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Isobaric Vapor−Liquid Equilibria of 1-Butanol + *N,N*-Dimethylformamide and 1-Pentanol + *N,N*-Dimethylformamide Systems at 50.00 and 100.00 kPa

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Isobaric vapor−liquid equilibria were obtained for the 1-butanol + *N,N*-dimethylformamide and 1-pentanol + *N,N*-dimethylformamide systems at 50.00 and 100.00 kPa. The activity coefficients were found to be thermodynamically consistent. The data were correlated with five liquid phase activity coefficient models (Margules, Van Laar, Wilson, NRTL, and UNIQUAC). Experimental vapor pressures of *N,N*-dimethylformamide are also included.

Introduction

The experimental determinations of vapor−liquid equilibria (VLE) are indispensable for the design of separation processes such as distillation columns, extractive distillation, and selection of solvents. Although these data can be estimated from available predictive VLE models, experimental data are required to update and improve the data bank used to fit the model parameters. Among these models, the group-contribution methods such as UNIFAC (Fredenslund et al., 1977; Gmehling et al., 1982; Skjold-Jørgensen et al., 1979) have been shown to be useful tools. There is a lack of VLE measurements for some groups (Gmehling and Schiller, 1993). One of the groups for which more measurements are desirable is the dialkylformamide (main group DMF).

In a recent literature review, only isothermal pressure−liquid composition VLE for the 1-butanol + *N,N*-dimethylformamide and 1-pentanol + *N,N*-dimethylformamide systems have been found (Wilson et al., 1991; Surovy and Dojcansky, 1974).

In this paper, isobaric VLE, at 50.00 and 100.00 kPa, for the above systems are presented. The vapor pressures of pure *N,N*-dimethylformamide were also determined. These results can contribute to improved estimation of the interaction parameters between the main groups DMF and OH.

Experimental Section

Chemicals. 1-Butanol, 1-pentanol, and *N,N*-dimethylformamide, high-purity grade from Aldrich Chemical, were used without further purification. The purity of these chemicals was checked by gas chromatography (GLC): 1-butanol, 99.94 mass %; 1-pentanol, 99.30 mass %; and *N,N*-dimethylformamide, 99.85 mass %. The physical properties of the three compounds are listed in Table 1 along with literature values (Lide, 1990).

Apparatus and Procedure. The apparatus used in this work is an all-glass, dynamic recirculating still described by Walas (1985), equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Bonn, Germany), can handle pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. In the boiler, with a volume of 80 cm^3, vapor bubbles are generated by external heating. The Cottrell pump ensures intimate contact between the liquid and vapor phases and also with the sensing temperature elements. The equilibrium temperature is measured with a digital Fischer thermometer with an accuracy of ±0.1 K. For the pressure measuring, a digital manometer with an accuracy of ±0.01 kPa is used.

Table 1. Physical Properties of Chemicals: Densities *d*, Refractive Indices *n*, and Boiling Points T_b

	d(293.15 K)/(g·cm^{-3})		n(293.15 K)		T_b (100.00 kPa)/K	
compd	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.
1-butanol	0.809 50	0.8098	1.3988	1.3993	390.15	390.49[b]
1-pentanol	0.814 68	0.8144	1.4099	1.4101	410.05	410.53[b]
N,N-dimethylformamide	0.948 69	0.9487	1.4301	1.4305	424.75	425.64[c]

[a] Lide (1990). [b] Calculated with the Antoine equation from Reid et al. (1977). [c] Calculated from the correlation proposed in AIChE *Data Compilation Tables of Properties of Pure Compounds* (Daubert and Danner, 1985).

The vapor pressures of *N,N*-dimethylformamide were determined with the same recirculating still.

In each VLE experiment, the pressure was fixed and the heating and shaking systems of the liquid mixture were turned on. The system was kept at the boiling point at least for 30 min to ensure that the steady state was reached. At this moment, 0.2 cm^3 samples of liquid and condensed vapor of the Cottrell pump were taken with special syringes under partial vacuum.

