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Vapor−Liquid Equilibria for Four Binary Systems at 363.15 K: *N*-Methylformamide + Hexane, + Benzene, + Chlorobenzene, and + Acetonitrile

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In this work experimental VLE data are presented for *N*-methylformamide + hexane, *N*-methylformamide + benzene, *N*-methylformamide + chlorobenzene, and *N*-methylformamide + acetonitrile at 363.15 K. The data were measured using a computer driven static vapor−liquid equilibrium device. The data were modeled with the NRTL excess Gibbs energy (g^E) model. Activity coefficients at infinite dilution for the low boiling compound were calculated using a differential pressure method and the NRTL equation.

Introduction

Vapor−liquid equilibrium (VLE) data are essential for the design of separation processes and equipment as well as for the extension of thermodynamic models. In this study isothermal, $P-x$ data were measured at 363.15 K for the four mixtures *N*-methylformamide + hexane, *N*-methylformamide + benzene, *N*-methylformamide + chlorobenzene, and *N*-methylformamide + acetonitrile using a computer-controlled, static apparatus. No literature data are available for *N*-methylformamide + hexane, + chlorobenzene, and + acetonitrile.

Experimental Section

Materials. The chemicals were purchased from commercial sources and were purified as previously explained.[1] This included drying over molecular sieves, degassing, and distilling. Final working purities were at least 99.9%.

Apparatus and Procedures. VLE data for this study were measured as isothermal $P-x$ data. The equipment used is the same as that used in previous studies[2] and has been described previously.[3,4] The experimental procedure is based on the work of Gibbs and Van Ness.[5]

The motor driven injection pumps were charged with the purified compounds, and the liquids were then pumped into the evacuated VLE cell through automated valves. The VLE cell was maintained at constant temperature by immersing in an oil bath. The overall compositions were determined from the metered quantities of liquid pumped into the cell. Liquid-phase composition (x_i) was calculated by solving mass and volume balances while taking into account the phase equilibrium.[3] A summary of the equipment used and the uncertainties in the measured properties are given in Table 1.

Table 1. Measured Parameters, Devices Used, and Experimental Uncertainty

measurement	device	uncertainty
T	Pt 100 (model 1506, Hart Scientific)	0.03 K
P	Digiquartz sensor (model 245A, Paroscientific)	20 Pa + 0.0001 (P/Pa)
x_i	N/A	0.002

Table 2. VLE Data for the System Hexane (1) + *N*-Methylformamide (2) at 363.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000	2.01	0.126	189.05	0.675	188.86
0.002	13.51	0.152	189.06	0.736	188.88
0.004	22.47	0.182	189.08	0.789	188.86
0.007	33.12	0.214	189.12	0.837	188.86
0.010	44.93	0.248	189.14	0.879	188.85
0.012	56.36	0.274	188.96	0.913	188.84
0.019	83.32	0.283	189.20	0.941	188.84
0.026	105.96	0.309	188.93	0.959	188.82
0.034	129.69	0.349	188.90	0.971	188.82
0.043	153.13	0.394	188.89	0.981	188.81
0.053	175.07	0.443	188.88	0.988	188.74
0.065	188.98	0.497	188.88	0.994	188.44
0.081	189.04	0.554	188.86	0.997	188.38
0.102	189.05	0.614	188.86	1.000	188.05

Results

VLE. Tables 2−5 list the VLE experimental $P-x$ data. The data are plotted in Figures 1−4. $P-x_i-y_i$ values were calculated with the NRTL model,[6] and y_i values were corrected by using the virial equation of state.[6] The calculated liquid phase (x_i) and vapor phase (y_i) values are also presented in Figures 1−4. Equation 1 defines the objective function (F) which was minimized to regress the NRTL parameters (Δg_{12}, Δg_{21}, and α_{12}) from the experimental data

$$F = \left(\frac{P_{\text{expt}} - P_{\text{calc}}}{P_{\text{expt}}}\right)^2 \qquad (1)$$

The regressed NRTL parameters (Δg_{12}, Δg_{21}, and α_{12}) are given in Table 6.

