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Gas Solubility Measurement and Modeling for the Nitrogen + Water System from 274.18 K to 363.02 K

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New experimental solubility data of N_2 in water are reported over a wide temperature range from (274.18 to 363.02) K and pressures up to 7.16 MPa. A static-analytic apparatus, taking advantage of a pneumatic capillary sampler, is used for fluid sampling. The experimental data generated in this work are compared with those reported in the open literature with good agreement. The Valderrama modification of the Patel−Teja equation of state combined with nondensity-dependent mixing rules is used for modeling the gas−liquid equilibrium. The solubility data generated in this work are used for tuning the binary interaction parameters between nitrogen and water. The model predictions are compared with independent experimental data on nitrogen solubility in water as well as water content of the gas phase. The results are in good agreement, demonstrating reliability of the technique and the thermodynamic approach used in this work.

Introduction

Accurate determination of nitrogen + water phase behavior, over wide temperature and pressure ranges, has many applications in science and engineering. For example, many natural gases contain nitrogen. The combination of the natural gas and water could result in condensate, ice, and hydrate formation at low-temperature conditions. Water and nitrogen could also coexist at high-temperature conditions, for example in nitrogen-enhanced oil recovery. Therefore, experimental data on water + nitrogen systems are crucial for successful developing and validating a predictive model capable of predicting the phase behavior of these systems over a wide temperature range.

However, preliminary studies show that most of the experimental data for hydrocarbons and for non-hydrocarbon gases (e.g., N_2, CO_2, and H_2S) have been reported at relatively high temperatures and the data reported at low temperatures are often inconsistent, and therefore these types of uncertainties may lead to large deviations for predictive methods.[1,2] Only a few studies have been reported on the solubility of nitrogen in water.

The solubilities of nitrogen in water have been reported by several authors, e.g., Goodman and Krase in 1931,[3] Frolich et al.[4] in 1931, Wiebe et al.[5] in 1932, Saddington and Krase[6] in 1934, Pray et al.[7] in 1952, Smith et al.[8] in 1962, O'Sullivan et al.[9] in 1966, Maslennikova et al.[10] in 1971, and more recently Japas and Franck[11] in 1985. Table 1 shows temperature and pressure conditions for nitrogen solubility data in water.

In this work, new solubility measurements of nitrogen in water have been generated in the (274.18 to 363.02) K temperature range for pressures up to 7.16 MPa. The different isotherms presented herein were obtained using an apparatus based on a static-analytic method taking advantage of a Rolsi capillary sampler.[1,12−14]

Table 1. Experimental Solubility of Nitrogen in Water at Pressures over Atmospheric Pressure

ref	T/K	P/MPa
Goodman and Krase[3]	273.15−442.15	10.133−30.398
Frolich et al.[4]	298.15	2.027−19.252
Wiebe et al.[5]	298.15	2.533−101.325
Saddington and Krase[6]	323.15−513.15	10.133−30.398
Pray et al.[7]	533.15−588.71	1.034−2.757
Smith et al.[8]	303.15	1.103−5.895
O'Sullivan et al.[9]	324.65	10.133−60.795
Maslennikova et al.[10]	473.15−613.15	10.538−50.156
Japas and Franck[11]	480−658	15.5−270.5

The Valderrama modification of the Patel−Teja equation of state (VPT-EoS)[15] with nondensity-dependent mixing rules[16] is used to model the gas−water equilibrium. The binary interaction parameters between nitrogen and water are tuned using our new nitrogen solubility data. Then, the new experimental data and some literature data are compared with the results of model. To further evaluate the performance of the model, some independent water content data in the literature are compared with the predictions of the model. Predictions are found to be in good agreement with the experimental data, demonstrating the reliability of the experimental technique and model used in this work.

Experimental Section

Materials. Nitrogen was purchased from Air Liquide with a certified purity greater than 99.995 vol. %. Ethane was purchased from Messer Griesheim with a certified purity greater than 99.995 vol. %. Helium (carrier gas), from Air Liquide, is pure grade with only traces of water (3 ppm) and of hydrocarbons (0.5 ppm). Deionized water was used after degassing.

