a function of charge composition at constant temperature, were reduced to equilibrium phase compositions and activity and fugacity coefficients. The Wilson activity coefficient equation (*1*) was used to represent the liquid-phase nonidealities because it has been shown to represent binary systems such as the one reported herein as well as or better than other equations (*2*). The Wilson equation for the excess Gibb's free energy for binary systems is as follows:

$$\frac{g^E}{RT} = -x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (x_2 + \Lambda_{21}x_1) \quad (1)$$

where x_i is the liquid mole fraction of component i. The activity coefficients are given by

$$\ln \gamma_1 = -[\ln (x_1 + \Lambda_{12}x_2)] + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (2)$$

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Table I. Vapor–Liquid Equilibrium Data by the *PTx* Method for the DMF/1-Butanol System at 65 °C

run no.	mol % DMF charge	mol % DMF liquid	mol % DMF vapor	pressure, mmHg measd	pressure, mmHg calcd	activity coeff DMF	activity coeff 1-butanol	relative volatility 1-butanol/DMF
1	100.00	100.00	100.00	33.79	33.79	1.000	0.846	1.97
1	97.01	97.01	94.26	34.57	34.78	1.000	0.851	1.98
1	94.20	94.21	89.09	35.52	35.72	1.000	0.857	1.99
1	89.08	89.08	80.18	37.15	37.50	0.999	0.867	2.02
1	81.76	81.77	68.58	40.01	40.14	0.996	0.881	2.06
1	73.19	73.20	56.47	43.41	43.41	0.990	0.898	2.11
1	73.05	73.06	56.28	43.52	43.47	0.990	0.898	2.11
1	64.91	64.92	46.14	46.97	46.76	0.983	0.914	2.16
1	55.94	55.95	36.32	50.67	50.59	0.971	0.931	2.23
2	54.53	54.54	34.90	51.12	51.21	0.969	0.933	2.24
2	54.41	54.42	34.77	51.27	51.27	0.968	0.933	2.24
1	49.21	49.22	29.80	53.64	53.61	0.959	0.943	2.28
2	46.11	46.12	27.03	55.04	55.05	0.953	0.948	2.31
2	37.88	37.89	20.31	58.92	58.98	0.934	0.962	2.39
2	30.12	30.14	14.81	62.77	62.84	0.912	0.974	2.48
2	23.01	23.02	10.41	66.58	66.50	0.887	0.984	2.58
2	16.96	16.97	7.12	69.59	69.69	0.863	0.991	2.67
2	10.51	10.52	4.07	73.15	73.13	0.834	0.996	2.77
2	5.43	5.44	1.96	75.91	75.84	0.808	0.999	2.87
2	2.79	2.80	0.97	77.00	77.25	0.793	1.000	2.93
2	0.00	0.00	0.00	78.73	78.73	0.776	1.000	2.99

av % dev: 0.21
Wilson activity coeff params: $\Lambda_{12} = 0.600$; $\Lambda_{21} = 1.764$
calc density, g/cm^3: DMF (1), 0.9089; 1-butanol (2), 0.7662

Table II. Vapor–Liquid Equilibrium Data by the *PTx* Method for the DMF/1-Butanol System at 125 °C

run no.	mol % DMF charge	mol % DMF liquid	mol % DMF vapor	pressure, mmHg measd	pressure, mmHg calcd	activity coeff DMF	activity coeff 1-butanol	relative volatility 1-butanol/DMF
1	100.00	100.00	100.00	338.66	338.66	1.000	0.787	2.23
1	97.37	97.38	94.29	351.07	349.93	1.000	0.794	2.25
1	92.75	92.77	84.84	370.13	370.55	0.999	0.808	2.29
1	86.07	86.10	72.46	403.58	402.13	0.996	0.827	2.35
1	78.68	78.73	60.40	439.49	439.56	0.991	0.848	2.43
1	68.93	68.98	46.75	494.41	493.26	0.980	0.875	2.53
1	60.27	60.32	36.55	546.08	544.98	0.966	0.899	2.64
2	54.56	54.67	30.77	577.34	580.77	0.954	0.914	2.71
1	52.71	52.76	28.95	593.26	593.25	0.950	0.919	2.74
2	47.41	47.54	24.34	625.30	628.13	0.937	0.932	2.82
2	38.91	39.07	17.84	684.88	687.47	0.912	0.951	2.95
2	30.67	30.84	12.57	748.72	747.92	0.882	0.968	3.10
2	20.12	20.28	7.11	834.12	828.55	0.838	0.985	3.32
2	11.07	11.19	3.43	909.22	899.61	0.793	0.995	3.55
2	7.63	7.71	2.24	931.93	926.75	0.774	0.998	3.64
2	7.23	7.30	2.11	928.42	929.95	0.772	0.998	3.65
2	2.44	2.47	0.66	975.10	967.40	0.744	1.000	3.79
2	0.00	0.00	0.00	986.29	986.30	0.729	1.000	3.87

