Isothermal Vapor−Liquid Equilibria of Binary Mixtures of Nitrogen with Dimethyl Sulfoxide, *N*-Methyl-2-pyrrolidone, and Diethylene Glycol Monobutyl Ether at Elevated Pressures

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High-pressure vapor−liquid phase equilibrium (*P*, *x*, *y*) were measured for the binary systems of nitrogen + dimethyl sulfoxide, nitrogen + *N*-methyl-2-pyrrolidone, and nitrogen + diethylene glycol monobutyl ether over a temperature rage between (323.15 and 393.15) K. In addition to the new data, the Soave−Redlich−Kwong, Peng−Robinson, and Patel−Teja equations of state accompanied by several types of mixing rule were also used to correlate these vapor−liquid phase behaviors. In general, the Patel−Teja equation incorporated with mixing rule-C (linear temperature-dependent combining rule for a_{ij}) yielded the best representation.

Introduction

The stripper agent is an important material for photolithography technology in the manufacture of semiconductors. In our laboratory, we are interested in investigating the recovery of stripper agent and reducing the pollution impact of the stripper agent on the environment. It is very important to have accurate and reliable vapor−liquid equilibrium (VLE) data, because those properties of such mixture systems cannot be predicted from pure component values. Therefore, VLE data for these mixtures are essential to design and operate new processes or establish environment-friendly industrial equipment. Nitrogen is the preferred carrier gas in most applications of separation processes because it is cheap, nontoxic, and nonreactive toward many materials. A stripper agent waste always includes the mixture system of dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and diethylene glycol monobutyl ether (DGBE). Hence a knowledge of the VLE data of N₂ + the components of stripper agent waste mixture system is required. In this paper, a semi-flow apparatus was used to measure the high-pressure VLE for N₂ + DMSO, N₂ + NMP, and N₂ + DGBE at temperatures from (323.15 to 393.15) K and pressures up to 100 bar. In addition to the new data, the Soave−Redlich−Kwong (SRK), Peng−Robinson (PR), and Patel−Teja (PT) equations of state using several types of mixing rules (MR) were also used to correlate the results. In general, the PT equation incorporated with MR-C (linear temperature-dependent combining rule for a_{ij}) yielded the best representation.

Experimental Section

Chemicals. Nitrogen with a purity of 99.99 % was supplied by San Fu Chemical Company (Taiwan). Dimethyl sulfoxide was obtained from Sigma-Aldrich. NMP and DGBE were purchased from Fluka Chemicals (Germany). The purities of

these liquids were greater than 99 %. All the chemicals were used without further purification.

Apparatus and Procedure. A semi-flow VLE apparatus, as shown in Figure 1, was used in this work. The detailed descriptions of the apparatus and the operation have been given else where.[1,2] The main portion of the apparatus is a presaturator, and an equilibrium cell with a total internal volume of 600 cm³ that was immersed into an oil thermostated bath (model EX-251HT, stability = 0.03 K, Neslab Co., USA) and the equilibrium temperature was measured by a micro-thermometer (model 1506, Hart Scientific, USA) with a platinum RTD probe to an uncertainty of ± 0.02 K. At the beginning of operation, liquid stripper agent solute (about 400 cm³) was charged into the presaturator and the equilibrium cell at the temperature of interest. Nitrogen then flowed continuously into the pressure vessels to contact with the liquid. Nitrogen flow rate was adjusted by micrometering valves and monitored by a wet test meter. The flow rate should be slow enough to ensure that phase equilibrium was attained in the equilibrium cell. After controlling the equilibrium condition at a constant pressure and temperature of interest for 3 h, the saturated vapor stream was diverted to a sampling flask, which was immersed in an ice bath after its pressure and temperature were reduced. The stripper agent solute was trapped in the flask and later weighed to determine its mass by an analytical electronic balance with a precision of ± 0.1 mg. The corresponding quantity of nitrogen liberated from the sample was measured with a wet test meter. Liquid sample was taken from the bottom of the equilibrium cell, while the pressure of the cell was maintained at a very small fluctuation by a vapor stream that passed continuously over the top of the equilibrium cell from the presaturator. Similar method was used for composition analysis of liquid samples, but a graduated cylinder, instead of the wet test meter, was employed to collect the liberated nitrogen. A pressure transducer (PDCR-330, 0−300 bar, Druck Ltd., UK) with a digital indicator (model DPI 261, Druck Ltd., UK) was employed to read the