All of the samples were analyzed with a Hewlett-Packard 5890 S-II gas chromatograph with a flame ionization detector. The GLC column was a 60 m, 0.2 mm i.d. fused silica capillary column, Supelcowax 10. Chromatographic conditions were as follows: oven temperature, 463.15 K; gas carrier, helium (30 cm^3·min^{-1}). The GLC response peaks were integrated with a Hewlett-Packard 3396 integrator.

The GLC was calibrated with gravimetrically prepared standard solutions. The standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made for each liquid and each vapor sample.

Results and Discussion

Vapor pressures $P_i°$ were calculated with the Antoine equation

$$\ln (P_i°/\mathrm{kPa}) = A - B/(C + T/K) \tag{1}$$

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Table 2. *N,N*-Dimethylformamide Vapor Pressure $P_i°$ Data as a Function of Temperature *T* and Antoine Constants

T/K	$P_i°$/kPa	T/K	$P_i°$/kPa	T/K	$P_i°$/kPa
338.25	4.60	392.55	38.40	416.15	78.86
362.25	12.90	396.45	43.55	418.15	83.52
369.05	16.79	400.45	49.41	420.55	89.22
373.75	19.99	402.55	52.75	422.65	94.68
379.15	24.29	406.05	58.67	424.55	99.61
383.25	28.06	409.45	64.86	425.05	100.78
388.15	33.19	411.75	69.43		

	A	B	C
N,N-dimethylformamide	14.54077	3628.89	−59.420

Table 3. Vapor−Liquid Equilibrium Data, Liquid Phase Mole Fraction x_1, Vapor Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i for the 1-Butanol(1) + *N,N*-Dimethylformamide (2) System at Constant Pressure *P*

P/kPa	x_1	y_1	T/K	γ_1	γ_2
50.00	0.000	0.000	401.55		
	0.013	0.028	400.65	0.737	0.991
	0.036	0.075	399.85	0.745	0.990
	0.059	0.118	399.05	0.741	0.991
	0.090	0.188	397.95	0.799	0.977
	0.126	0.253	396.55	0.806	0.979
	0.170	0.335	394.75	0.840	0.972
	0.218	0.415	393.05	0.862	0.959
	0.268	0.489	391.35	0.878	0.945
	0.333	0.579	389.15	0.905	0.919
	0.397	0.649	387.05	0.916	0.911
	0.482	0.726	384.45	0.929	0.904
	0.545	0.779	382.75	0.940	0.880
	0.598	0.822	381.15	0.960	0.848
	0.660	0.870	379.55	0.977	0.776
	0.717	0.902	378.05	0.988	0.742
	0.766	0.930	376.75	1.004	0.671
	0.807	0.941	375.75	1.003	0.708
	0.851	0.960	374.65	1.013	0.650
	0.887	0.970	373.85	1.014	0.660
	0.918	0.977	373.15	1.015	0.716
	0.940	0.983	372.55	1.021	0.740
	0.965	0.991	372.25	1.015	0.684
	1.000	1.000	371.85		
100.00	0.000	0.000	424.75		
	0.012	0.028	423.85	0.821	1.005
	0.030	0.069	423.15	0.806	1.000
	0.052	0.116	422.05	0.800	1.002
	0.089	0.188	420.45	0.791	1.001
	0.138	0.280	418.35	0.812	0.995
	0.220	0.431	414.45	0.879	0.971
	0.312	0.550	411.15	0.878	0.957
	0.426	0.685	406.85	0.917	0.913
	0.531	0.777	403.45	0.931	0.878
	0.618	0.841	400.25	0.963	0.848
	0.699	0.900	398.05	0.981	0.723
	0.740	0.918	396.65	0.991	0.722
	0.798	0.936	395.05	0.990	0.764
	0.861	0.960	393.35	0.999	0.733
	0.867	0.964	393.25	0.999	0.697
	0.901	0.971	392.25	1.004	0.765
	0.908	0.975	392.05	1.006	0.718
	0.931	0.981	391.55	1.006	0.747
	0.963	0.990	390.55	1.016	0.762
	1.000	1.000	390.15		

Table 4. Vapor−Liquid Equilibrium Data, Liquid Phase Mole Fraction x_1, Vapor Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i for the 1-Pentanol (1) + *N,N*-Dimethylformamide (2) System at Constant Pressure *P*