Apparatus and Experimental Procedures. The apparatus used in this work (Figure 1) is based on a static-analytic method with fluid phase sampling. This apparatus is similar to that described originally by Laugier and Richon.[17]

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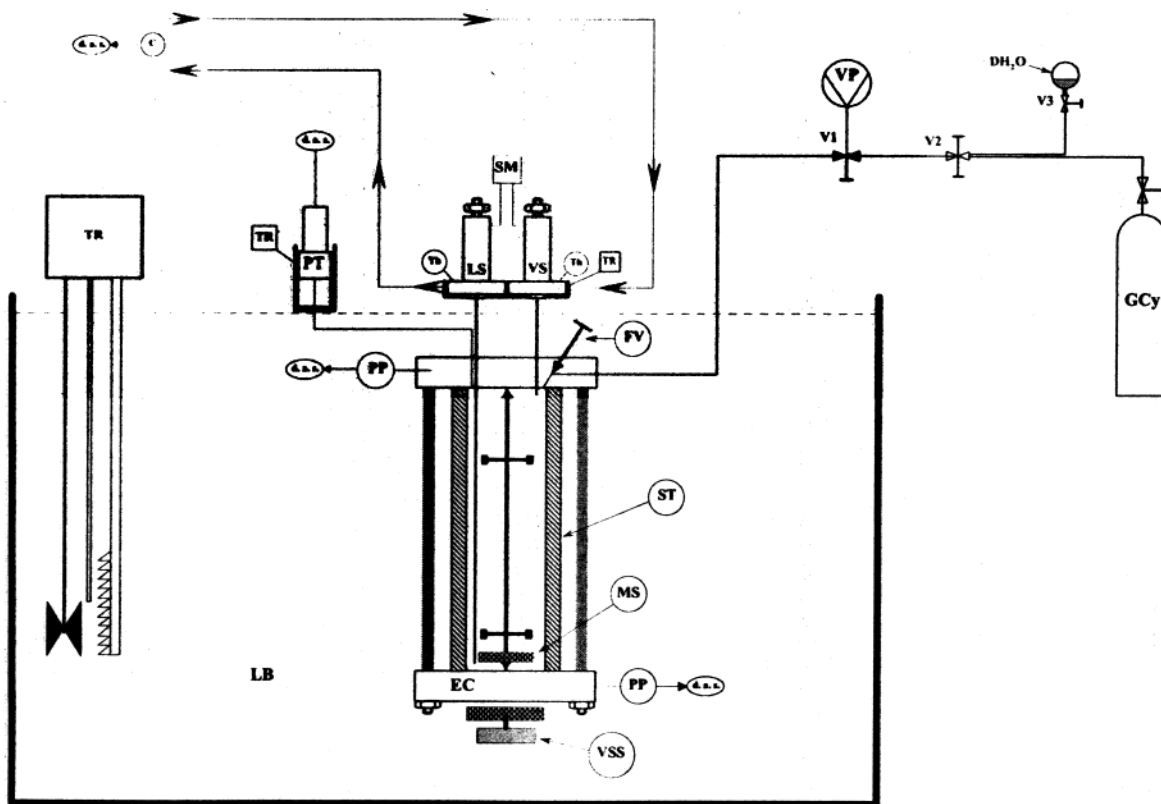
Figure 1. Flow diagram of the equipment: C, carrier gas; d.a.s, data acquisition system; DH$_2$O, degassed water; EC, equilibrium cell; FV, feeding valve; GCy, gas cylinder; LB, liquid bath; LS, liquid sampler; PP, platinum-resistance thermometer probe; PT, pressure transducer; SM, sampler monitoring; ST, sapphire tube; Th, thermocouple; TR, temperature regulator; Vi, valve i; VS, vapor sampler; VSS: variable speed stirrer; VP, vacuum pump.

The phase equilibrium is achieved in a cylindrical cell made of sapphire; the cell volume is about 28 cm^3 (internal diameter = 25 mm), and it can be operated up to 8 MPa between (223.15 and 473.15) K. The cell is immersed in an Ultra-Kryomat Lauda constant-temperature liquid bath that controls and maintains the desired temperature within ±0.02 K. To perform accurate temperature measurements in the equilibrium cell and to check for thermal gradients, temperature is measured at two locations corresponding to the vapor and liquid phases through two 100-Ω platinum-resistance thermometer devices (Pt100) connected to an HP data acquisition unit (HP34970A). These two Pt100 thermometers are carefully and periodically calibrated against a 25-Ω reference platinum resistance thermometer (TINSLEY Precision Instruments). The resulting uncertainty is not higher than ±0.02 K. The 25-Ω reference platinum-resistance thermometer was calibrated by the Laboratoire National d'Essais (Paris) based on the 1990 International Temperature Scale. Pressures are measured by means of a Druck pressure transducer connected to the HP data acquisition unit (HP34970A); the pressure transducers are maintained at a constant temperature (temperature higher than the highest temperature of the study) by means of a specially made air thermostat, which is controlled using a PID regulator (WEST, model 6100). The pressure transducer is calibrated against a dead-weight pressure balance (Desgranges & Huot 5202S, CP (0.3 to 40) MPa, Aubervilliers, France). Pressure measurement uncertainties are estimated to be within ±1 kPa in the (0.2 to 7) MPa range.