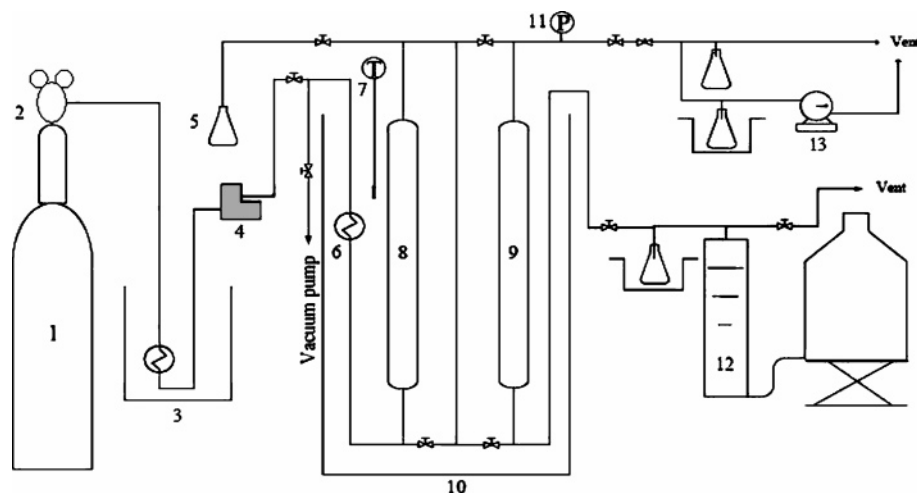* Corresponding author. E-mail: wengwl@must.edu.tw. Fax: +886-3-6007577.

Figure 1. Schematic diagram for the semi-flow VLE apparatus: 1, nitrogen cylinder; 2, regulator; 3, precool equipment; 4, liquid pump; 5, heavy component input equipment; 6, preheat loop; 7, thermometer; 8, presaturator; 9, equilibrium cell; 10, thermostated bath; 11, pressure transducer; 12, graduated cylinder; 13, wet test meter.

Table 1. Vapor−Liquid Equilibrium Data for Nitrogen (1) + Dimethyl Sulfoxide (2)

T/K	P/bar	y_2	x_1	$K_2 = y_2/x_2$	$K_1 = y_1/x_1$
323.15	30.0	0.0007	0.0026	0.0007	384.4
	40.0	0.0005	0.0035	0.0005	285.6
	50.0	0.0004	0.0044	0.0004	227.2
	60.0	0.0004	0.0052	0.0004	192.2
	70.0	0.0003	0.0059	0.0003	169.4
	80.0	0.0003	0.0067	0.0003	149.2
	90.0	0.0003	0.0074	0.0003	135.1
	100.0	0.0003	0.0080	0.0003	125.0
353.15	30.0	0.0012	0.0032	0.0012	312.1
	40.0	0.0010	0.0042	0.0010	237.9
	50.0	0.0009	0.0052	0.0009	192.1
	60.0	0.0008	0.0063	0.0008	158.6
	70.0	0.0007	0.0073	0.0007	136.9
	80.0	0.0007	0.0084	0.0007	119.0
	90.0	0.0006	0.0094	0.0006	106.3
	100.0	0.0006	0.0104	0.0006	96.1
393.15	30.0	0.0036	0.0043	0.0036	231.7
	40.0	0.0031	0.0057	0.0031	174.9
	50.0	0.0025	0.0070	0.0025	142.5
	60.0	0.0022	0.0083	0.0022	120.2
	70.0	0.0020	0.0096	0.0020	104.0
	80.0	0.0020	0.0112	0.0020	89.1
	90.0	0.0019	0.0126	0.0019	79.2
	100.0	0.0018	0.0146	0.0018	68.4

Table 2. Vapor−Liquid Equilibrium Data for Nitrogen (1) + *N*-Methyl-2-pyrrolidone (2)