Infinite Dilution Activity Coefficients. Infinite dilution activity coefficients (γ^∞) were determined from the NRTL parameters[6] and also from the pressure differential

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Table 3. VLE Data for the System Benzene (1) + *N*-Methylformamide (2) at 363.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000	1.95	0.221	82.85	0.807	129.39
0.002	3.15	0.258	90.36	0.849	130.44
0.004	4.46	0.297	96.99	0.886	131.41
0.007	5.92	0.337	102.82	0.917	132.38
0.010	7.40	0.359	105.32	0.942	133.30
0.012	8.74	0.378	107.84	0.961	134.26
0.021	13.43	0.400	109.72	0.974	135.04
0.032	19.06	0.418	111.99	0.982	135.66
0.046	25.55	0.444	113.66	0.989	136.18
0.061	32.63	0.492	117.17	0.993	136.55
0.080	40.30	0.543	120.18	0.997	136.94
0.101	48.47	0.596	122.75	0.999	137.15
0.125	56.77	0.650	124.87	1.000	137.28
0.154	65.78	0.704	126.62		
0.186	74.56	0.757	128.09		

Table 4. VLE Data for the System Chlorobenzene (1) + *N*-Methylformamide (2) at 363.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000	2.10	0.189	17.86	0.732	27.17
0.002	2.34	0.223	19.39	0.786	27.44
0.003	2.52	0.260	20.73	0.831	27.65
0.005	2.76	0.299	21.91	0.871	27.85
0.008	3.18	0.330	22.77	0.906	28.03
0.012	3.67	0.338	22.91	0.933	28.18
0.017	4.32	0.369	23.60	0.955	28.30
0.024	5.20	0.378	23.73	0.970	28.36
0.034	6.36	0.413	24.36	0.979	28.39
0.047	7.69	0.417	24.43	0.986	28.39
0.062	9.15	0.460	25.03	0.991	28.38
0.080	10.80	0.511	25.61	0.996	28.36
0.101	12.53	0.564	26.10	0.999	28.34
0.127	14.37	0.620	26.52	1.000	28.33
0.156	16.16	0.676	26.87		

Table 5. VLE Data for the System Acetonitrile (1) + *N*-Methylformamide (2) at 363.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000	2.13	0.286	52.47	0.841	113.04
0.005	3.14	0.331	58.76	0.876	116.67
0.008	3.93	0.377	64.74	0.905	119.69
0.013	5.03	0.423	70.38	0.929	122.37
0.018	6.05	0.469	75.64	0.949	124.67
0.026	7.70	0.513	80.51	0.964	126.56
0.041	10.82	0.554	84.93	0.976	128.04
0.058	14.20	0.576	87.31	0.984	129.02
0.080	18.46	0.594	88.97	0.989	129.68
0.105	23.09	0.622	91.93	0.992	130.17
0.133	28.22	0.668	96.46	0.995	130.55
0.165	33.78	0.714	100.85	0.998	130.85
0.200	39.59	0.759	105.10	0.999	131.01
0.242	46.05	0.802	109.19	1.000	131.21

method.[7] The equation for the NRTL method is given by

$$\ln \gamma_i^\infty = \tau_{ij} \exp(-\alpha_{12}\tau_{ij}) + \tau_{ji} \tag{2}$$

The simplified equation for the pressure differential method is

$$\gamma_i^\infty = \frac{(P^E/x_ix_j)^\infty}{P_i^{sat}} + 1 \tag{3}$$

where P_i^{sat} is the saturated vapor pressure for component i and

$$P^E = |P - \sum x_i P_i^{sat}| \tag{4}$$

where P refers to the actual system pressure.