The HP on-line data acquisition unit is connected to a personal computer through a RS-232 interface. This system allows real time readings and storage of temperatures and pressures throughout the different isothermal runs.

Table 2. Critical Properties and Acentric Factors[19]

compound	P_c/MPa	T_c/K	v_c/m^3·kmol^{-1}	ω
water	22.048	647.30	0.0560	0.3442
nitrogen	3.394	126.05	0.0901	0.0403

The analytical work was carried out using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system fitted with BORWIN software (ver 1.5, from JMBS, Le Fontanil, France). The analytical column is a Hayesep T 100/120 Mesh column (silcosteel tube; length, 1.5 m; diameter, $^1/_8$ in.). The TCD was used to detect the water; it was repeatedly calibrated by injecting known amount of water through "liquid-type" syringes. The uncertainties on the calculated moles of water are estimated to be within ±1.5% in the 2.5×10^{-5} to 3×10^{-4} mol range. The TCD was first calibrated by introducing known moles of ethane through a "gas-type" syringe; with the moles known within ±1%. After this careful ethane calibration, different ethane + nitrogen mixtures of known low nitrogen composition were prepared inside the equilibrium cell. Then, samples of different (a priori) unknown sizes are withdrawn directly from the cell through the ROLSI sampler for gas chromatography analyses. Knowing the composition of the mixture and the number of sampled moles of ethane (through the response of the TCD), it is possible to estimate the amount of nitrogen and hence calibrate the TCD for this compound. The resulting relative uncertainty in the moles of nitrogen is about ±2.5%.

Experimental Procedures. The equilibrium cell and its loading lines is evacuated down to 0.1 Pa prior to introduction of about 5 cm^3 of degassed water. Then, nitrogen is introduced into the cell directly from the commercial cylinder to pressure level corresponding to the

Table 3. Experimental and Calculated Nitrogen Mol Fraction in the Aqueous Phase in the Nitrogen (1) + Water (2) System

T/K	P_{exp}/MPa	$x_1 \times 10^3$ (exp)	AAD[a] % (exp)	$x_1 \times 10^3$ (cal)	AD %
274.19	0.979	0.176	2.4	0.170	3.2
274.19	1.900	0.325	1.2	0.325	0.0
274.18	3.006	0.511	1.1	0.504	1.4
274.18	3.837	0.636	1.3	0.634	0.4
274.19	4.868	0.795	1.4	0.789	0.7
274.21	5.993	0.963	0.6	0.952	1.1
274.26	6.775	1.073	2.2	1.061	1.1
278.15	0.971	0.155	1.4	0.156	0.4
278.21	1.763	0.286	2.9	0.279	2.5
278.19	2.990	0.468	1.9	0.463	1.1
278.19	3.990	0.613	1.1	0.607	0.9
278.16	4.934	0.739	1.4	0.739	0.0
278.05	5.900	0.871	2.2	0.872	0.1
278.17	6.916	1.015	1.2	1.003	1.1
283.12	1.012	0.144	1.3	0.148	2.9
283.13	2.413	0.344	1.5	0.345	0.2
283.13	4.877	0.668	0.6	0.669	0.1
283.18	5.825	0.797	0.5	0.787	1.3
283.16	7.160	0.954	1.7	0.948	0.6
288.11	0.966	0.132	3.4	0.130	1.4
288.09	2.395	0.316	2.9	0.315	0.3
288.11	4.042	0.517	0.3	0.518	0.2
288.11	5.444	0.683	0.3	0.683	0.0
288.11	7.003	0.861	0.2	0.858	0.3
293.12	0.984	0.119	0.9	0.122	2.3
293.08	2.511	0.302	1.2	0.305	1.0
293.09	3.964	0.470	2.4	0.472	0.4
293.09	5.655	0.657	0.7	0.657	0.0
293.09	6.945	0.788	0.5	0.792	0.5
298.07	1.004	0.114	1.4	0.116	2.2
298.10	2.233	0.259	2.3	0.254	1.8
298.10	3.717	0.411	0.7	0.415	0.9
298.08	4.745	0.521	0.6	0.522	0.3
298.04	6.967	0.746	0.4	0.745	0.1
308.23	1.040	0.103	1.6	0.107	3.2
308.18	2.196	0.215	2.7	0.222	3.2
308.18	4.180	0.400	0.5	0.413	3.1
308.19	7.032	0.655	1.2	0.670	2.3
323.13	0.915	0.084	0.1	0.082	3.1
323.13	2.031	0.185	1.5	0.180	2.4
323.13	3.542	0.303	2.8	0.309	2.2
323.13	4.957	0.417	1.8	0.427	2.3
323.14	7.043	0.593	1.8	0.593	0.0
342.99	0.992	0.077	0.7	0.078	1.6
342.92	2.424	0.193	0.7	0.192	0.4
342.98	4.956	0.390	1.0	0.385	1.1
342.98	6.941	0.535	1.0	0.530	0.9
362.90	1.001	0.074	2.0	0.073	0.8
362.90	1.900	0.146	1.1	0.143	2.1
363.00	3.396	0.252	1.4	0.256	1.5
362.92	4.776	0.358	1.7	0.357	0.1
363.02	6.842	0.515	1.0	0.505	1.8