T/K	P/bar	y_2	x_1	$K_2 = y_2/x_2$	$K_1 = y_1/x_1$
323.15	30.0	0.0005	0.0060	0.0005	166.6
	40.0	0.0004	0.0078	0.0004	128.2
	50.0	0.0003	0.0098	0.0003	102.0
	60.0	0.0003	0.0119	0.0003	84.0
	70.0	0.0002	0.0136	0.0002	73.5
	80.0	0.0002	0.0159	0.0002	62.9
	90.0	0.0002	0.0175	0.0002	57.1
	100.0	0.0002	0.0189	0.0002	52.9
353.15	30.0	0.0008	0.0066	0.0008	151.4
	40.0	0.0007	0.0089	0.0007	112.3
	50.0	0.0005	0.0112	0.0005	89.2
	60.0	0.0005	0.0134	0.0005	74.6
	70.0	0.0004	0.0158	0.0004	63.3
	80.0	0.0004	0.0178	0.0004	56.2
	90.0	0.0004	0.0199	0.0004	50.2
	100.0	0.0004	0.0215	0.0004	46.5
393.15	30.0	0.0028	0.0083	0.0028	120.1
	40.0	0.0022	0.0109	0.0022	91.5
	50.0	0.0019	0.0138	0.0019	72.3
	60.0	0.0017	0.0165	0.0017	60.5
	70.0	0.0015	0.0192	0.0015	52.0
	80.0	0.0014	0.0214	0.0014	46.7
	90.0	0.0014	0.0237	0.0014	42.1
	100.0	0.0013	0.0260	0.0013	38.4

cell's pressure. The fluctuation of pressure was regulated within ± 0.1 bar during the sampling course. The uncertainty of reported pressures was estimated to be less than ± 0.1 %. At least four samples were taken for analyzing the phase composition at each equilibrium condition. In general, the compositions were reproduced to 2 % for the minor component in the replicated samples. However, the uncertainty of the reported vapor-phase more fractions could be ± 10 % when the value was as low as 10^{-4}.

Results

The equilibrium phase compositions as well as the equilibrium vaporization ratios ($K_i = y_i/x_i$) for nitrogen (1) + DMSO (2), nitrogen (1) + NMP (2), and nitrogen (1) + DGBE (2) are listed in Tables 1 to 3, respectively. In those three binary systems, the saturated vapor compositions of the stripper agent solutes (y_2) increase with increasing temperature and decrease with increasing pressure within the investigated conditions.

Figure 2 shows that y_2 can be correlated with the molar density of nitrogen (ρ_{N_2}) by a quadratic function:

$$\ln y_2 = A + B\rho_{N_2} + C(\rho_{N_2})^2 \tag{1}$$

where ρ_{N_2} was calculated from the PT equation of state[3] at the same T and P as the corresponding mixture. The coefficients of A, B, and C were obtained by fitting the equation to the experimental values with a linear-regression method. The above empirical equation quantitatively interpolates the y_2 isotherms. Table 4 reports the best-fitted results.

We also find that the solubilities of nitrogen in the liquid phase (x_1) increase with both increasing temperature and pressure. Figure 3 presents the relation for nitrogen + dimethyl sulfoxide. The pressure dependence is about linear. Furthermore, each gas solubility isotherm was correlated by the

Table 3. Vapor−Liquid Equilibrium Data for Nitrogen (1) + Diethylene Glycol Monobutyl Ether (2)

T/K	P/bar	y_2	x_1	$K_2 = y_2/x_2$	$K_1 = y_1/x_1$
323.15	30.0	0.0001	0.0121	0.0001	82.6
	40.0	0.0001	0.0157	0.0001	63.7
	50.0	0.0001	0.0201	0.0001	49.7
	60.0	0.0001	0.0243	0.0001	41.1
	70.0	0.0001	0.0289	0.0001	34.6
	80.0	0.0001	0.0330	0.0001	30.3
	90.0	0.0001	0.0372	0.0001	26.9
	100.0	0.0000	0.0415	0.0000	24.1
353.15	30.0	0.0003	0.0132	0.0003	75.7
	40.0	0.0002	0.0187	0.0002	53.5
	50.0	0.0002	0.0234	0.0002	42.7
	60.0	0.0002	0.0291	0.0002	34.4
	70.0	0.0002	0.0338	0.0002	29.6
	80.0	0.0001	0.0386	0.0001	25.9
	90.0	0.0001	0.0430	0.0001	23.3
	100.0	0.0001	0.0482	0.0001	20.7
393.15	30.0	0.0008	0.0144	0.0008	69.4
	40.0	0.0007	0.0206	0.0007	48.5
	50.0	0.0006	0.0264	0.0006	37.9
	60.0	0.0005	0.0312	0.0005	32.0
	70.0	0.0005	0.0364	0.0005	27.5
	80.0	0.0004	0.0420	0.0004	23.8
	90.0	0.0004	0.0479	0.0004	20.9
	100.0	0.0004	0.0530	0.0004	18.9