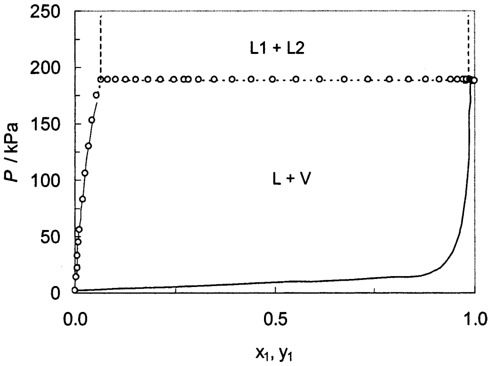

Figure 1. Experimental and calculated $P-x$ (y) data for the system hexane (1) + *N*-methylformamide (2) at 363.15 K: ○, experimental data; —, NRTL.

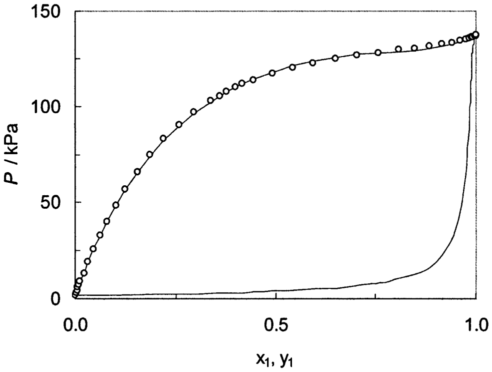

Figure 2. Experimental and calculated $P-x$ (y) data for the system benzene (1) + *N*-methylformamide (2) at 363.15 K: ○, experimental data; —, NRTL.

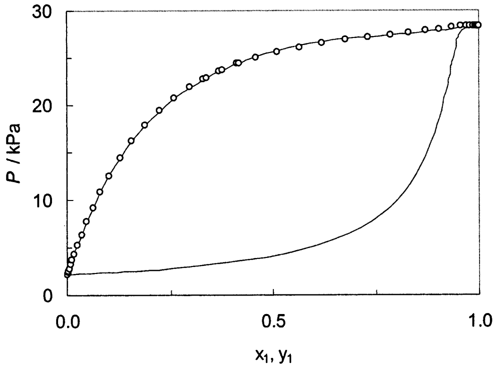

Figure 3. Experimental and calculated $P-x$ (y) data for the system chlorobenzene (1) + *N*-methylformamide (2) at 363.15 K: ○, experimental data; —, NRTL.

Table 6. Regressed NRTL Parameters for the Experimental VLE Data at 363.15 K

system	Δg_{12} J·mol^{-1}	Δg_{21} J·mol^{-1}	α_{12}
hexane (1) + *N*-methylformamide (2)	8108	7378	0.373
benzene (1) + *N*-methylformamide (2)	6641	2306	0.497
chlorobenzene (1) + *N*-methylformamide (2)	6220	2689	0.503
acetonitrile (1) + *N*-methylformamide (2)	2212	794.7	0.989

Determination of the limiting values, $(P^E/x_ix_j)^\infty$, according to the method of Maher and Smith[8] is shown for the *N*-methylformamide + chlorobenzene system in Figure 5. As discussed previously,[9] derivation of γ^∞ values from $P-x$ data is difficult for high boiling substances (such as *N*-methylformamide) in low boiling components. Thus, only

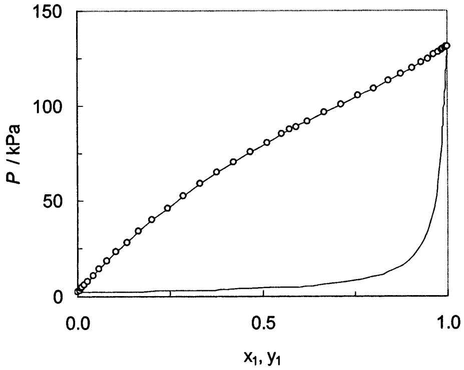

Figure 4. Experimental and calculated $P-x$ (y) data for the system acetonitrile (1) + N-methylformamide (2) at 363.15 K: ○, experimental data; —, NRTL.