[a] With AAD (exp) = $(1/N) \sum^N |\overline{x_{1,exp}} - x_{1,exp}/\overline{x_{1,exp}}|$ and absolute deviation (AD) = $|(x_{1,exp} - x_{1,cal})/x_{1,exp}|$.

pressure of the first measurement. More nitrogen is introduced after each sampling and analyses steps up to the highest pressure of the studied solubility curve. After introduction of the gas into the cell, an efficient stirring is started, pressure is stabilized within a few minutes, and solubility measurements were performed when pressure was constant. (Furthermore, pressure is verified to be constant all along the sample analyses.)

For each equilibrium condition, at least 10 samples of liquid phase are withdrawn using the pneumatic samplers ROLSI[18] and analyzed in order to check for measurement repeatability (calculation of the average absolute deviation (AAD) (exp) in Table 3). As the volume of the withdrawn samples is very small (typically less than 1 μL) compared to the volume of the liquid phase present in the equilibrium

cell (around 5000 μL), it is possible to withdraw many samples without disturbing the phase equilibrium.

Thermodynamic Model

Pure Compound Properties. The critical temperature (T_C), critical pressure (P_C), critical volume (v_C), and acentric factor (ω) for each pure compound are provided in Table 2.

Model. A general phase equilibrium model based on uniformity of the fugacity of each component throughout all the phases[20,21] was used to model the gas–water equilibrium. The VPT-EoS[15] with the nondensity-dependent mixing rules[16] was employed for calculating fugacities in fluid phases. This combination has proved to be a strong tool in modeling systems with polar as well as nonpolar components.[16]

The VPT-EoS[15] is given by

$$P = \frac{RT}{v - b} - \frac{\bar{a}\alpha(T_r)}{v(v + b) + c(v - b)} \quad (1)$$

with

$$\bar{a} = \frac{\Omega_a R^2 T_c^2}{P_c} \quad (2)$$

$$b = \frac{\Omega_b R T_c}{P_c} \quad (3)$$

$$c = \frac{\Omega_{c^*} R T_c}{P_c} \quad (4)$$

$$\alpha(T_r) = [1 + F(1 - T_r^\Psi)]^2 \quad (5)$$

where P is the pressure, T is the temperature, v is the molar volume, R is the universal gas constant, and $\Psi = 0.5$. The subscripts c and r denote critical and reduced properties, respectively.