KI equation[4] to determine Henry's constant. The KI equation was defined as

$$\ln(f_1/x_1) = \ln H_{1,2}^* + [A'(x_2^2 - 1)/RT] + \overline{V_1^\infty}(P - P_2^*)/RT \tag{2}$$

where R is gas constant, $H_{1,2}^*$ is Henry's constant of nitrogen at the saturated pressure of the solvent (P_2^*), A' represents the Margules constant, and $\overline{V_1^\infty}$ refers to the partial molar volume of nitrogen at infinite dilution. The fugacity of nitrogen component (f_1) was obtained from the Lewis fugacity rule where the fugacity of pure nitrogen was calculated by the BWR equation.[5] Because the vapor compositions of nitrogen (y_1) are approximate the value of 1, the estimated fugacity of nitrogen component (f_1) should be reliable and close to experimental fugacity, f_i^{exp}. They are the best experimentally recommended values of the fugacity of nitrogen component (f_1). The value of
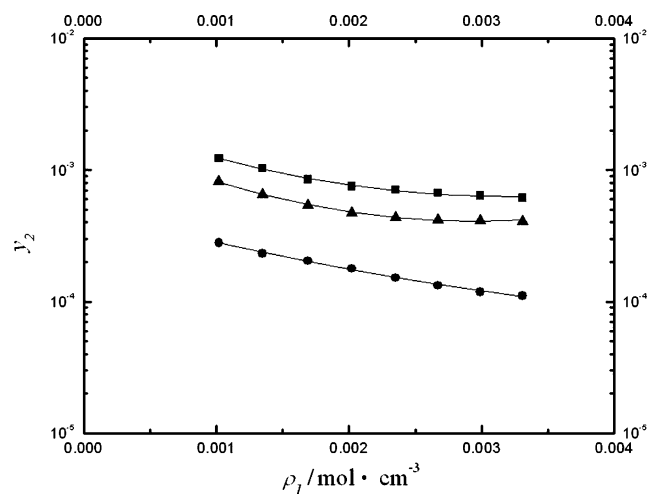

Figure 2. Correlations between the saturated vapor compositions of the stripper agent solutes and the molar density of nitrogen at 353.15 K: ■, N_2 (1) + dimethyl sulfoxide (2); ▲, N_2 (1) + N-methyl-2-pyrrolidone (2); ●, N_2 (1) + diethylene glycol monobutyl ether (2); −, calculated from eq 1.

Table 4. Correlation for Saturated Vapor Compositions (eq 1)

substance	T / K	n	A	$10^{-3}B$ / cm^3·mol^{-1}	$10^{-5}C$ / cm^6·mol^{-2}	10^2AAD^a
N_2 + DMSO	323.15	8	−6.26	−11.18	15.56	0.004
	353.15	8	−5.95	−8.79	13.53	0.001
	393.15	8	−4.82	−10.42	18.34	0.004
N_2 + NMP	323.15	8	−6.65	−10.54	15.74	0.000
	353.15	8	−6.19	−11.03	18.72	0.001
	393.15	8	−5.07	−10.62	18.26	0.002
N_2 + DGBE	323.15	8	−8.38	−7.04	6.76	0.008
	353.15	8	−7.60	−6.17	4.72	0.000
	393.15	8	−6.53	−7.39	9.62	0.000

$$^a \quad \text{AAD} = \sum_{k=1}^{n} \left| y_{2,k}^{\text{calcd}} - y_{2,k}^{\text{exp}} \right|/n.$$

$\overline{V_1^\infty}$ was estimated by the generalized equation of Brelvi and O'Connell[6] while the liquid density of nitrogen was calculated from the modified Rackett model.[7] The values of $H_{1,2}^*$ and the Margules constant were then determined by fitting the solubility data to the KI equation. Table 5 lists the calculated results, and Figure 4 illustrates the temperature effects on Henry's constants, which show that Henry's constants decrease with increasing temperature.