av % dev: 0.34
Wilson activity coeff params: $\Lambda_{12} = 0.845$; $\Lambda_{21} = 1.484$
calcd density, g/cm^3: DMF (1), 0.8517; 1-butanol (2), 0.7015
temp dependence of Wilson eq params (based on data at both isotherms): $\lambda_{12} - \lambda_{11}$ (J/mol) = 5954.90 − 11.8275 (T (K)); $\lambda_{12} - \lambda_{22}$ (J/mol) = −2791.41 + 2.000333 (T (K))

$$\ln \gamma_2 = -[\ln (x_2 + \Lambda_{21}x_1)] - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (3)$$

The two adjustable parameters Λ_{12} and Λ_{21} are related to the pure-component molar volumes and to characteristic energy differences by the following equations:

$$\Lambda_{12} \equiv \frac{v_2}{v_1}\exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT}\right] \qquad (4)$$

$$\Lambda_{21} \equiv \frac{v_1}{v_2}\exp\left[-\frac{\lambda_{12} - \lambda_{22}}{RT}\right] \qquad (5)$$

where v_i is the liquid molar volume of component i and λ_{ij} is the interaction energy between the molecules designated by the subscripts. The differences in the characteristic energies are treated as temperature-dependent parameters. Since data were measured at two temperatures, only a straight line temperature dependence is possible, but a straight line is usually adequate over a limited temperature range.

The Soave equation of state (*3*) was used to represent the vapor phase in the data reduction procedure.

To derive equilibrium phase compositions from *PTx* data, an interative procedure is used to solve the fundamental equation of vapor–liquid equilibrium, given as follows:

$$Py_i\phi_i = P_i^{\circ}\phi_i^{\circ}x_i\gamma_i \exp\left[\int_{P_i^{\circ}}^{P}\frac{\bar{V}_i}{RT}\,dP\right] \qquad (6)$$

where P is the total pressure, y_i is the vapor mole fraction of component i, ϕ_i is the fugacity coefficient of component i, P_i° is the vapor pressure of component i at the temperature of interest, ϕ_i° is the fugacity coefficient of component i at system

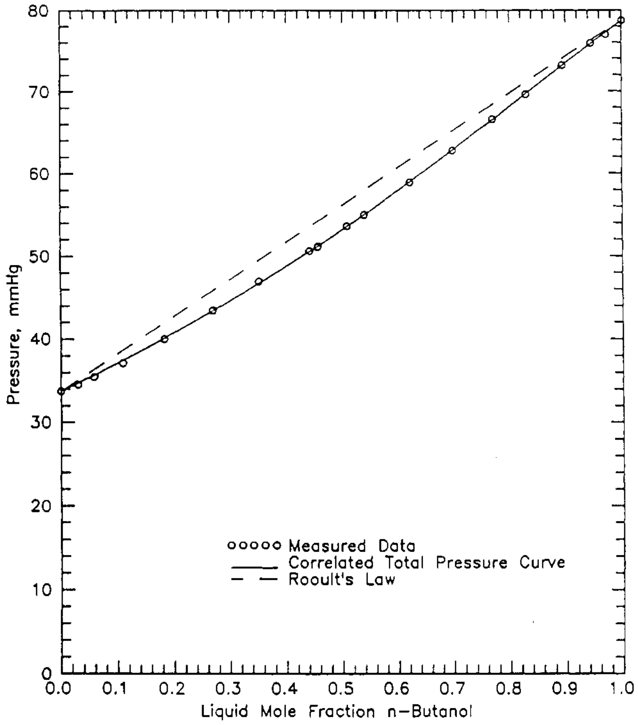

Figure 2. Total pressure versus liquid composition for the DMF/1-butanol system at 65 °C.