The coefficients Ω_a, Ω_b, Ω_{c^*}, and F are given by

$$\Omega_a = 0.66121 - 0.76105 Z_c \quad (6)$$

$$\Omega_b = 0.02207 + 0.20868 Z_c \quad (7)$$

$$\Omega_{c^*} = 0.57765 - 1.87080 Z_c \quad (8)$$

$$F = 0.46283 + 3.58230(\omega Z_c) + 8.19417(\omega Z_c)^2 \quad (9)$$

where Z_c is the critical compressibility factor and ω is the acentric factor. Tohidi-Kalorazi[22] relaxed the α function for water, α_w, using experimental water vapor pressure data in the range of 258.15 to 374.15 K to improve the predicted water fugacity

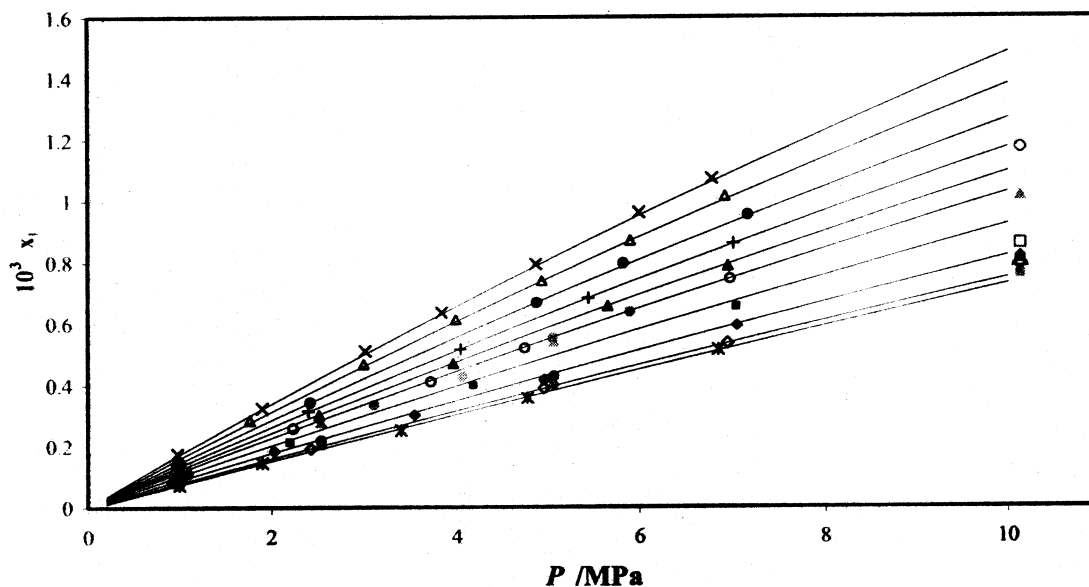$$\alpha_w(T_r) = 2.4968 - 3.0661 T_r + 2.7048 T_r^2 - 1.2219 T_r^3 \quad (10)$$

The above relation is used in the present work.

In this work, the NDD mixing rules developed by Avlonitis et al.[16] are applied to describe mixing in the a parameter