Data Reduction with Cubic Equations of State. The new VLE data were correlated by the SRK,[8] PR,[9] and PT equations of state with various mixing rules. The mixture constants a_m,
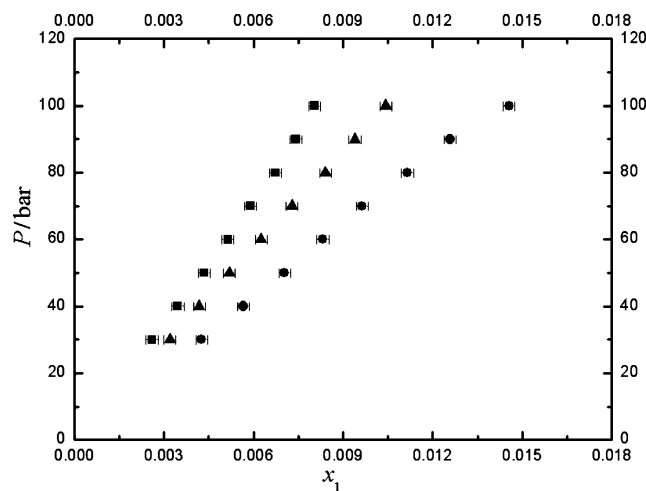

Figure 3. Variations of nitrogen solubility in dimethyl sulfoxide with pressure and temperature: ■, 323.15 K; ▲, 353.15 K; ●, 393.15 K; cross bars, the uncertainties of composition measurements.

Table 5. Calculated Results from the KI Equation

mixture	T / K	$H_{1,2}^*$ / bar	$10^{-3}A'$ / cm^3·bar·mol^{-1}	$\overline{V_1^\infty}$ / cm^3·mol^{-1}	10^2AAD^a
N_2 + DMSO	323.15	10982	14.4	33.4	0.80
	353.15	9426	115.9	35.2	0.56
	393.15	7146	114.2	38.8	1.26
N_2 + NMP	323.15	4956	59.0	36.2	0.92
	353.15	4431	56.5	37.3	0.99
	393.15	3496	5.0	40.1	1.16
N_2 + DGBE	323.15	2548	80.6	50.9	0.71
	353.15	2243	83.7	56.8	1.55
	393.15	2048	92.1	73.6	1.45

$$^a \quad \text{AAD} = \left(\frac{1}{n}\right)\sum_{k=1}^{n} \frac{\left|(f_1/x_1)_k^{\text{calcd}} - (f_1/x_1)_k^{\text{exp}}\right|}{(f_1/x_1)_k^{\text{exp}}}.$$
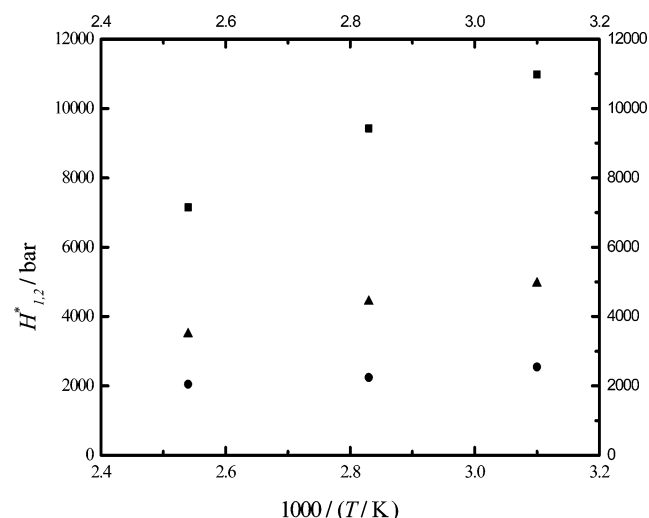
Figure 4. Temperature dependence of Henry's constants of the nitrogen/stripper agent solute systems: ■, N$_2$ (1) + dimethyl sulfoxide (2); ▲, N$_2$ (1) + *N*-methyl-2-pyrrolidone (2); ●, N$_2$ (1) + diethylene glycol monobutyl ether (2).