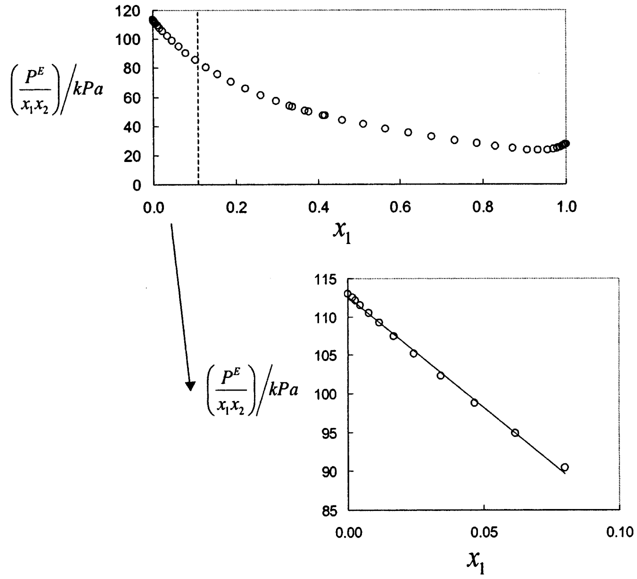

Figure 5. Determination of the limiting values, $(P^E/x_ix_j)^\infty$, according to the method of Maher and Smith[8] for the chlorobenzene (1) + N-methylformamide (2) system.

Table 7. γ^∞ Values for the Four Binary Systems Determined from VLE Data at 363.15 K

system	$\gamma_1^{\infty\,a}$	$\gamma_1^{\infty\,b}$
hexane (1) + N-methylformamide (2)	30.9	42.2
benzene (1) + N-methylformamide (2)	4.5	4.3
chlorobenzene (1) + N-methylformamide (2)	5.1	5.0
acetonitrile (1) + N-methylformamide (2)	1.9	1.7

[a] Calculated using eq 2. [b] Calculated using eq 3.

γ^∞ values with N-methylformamide as the solvent are considered. Table 7 compares the γ^∞ values calculated by these two methods for the four binary systems.

Conclusions

In this work experimental VLE data are presented for N-methylformamide + hexane, N-methylformamide + benzene, N-methylformamide + chlorobenzene, and N-methylformamide + acetonitrile at 363.15 K. The NRTL model fits the pressure data within 1.5 kPa for the systems N-methylformamide + benzene, + chlorobenzene, and + acetonitrile, as shown in Figure 6. The model does not fit the N-methylformamide + hexane system well; however, of the models assessed, it gave the best fit. The N-methylformamide + hexane system forms two liquid phases, as is indicated in Figure 1.

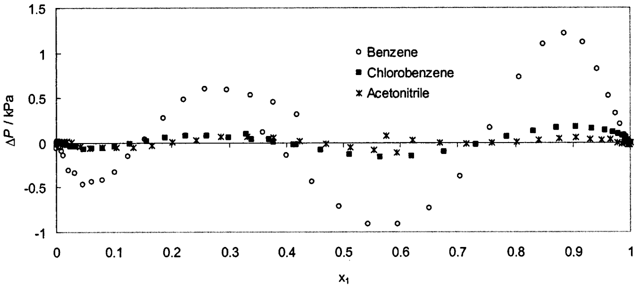

Figure 6. Pressure difference (ΔP) between actual pressures and model pressures for the N-methylformamide (2) + benzene (1), + chlorobenzene (1), and + acetonitrile (1) systems at 363.15 K.

γ^∞ values are presented for all four systems, calculated both from the fitted NRTL equation and from the generally more reliable method of Maher and Smith.[8] The two methods give similar results for the N-methylformamide + benzene, + chlorobenzene, and + acetonitrile systems, as shown in Table 7.

Acknowledgment

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