P/kPa	x_1	y_1	T/K	γ_1	γ_2
50.00	0.000	0.000	401.55		
	0.038	0.046	401.45	0.812	0.974
	0.055	0.068	401.15	0.851	0.977
	0.090	0.109	400.85	0.842	0.979
	0.127	0.155	400.05	0.871	0.992
	0.169	0.206	399.85	0.879	0.985
	0.221	0.271	399.45	0.895	0.977
	0.286	0.350	398.85	0.914	0.968
	0.365	0.444	398.05	0.935	0.955
	0.451	0.541	397.05	0.954	0.943
	0.544	0.640	396.15	0.969	0.915
	0.633	0.733	395.15	0.990	0.871
	0.708	0.803	394.15	1.005	0.837
	0.773	0.856	393.25	1.015	0.812
	0.828	0.894	392.55	1.017	0.802
	0.871	0.924	391.95	1.023	0.778
	0.903	0.942	391.25	1.033	0.810
	0.926	0.959	390.75	1.044	0.777
	0.946	0.969	390.55	1.041	0.802
	1.000	1.000	390.05		
100.00	0.000	0.000	424.75		
	0.009	0.012	424.65	0.834	0.997
	0.032	0.043	424.45	0.855	0.994
	0.074	0.096	424.05	0.835	0.992
	0.108	0.140	423.55	0.840	0.994
	0.146	0.188	423.05	0.851	0.993
	0.179	0.231	422.55	0.864	0.992
	0.221	0.287	421.95	0.885	0.986
	0.269	0.355	421.25	0.920	0.969
	0.332	0.429	420.35	0.925	0.964
	0.393	0.514	419.45	0.966	0.924
	0.451	0.578	418.65	0.970	0.908
	0.523	0.649	417.65	0.971	0.893
	0.590	0.710	416.65	0.973	0.883
	0.659	0.778	415.65	0.985	0.838
	0.716	0.823	414.65	0.992	0.824
	0.766	0.859	413.75	0.997	0.820
	0.804	0.885	413.05	1.001	0.815
	0.842	0.909	412.25	1.009	0.817
	0.871	0.928	411.85	1.009	0.797
	0.896	0.944	411.45	1.011	0.790
	0.917	0.955	411.05	1.013	0.795
	0.936	0.965	410.75	1.013	0.805
	0.953	0.975	410.55	1.013	0.788
	1.000	1.000	410.05		

For 1-butanol and 1-pentanol, the constants given in Aucejo et al. (1994a,b) were used. The experimental vapor pressure data of pure *N,N*-dimethylformamide are listed in Table 2. The constants in eq 1 (Table 2) were fitted by a nonlinear optimization method to minimize the mean relative deviation in $P_i°$. Experimental data were compared with the values calculated from the correlations proposed in Gmehling et al. (1978) and in the AIChE *Data Compilation Tables of Properties of Pure Compounds* (Daubert and Danner, 1985), the mean relative deviations being 3.25% and 3.57%, respectively.

The experimental VLE data for both binary systems at 50.00 and 100.00 kPa are given in Tables 3 and 4.

To calculate the liquid phase activity coefficients, γ_i, the Poynting factor was considered as unity at the experimental conditions. The fugacity coefficients were calculated on the basis of the virial equation of state with the second virial coefficient being estimated by means of correlation proposed in the AIChE *Data Compilation Tables of Properties of Pure Compounds* (Daubert and Danner, 1985). For every experimental pressure−temperature−composition condition, the calculated fugacity coefficients were close to unity (1.006 maximum, 0.985 minimum), and were not considered in the analysis of the VLE data. So, the experimental liquid phase activity coefficients γ_i were calculated from

$$\gamma_i = Py_i/x_iP_i° \qquad (2)$$

Table 5. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution γ_i^∞, and Mean Absolute Deviations MAD(*y*) and MAD(*T*)