b_m, and c_m in those equations of state were calculated from

$$\theta_m = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \theta_{ij} \tag{3}$$

where x_i is the mole fraction of component i and θ represents the equation constant a, b, or c. The subscript ij represents $i-j$ pair interaction properties. The combining rule of c_{ij} for the PT

equation was given by

$$c_{ij} = (c_i + c_j)/2 \tag{4}$$

Three types of combining rules were employed to calculate a_{ij} and b_{ij}. The combining rules for a_{ij} and b_{ij} in MR-A (one-fluid, one-parameter van der Waals mixing rule) were defined as follows:

$$a_{ij} = (1 - k_{aij})(a_i a_j)^{0.5} \tag{5}$$

and

$$b_{ij} = (b_i + b_j)/2 \tag{6}$$

where k_{aij} was a binary interaction constant. In MR-B (one-fluid, two-parameter van der Waals mixing rule), an additional cross parameter k_{bij} was introduced in the combining rule of b_{ij}:

$$b_{ij} = (1 - k_{bij})(b_i + b_j)/2 \tag{7}$$

MR-C included eq 6 for b_{ij} and the linear temperature-dependent combining rule[10] for a_{ij}:

$$a_{ij} = \left(1 - k_{1ij} + k_{2ij}\frac{T}{1000}\right)(a_i a_j)^{0.5} \tag{8}$$

where k_{1ij} and k_{2ij} were binary interaction constants. The optimal interaction parameters, including k_{aij}, k_{bij}, k_{1ij}, and k_{2ij} were determined from the bubble pressure calculations by minimization of the objective function π with a modified Levenberg−

Table 6. Parameters of Pure Compounds

substance	$T_c{}^a$/K	$P_c{}^a$/bar	ω^a	m^b	κ^c	$\zeta_c{}^d$	F^d	A^e	B^e	C^e	D^e	E^e
nitrogen	126.2	33.98	0.037	0.5380	0.43133	0.326	0.500					
DMSO	729	56.5	0.281	0.9084	0.78670	0.309	0.797	5.63E+01	−7.62E+03	−4.63E+00	4.38E−07	2.00E+00
NMP	724	47.8	0.358	1.0209	0.89218	0.304	0.883	6.92E+01	−8.55E+03	−6.44E+00	2.93E−18	6.00E+00
DGBE	654	25.6	0.932	1.7941	1.57757	0.276	1.416	2.12E+02	−1.76E+04	−2.67E+01	3.49E−17	6.00E+00

^{a} Taken from DIPPR, NIST Standard Reference Database II. ^{b} Estimated from generalized correlation reported as Soave−Redlich−Kwong,[8] where $m = 0.480 + 1.574\omega − 0.176\omega^2$. ^{c} Estimated from generalized correlation reported as Peng and Robinson,[9] where $\kappa = 0.37464 + 1.54226\omega − 0.26992\omega^2$. ^{d} Estimated from generalized correlation reported as Patel and Teja[3] where $\zeta_c = 0.329032 − 0.0767992\omega + 0.0211947\omega^2$ and $F = 0.452413 + 1.30982\omega − 0.295937\omega^2$. ^{e} $P^{vap} = \exp(A + (B/T) + C \ln T + DT^E)$ where P^{vap}/Pa and T/K, the coefficients were taken from DIPPR, NIST Standard Reference Database II