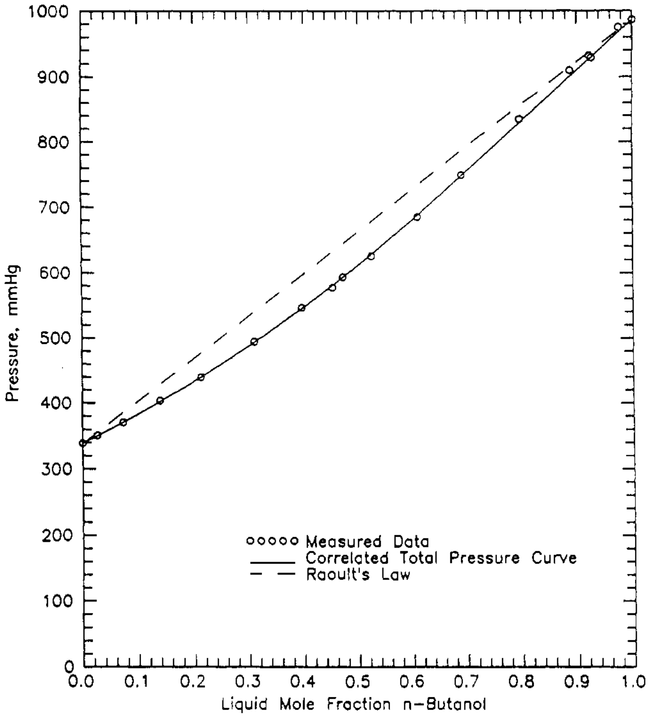

Figure 3. Total pressure versus liquid composition for the DMF/1-butanol system at 125 °C.

temperature and the corresponding vapor pressure of component *i*, x_i is the liquid composition of component *i*, γ_i is the activity coefficient of component *i*, and the exponential term is the Poynting correction where $\bar{V}_i$ is the partial molar volume of component *i*. This volume is obtained from literature density data for each component adjusted to the temperature of the measurements using the Rackett equation (*4*).

The procedure consists of fitting the pressure data to eq 6 across the entire composition range by adjusting the activity coefficient parameters of the Wilson equation. As a beginning

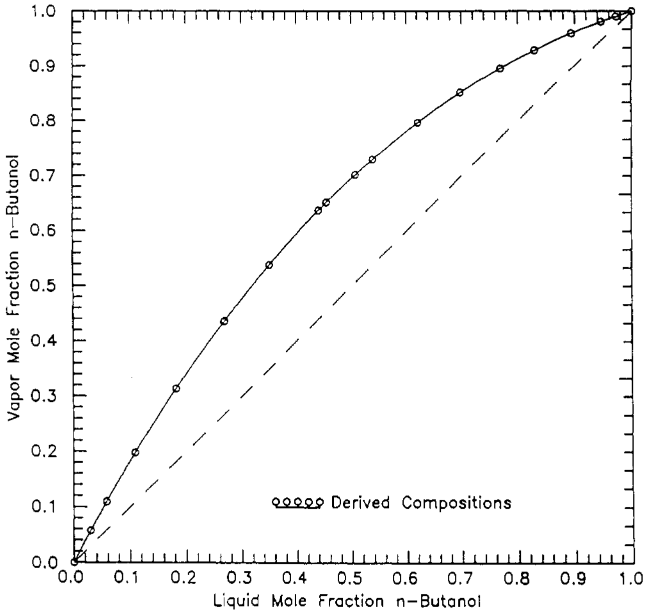

Figure 4. Vapor composition versus liquid composition for the DMF/1-butanol system at 65 °C.

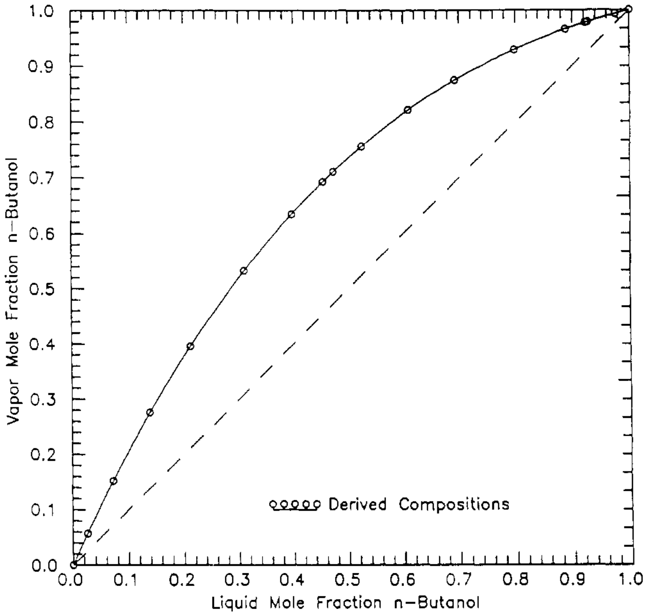

Figure 5. Vapor composition versus liquid composition for the DMF/1-butanol system at 125 °C.