P/kPa	model	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD(*y*)	MAD(*T*)
		1-Butanol (1) + *N,N*-Dimethylformamide (2) System						
50.00	Margules	−0.3221^a	−0.5676^a		0.72	0.57	0.0120	0.45
	Van Laar	−0.3555^a	−0.5722^a		0.70	0.56	0.0119	0.44
	Wilson	32.92^b	−1170.88^b		0.78	0.82	0.0100	0.50
	NRTL	237.51^b	−1355.67^b	0.47^a	0.82	0.80	0.0113	0.43
	UNIQUAC	795.95^b	−1132.95^b		0.84	0.83	0.0111	0.42
100.00	Margules	−0.2751^a	−0.4044^a		0.76	0.67	0.0071	0.26
	Van Laar	−0.2967^a	−0.3928^a		0.74	0.67	0.0070	0.25
	Wilson	34.51^b	−953.80^b		0.80	0.84	0.0061	0.30
	NRTL	242.16^b	−1264.29^b	0.47^a	0.84	0.82	0.0065	0.24
	UNIQUAC	821.24^b	−1073.30^b		0.86	0.86	0.0064	0.24
		1-Pentanol (1) + *N,N*-Dimethylformamide (2) System						
50.00	Margules	−0.2142^a	−0.2806^a		0.81	0.75	0.0077	0.45
	Van Laar	−0.2200^a	−0.2801^a		0.80	0.75	0.0077	0.45
	Wilson	40.62^b	−525.78^b		0.82	0.87	0.0066	0.38
	NRTL	249.34^b	−989.05^b	0.47^a	0.88	0.86	0.0074	0.44
	UNIQUAC	870.60^b	−960.56^b		0.87	0.89	0.0071	0.42
100.00	Margules	−0.2230^a	−0.2707^a		0.80	0.76	0.0094	0.15
	Van Laar	−0.2407^a	−0.2658^a		0.79	0.77	0.0078	0.20
	Wilson	34.77^b	−552.76^b		0.82	0.87	0.0067	0.20
	NRTL	250.67^b	−1032.37^b	0.47^a	0.87	0.86	0.0077	0.19
	UNIQUAC	876.75^b	−973.44^b		0.88	0.89	0.0083	0.13

[a] Dimensionless. [b] J·mol^{-1}.

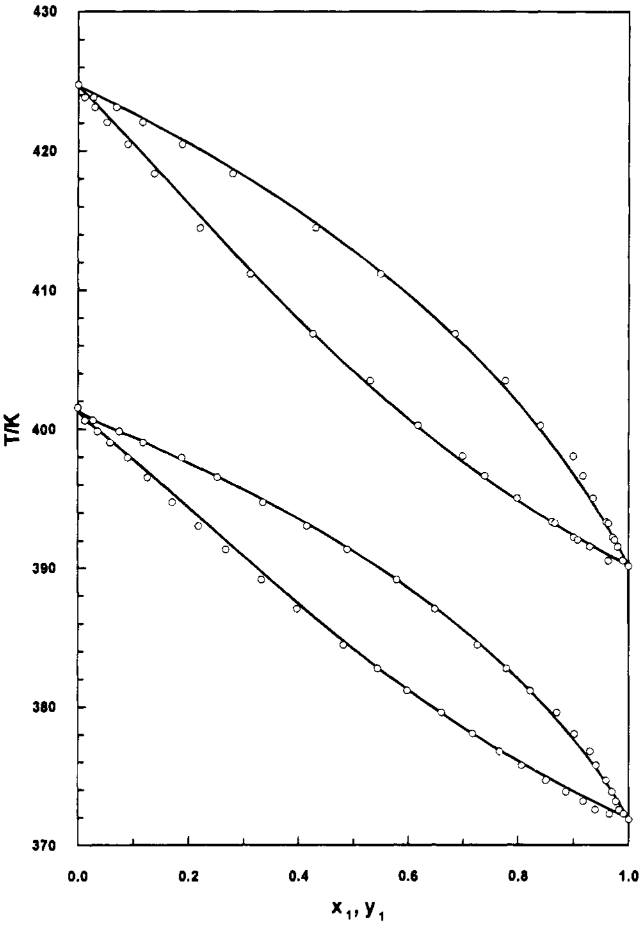

Figure 1. Temperature *T* vs composition (x_1, y_1) for the system 1-butanol (1) + *N,N*-dimethylformamide (2) at constant pressure, *P* = 100.00 and 50.00 kPa: ○, experimental; —, Wilson model.