Table 7. Bubble Pressure Calculations from the Soave−Redlich−Kwong, Peng−Robinson, and Patel−Teja Equations of State

mixture ID^a	mixing rule-A			mixing rule-B				mixing rule-C			
	k_{aij}	$10^2\Delta P/P$	$10^2\Delta y_2$	k_{aij}	k_{bij}	$10^2\Delta P/P$	$10^2\Delta y_2$	k_{1ij}	k_{2ij}	$10^2\Delta P/P$	$10^2\Delta y_2$
				Soave−Redlich−Kwong Equation of State							
M1	0.4408	5.26	0.040	−0.4985	−0.1789	2.67	0.084	0.1195	0.9315	1.81	0.030
M2	0.2474	3.55	0.023	0.1235	−0.0223	3.14	0.025	0.0909	0.4616	1.70	0.019
M3	0.2711	7.92	0.010	0.1518	−0.0169	7.78	0.011	−0.2293	1.4889	5.01	0.008
overall AAD		5.58	0.024			4.53	0.040			2.84	0.019
				Peng−Robinson Equation of State							
M1	0.4358	4.04	0.041	0.1218	−0.0688	3.68	0.056	0.2384	0.5753	1.90	0.034
M2	0.2686	2.82	0.025	0.1575	−0.0230	2.72	0.029	0.1373	0.3735	1.68	0.023
M3	0.2986	7.36	0.012	0.0737	−0.0370	7.33	0.015	−0.0582	1.0565	5.04	0.009
overall AAD		4.74	0.026			4.58	0.033			2.87	0.022
				Patel−Teja Equation of State							
M1	0.4023	3.45	0.039	−0.1059	−0.1117	2.51	0.063	0.2208	0.5298	1.76	0.034
M2	0.2045	1.72	0.023	0.0804	−0.0263	1.62	0.026	0.1443	0.1656	1.52	0.022
M3	0.1247	4.45	0.011	0.1010	−0.0045	4.41	0.011	0.0540	0.2050	4.34	0.010
overall AAD		3.21	0.024			2.85	0.033			2.54	0.022

^{a} M1, N$_2$ (1) + DMSO (2); M2, N$_2$ (1) + NMP (2); M3, N$_2$ (1) + DGBE (2).
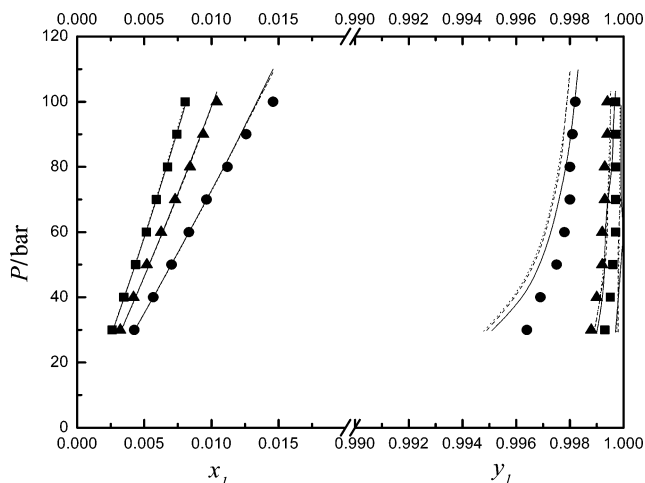
Figure 5. Comparison of VLE calculations from the SRK, PR, and PT equations of state with MR-C for the nitrogen (1) + dimethyl sulfoxide (2): ■, 323.15 K; ▲, 353.15 K; ●, 393.15 K; —, calculated from SRK; - - -, calculated from PR; · · ·, calculated from PT.
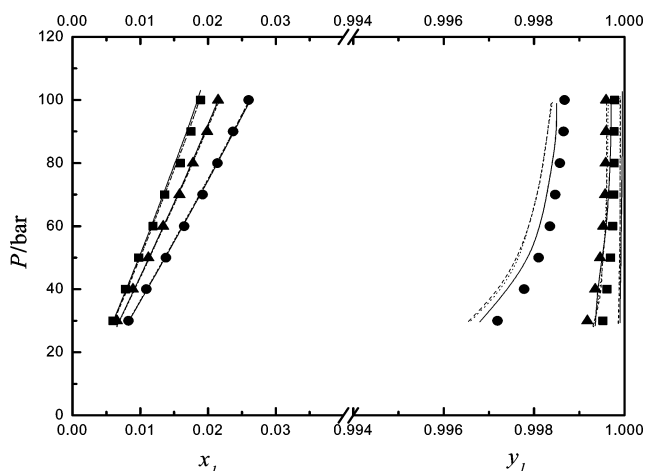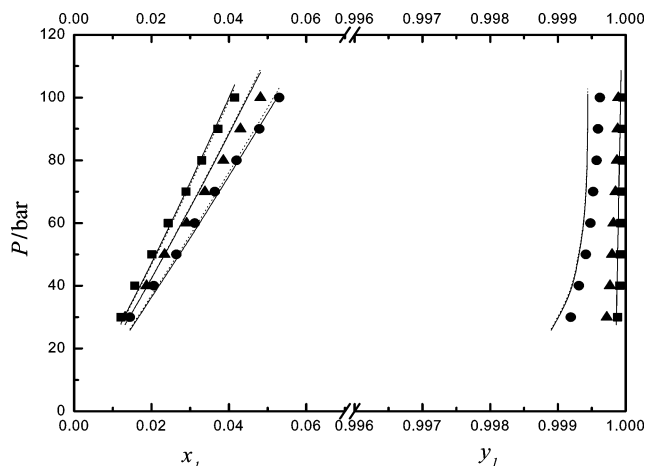