point, the ideal-solution parameters are selected. The activity coefficients are then calculated assuming the liquid composition is the same as the charge composition. Then assuming the fugacity coefficients are unity, eq 6 is solved for the product Py_i for each component. The calculated pressure is then the sum of these products:

$$P_{\mathrm{calc}} = \Sigma(Py_i) \tag{7}$$

The vapor mole fraction for each component is then determined:

$$y_i = (Py_i)/P_{\mathrm{calc}} \tag{8}$$

With values for the vapor-phase composition, the fugacity coefficients can be calculated from the equation of state.

The next step is to correct the liquid composition for the amounts of each component in the vapor and to return to the step in which the activity coefficients were calculated and

Table III. Physical Properties and Vapor Pressures Used in Data Reduction

compound	mol wt	T_c, K	P_c, atm	Z_c	ω	ref ρ, g/cm^3	temp for ρ, K
DMF	73.10	643.15[a]	43.5[a]	0.266	0.3094	0.9487[b]	293.15
1-butanol[c]	74.123	563.10	43.6	0.259	0.593	0.810	293.15

compound	temp, °C	vapor pressure, mmHg measd	vapor pressure, mmHg lit.	% dev
DMF	65	33.79	33.46[d]	0.99
	125	338.66	333.77[d]	1.47
1-butanol	65	78.73	79.10[e]	-0.47
	125	986.29	984.13[e]	0.22

[a] *Dimethylformamide (DMF). Properties, Uses, Storage and Handling.* E. I. du Pont de Nemours & Co.: Wilmington, DE, 1986. [b] Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1985. [c] Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987. [d] Riddick, J. A.; Bunger, W. B. *Organic Solvents: Physical Properties and Methods of Purification*, 3rd ed.; Wiley Interscience: New York, 1970. [e] Kemme, H. R.; Kreps, S. I. *J. Chem. Eng. Data* **1969**, *14*, 98–102.

continue iterating until the calculated pressure converges. As part of each iteration step, the amount of material taken out of the cell as degas is subtracted from the total charge at the calculated vapor composition.

This procedure is performed for each of the measurement points across the composition range. The calculated pressures are compared to the measured pressures, the activity coefficient parameters are adjusted, and the entire procedure is repeated until the calculated pressure curve agrees well with the measured pressure points.

Results and Discussion

Tables I and II contain the measurement results at 65 and 125 °C, respectively. Each table contains the following information for each measured data point: run number, equilibrium charge, liquid and vapor compositions, measured and calculated pressure, activity coefficients of DMF and 1-butanol, and the relative volatility of 1-butanol/DMF. The average absolute deviation of the pressure fit is given in each table, and at the bottom of the tables are the Wilson activity coefficient equation parameters and liquid densities used to correlate the measured data. The temperature dependence of the Wilson parameters is given at the bottom of Table II.

Plots of the total pressure versus liquid composition at 65 and 125 °C are shown in Figures 2 and 3. Moderate negative deviation from Raoult's law behavior at both isotherms is seen in the figures. Figures 4 and 5 show y–x plots for each isotherm.

Table III gives critical constants and other physical property data used in the data reduction. Table III also compares pure component vapor pressures measured during the project with literature values.

List of Symbols

g^E	excess Gibb's free energy
P	pressure
P_{calc}	calculated pressure
P_i°	vapor pressure of component i
R	gas constant
T	absolute temperature, K
v_i	liquid molar volume of component i
$\bar{V}_i$	partial molar volume of component i
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i

Greek Symbols

γ_i	activity coefficient of component i
λ_{ij}	interaction energy between molecules designated by subscripts in Wilson equation
$\Lambda_{12},\Lambda_{21}$	adjustable parameters, Wilson equation
ϕ_i	fugacity coefficient of component i
ϕ_i°	fugacity coefficient of component i at system temperature and corresponding vapor pressure of component i
ρ	density
ω	acentric factor

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