The thermodynamic consistency of the VLE experimental data was checked against the point-to-point test of Van Ness et al. (1973), as modified by Fredenslund et al. (1977), using a four-parameter Legendre polynomial. The selected objective function to minimize was the sum of the squared relative deviations in the total pressure, SSRD(*P*)

$$\mathrm{SSRD}\ (P) = \sum\left(\frac{P_{\mathrm{exptl}} - P_{\mathrm{calcd}}}{P_{\mathrm{exptl}}}\right)^2 \tag{3}$$

According to this test, the experimental data are consistent if the mean absolute deviation in *y*, MAD(*y*), is less than 0.01. The following values were obtained: For the 1-butanol + *N,N*-dimethylformamide system, MAD(*y*) = 0.0081 at 50.00 kPa and 0.0066 at 100.00 kPa; for the 1-pentanol + *N,N*-dimethylformamide system, MAD(*y*) = 0.0090 and 0.0086 at 50.00 and 100.00 kPa, respectively.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (Gmehling and Onken, 1977). To fit the binary parameters, a nonlinear optimization method was used to minimize the objective function

$$F = \sum_n \sum_i \left(\frac{\gamma_{\mathrm{exptl}} - \gamma_{\mathrm{calcd}}}{\gamma_{\mathrm{exptl}}}\right)^2_{i,n} \tag{4}$$

where *n* is the number of data points. The adjustable parameters A_{12}, A_{21}, and α_{12} for the correlation equations, mean absolute deviations, and activity coefficients at infinite dilution γ_i^∞ are given in Table 5. All models represent the data quite well. As an example, the results predicted with the Wilson model for the 1-butanol + *N,N*-dimethylformamide system are shown in Figure 1 along with the experimental data. The systems show negative deviations from ideality, as can be seen from the activity coefficients at infinite dilution. For both systems, the VLE is slightly influenced by pressure.

Literature Cited

Aucejo, A.; Burguet, M. C.; Montón, J. B.; Muñoz, R.; Sanchotello, M.; Vázquez, M. I. Vapor–Liquid Equilibria for Systems of 1-Butanol with 2-Methyl-1-butanol, 3-Methyl-1-butanol, 2-Methyl-2-butanol, 3-Methyl-2-butanol at 30 and 100 kPa. *J. Chem. Eng. Data* **1994a**, *39*, 271.

Aucejo, A.; Burguet, M. C.; Montón, J. B.; Muñoz, R.; Sanchotello, M.; Vázquez, M. I. Isothermal Vapor–Liquid Equilibria of 1-Pentanol with 2-Methyl-1-butanol, 2-Methyl-2-butanol, 3-Methyl-2-butanol. *J. Chem. Eng. Data* **1994b**, *39*, 578.

Daubert, T. E.; Danner, R. P. *Data Compilation Tables of Properties of Pure Compounds*; AIChE: New York, 1985.

Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor–Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

Gmehling, J., Onken, U., Eds. *Vapor–Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt/Main, 1977; Vol. 1, Part 1.

Gmehling, J., Onken, U., Eds. *Vapor–Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt/Main, 1978; Vol. 1, Part 2b.

Gmehling, J.; Rasmussen, P.; Fredenslund, Aa. Vapor–Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension 2. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118.

Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178.

Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics,* 71st ed.; CRC Press: Boca Raton, FL, 1990.

Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids,* 3rd ed.; McGraw-Hill: New York, 1977.

Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. Vapor–Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714.

Surovy, J.; Dojcansky, J. Dependence of the vapor pressure and activity coefficients on the composition of some two-components polar solvents. *Chem. Zvesti* **1974**, *28*, 313.

Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor–Liquid Equilibrium: Part I. An Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238.

Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, 1985.

Wilson, H. L.; Wilding W. V.; Nelditch, D. Vapor–Liquid Equilibrium Measurements on the *N,N*-Dimethylformamide/1-Butanol System at 65 and 125 °C. *J. Chem. Eng. Data* **1991**, *36*, 346.

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