$$a = \bar{a}\alpha(T_r) = a^C + a^A \quad (11)$$

where a^C is given by the classical quadratic mixing rules as follows

$$a^C = \sum_i \sum_j x_i x_j a_{ij} \quad (12)$$

Figure 2. Nitrogen mole fraction, x_1, in water-rich phase as a function of pressure at various temperatures. New solubility data: ×, 274.2 K; △, 278.2 K; ●, 283.1 K; +, 288.1 K; ▲, 293.1 K; ○, 298.1 K; ■, 308.2 K; ◆, 323.1 K; ◇, 343.0 K; *, 363.0 K; Literature data: ●, 303.1 K from Smith et al.;[8] ○, 273.1 K from Goodmann and Krase;[3] □, 298.1 K from Goodmann and Krase [3]; △, 324.6 K from O'Sullivan et al.;[9] ◇, 338.1 K from Saddington and Krase;[6] solid lines, calculated with the VPT-EoS[15] and NDD mixing rules[16] with parameters from Table 4.
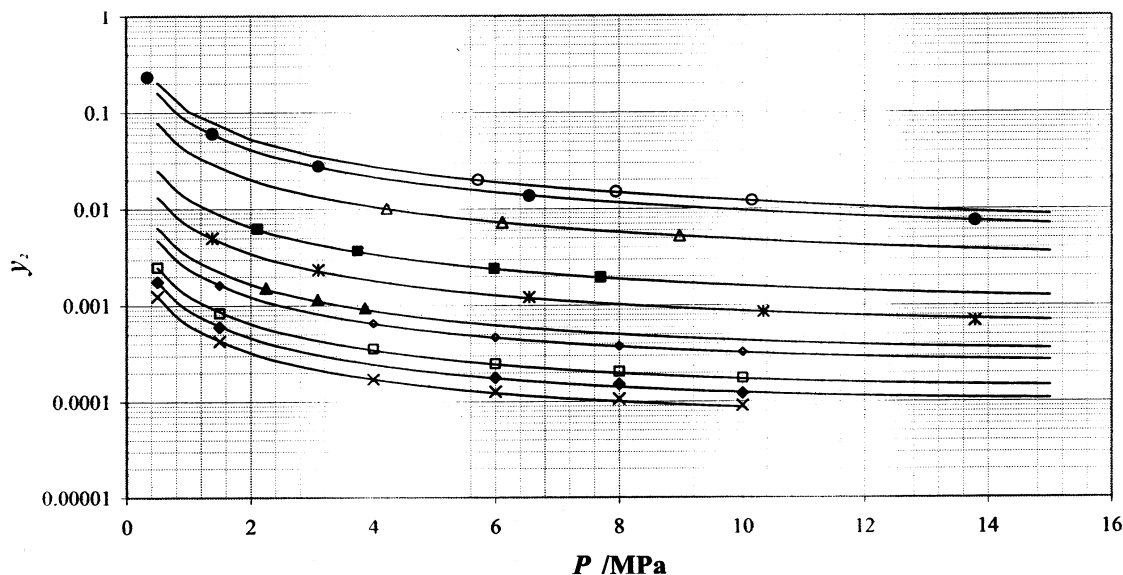
Figure 3. Water content, y_2, in the gas phase of the nitrogen (1) + water (2) system. Literature data: ×, 273.15 K from Althaus;[23] ◆, 278.15 K from Althaus;[23] □, 283.15 K from Althaus;[23] ◇, 293.15 K from Althaus;[23] ▲, 298.15 K from Rigby and Prausnitz;[26] *, 310.9 K from Namiot and Bondareva;[30] ■, 323.15 K from Rigby and Prausnitz;[26] △, 348.15 K from Rigby and Prausnitz;[26] ●, 366.95 K from Namiot and Bondareva;[30] ○, 373.15 K from Rigby and Prausnitz;[26] solid lines, calculated with the VPT-EoS[15] and NDD mixing rules[16] with parameters from Table 4.

and b, c, and a_{ij} parameters are expressed by

$$b = \sum_i x_i b_i \qquad (13)$$

$$c = \sum_i x_i c_i \qquad (14)$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \qquad (15)$$

where k_{ij} is the standard binary interaction parameter.

The term a^A corrects for asymmetric interaction, which cannot be efficiently accounted for by classical mixing rules

$$a^A = \sum_p x_p^2 \sum_i x_i a_{pi} l_{pi} \qquad (16)$$

$$a_{pi} = (a_p a_i)^{1/2} \qquad (17)$$

$$l_{pi} = l_{pi}^0 - l_{pi}^1 (T - T_0) \qquad (18)$$

where p is the index of polar components and T_0 is the ice point in K.

Table 4. Binary Interaction Parameters between Nitrogen (1) and Water (2) for the VPT-EoS[15] and the NDD Mixing Rules[16]

system	$k_{21}{}^a$	$l_{21}{}^{0\,a}$	$l_{21}{}^{1} \times 10^4\,{}^a$
nitrogen−water	0.4788	2.6576	65.1018

^{a} $l_{12}^0 = 0$, $l_{12}^1 = 0$, and $k_{12} = k_{21}$.

Table 5. Experimental Water Content of the Gas Phase in the Water + Nitrogen System[1]

ref	*T*/K	*P*/MPa
Althaus[23]	248.15−293.15	0.500−10.000
Kosyakov et al.[24]	233.16−293.16	1.010−12.120
Maslennikova et al.[25]	298.15−623.15	5.066−50.663
Rigby and Prausnitz[26]	298.15−373.15	2.109−10.152
Sidorov et al.[27]	373.15	5.066−40.530
Gillespie and Wilson[28]	310.93−588.71	0.345−13.786
Kosyakov et al.[29]	233.15−273.15	1.013−10.130
Namiot and Bondareva[30]	310.95−366.45	0.340−13.790
Bukacek[31]	377.65−378.09	6.983−68.274
Saddington and Krase[6]	323.15−503.15	10.133−30.398
Bartlett[32]	323.15	10.133−101.325

By use of the VPT-EoS[15] and the nondensity-dependent mixing rules,[16] the fugacity of each component in all fluid phases is calculated from

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,nj \neq i} - RT/V \right] dV - \ln Z \quad \text{for}$$
$$i = 1, 2, ..., M \quad (19)$$

$$f_i = x_i \phi_i P \quad (20)$$

where ϕ_i, V, M, n_i, Z, and f_i are the fugacity coefficient of component i in the fluid phases, volume, number of components, number of moles of component i, compressibility factor of the system, and fugacity of component i in the fluid phases, respectively.