Figure 7. Comparison of VLE calculations from the Patel−Teja equation of state with different mixing rules for the nitrogen (1) + diethylene glycol monobutyl ether (2): ■, 323.15 K; ▲, 353.15 K; ●, 393.15 K; —, calculated from MR-A; - - -, calculated from MR-B; · · ·, calculated from MR-C.

equation or the PR equation. Good agreements between the calculated results from these cubic equations of state with MR-C and experimental values have been obtained for N_2 + DMSO and N_2 + NMP mixture systems. Figures 5 and 6 show that these cubic equations of state with MR-C can quantitatively describe the vapor−liquid phase behaviors for N_2 + DMSO and N_2 + NMP systems, respectively. As the comparison made in Figure 7, it is indicated that the VLE equilibrium calculations for the N_2 + DGBE system from the PT equation are approximately comparable, regardless of which various mixing rule was used. In general, the PT equation with MR-C produces the best correlated results for those three nitrogen + stripper agent solute systems.

Conclusion

The VLE data were determined experimentally for three binary systems of nitrogen with DMSO, NMP, or DGBE at temperatures from (323.15 to 393.15) K and pressures up to 100 bar. The saturated vapor compositions of the stripper agent solutes could be correlated with the molar density of nitrogen within the entire investigated conditions. The study also found that nitrogen solubilities in the stripper agent solutes increased with increasing temperature and that Henry's constants of the nitrogen decreased with increasing temperature. According to the results of the bubble pressure calculations, these cubic equations of state with MR-C could satisfactorily represent the phase-equilibrium behavior of nitrogen + DMSO and nitrogen + NMP systems. However, the VLE calculations for the N_2 + DGBE system from the PT equation are approximately comparable, regardless of which various mixing rule was used. Generally, the PT equation with MR-C yielded the best results for those three investigated systems.

Figure 6. Comparison of VLE calculations from the SRK, PR, and PT equations of state with MR-C for the nitrogen (1) + N-methyl-2-pyrrolidone (2): ■, 323.15 K; ▲, 353.15 K; ●, 393.15 K; —, calculated from SRK; - - -, calculated from PR; · · ·, calculated from PT.

Marquardt algorithm:

$$\pi = \sum_{k=1}^{n} \left(\frac{|P_k^{calcd} - P_k^{exp}|}{P_k^{exp}} + \left| y_{2,k}^{calcd} - y_{2,k}^{exp} \right| \right) / n \qquad (9)$$

where n is the number of data points. The superscripts exp and calcd denote the experimental value and the calculated value, respectively. The pure component parameters used in VLE calculations and determining Henry's constants are given in Table 6. Table 7 reports the results of the data reductions where the absolute average deviations (AAD) of $\Delta P/P$ and Δy_2 are defined as

$$\Delta P/P = \frac{1}{n} \sum_{k=1}^{n} \frac{|P_k^{calcd} - P_k^{exp}|}{P_k^{exp}} \qquad (10)$$

$$\Delta y_2 = \frac{1}{n} \sum_{k=1}^{n} |y_{2,k}^{calcd} - y_{2,k}^{exp}| \qquad (11)$$

As seen from Table 7, the values of the objective function π from the PT equation are smaller than those from the SRK

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