Results and Discussions

The experimental and calculated gas solubility data are reported in Table 3 and plotted in Figure 2.

As mentioned before, the binary interaction parameters between nitrogen and water are adjusted directly to the measured nitrogen solubility data through a Simplex algorithm using the objective function, FOB, displayed in eq 21

$$\text{FOB} = \frac{1}{N} \sum_1^N \left| \frac{x_{i,\text{exp}} - x_{i,\text{cal}}}{x_{i,\text{exp}}} \right| \quad (21)$$

where N is the number of data points, $x_{i,\text{exp}}$ is the measured property, and $x_{i,\text{cal}}$ is the calculated property. Table 4 reports binary interaction parameter values adjusted between nitrogen and water used in this work.

Our isothermal $P−x$ data sets for the nitrogen−water are well represented with the VPT-EoS[15] and the nondensity-dependent mixing rules[16] (AAD = $(1/N\sum^N)|(x_{\text{exp}} - x_{\text{cal}})/x_{\text{exp}}| = 1.2\%$). Some nitrogen solubility data reported in the literature are plotted in Figure 2. There is good agreement between the different authors, with the exception of the data reported by Goodman and Krase,[3] whose solubility data are lower than those predicted by the model and those reported by the other authors.

To further evaluate the performance of the model, some experimental gas water content data in the literature are compared with the predictions of the model. Table 5 shows

Table 6. Experimental and Predicted Water Mol Fraction, y_2, in the Gas Phase of the Nitrogen (1) + Water (2) System

T/K	*P*/MPa	y_2, exp	y_2, predicted	AD %
		Rigby and Prausnitz[26]		
298.15	2.249	0.001529	0.001521	0.52
	3.090	0.001149	0.001138	0.96
	3.870	0.000941	0.000933	0.85
323.15	2.109	0.006260	0.006220	0.64
	3.742	0.003680	0.003662	0.49
	5.982	0.002420	0.002428	0.33
	7.700	0.001956	0.001969	0.66
348.15	4.221	0.010090	0.010113	0.23
	6.115	0.007210	0.007269	0.82
	8.972	0.005230	0.005252	0.42
373.15	5.717	0.019940	0.020022	0.41
	7.948	0.015030	0.014974	0.37
	10.152	0.012180	0.012163	0.14
		Namiot and Bondareva[30]		
310.95	1.380	0.005020	0.004963	1.14
	3.100	0.002360	0.002326	1.44
	6.550	0.001220	0.001215	0.41
	10.340	0.000850	0.000852	0.24
	13.790	0.000690	0.000695	0.72
366.45	0.340	0.233000	0.236873	1.66
	1.380	0.060500	0.059820	1.12
	3.100	0.027700	0.027572	0.46
	6.550	0.013700	0.013933	1.70
	13.790	0.007470	0.007490	0.27
		Althaus[23]		
273.15	0.500	0.001245	0.001249	0.32
	1.500	0.000427	0.000434	1.64
	4.000	0.000171	0.000181	5.85
	6.000	0.000127	0.000130	2.36
	8.000	0.000106	0.000106	0.00
	10.000	0.000091	0.000091	0.00
278.15	0.500	0.001780	0.001781	0.06
	1.500	0.000601	0.000618	2.83
	6.000	0.000178	0.000184	3.37
	8.000	0.000151	0.000149	1.32
	10.000	0.000122	0.000128	4.92
283.15	0.500	0.002504	0.002504	0.00
	1.500	0.000838	0.000868	3.58
	4.000	0.000354	0.000358	1.13
	6.000	0.000248	0.000256	3.23
	8.000	0.000205	0.000206	0.49
	10.000	0.000176	0.000176	0.00
293.15	1.500	0.001632	0.001645	0.80
	4.000	0.000654	0.000673	2.91
	6.000	0.000467	0.000479	2.57
	8.000	0.000375	0.000383	2.13
	10.000	0.000326	0.000326	0.00

a list of the experimental data for the water + nitrogen system.[1] As it can be seen, most of these data have been reported at relatively high-temperature conditions. Table 6 shows a comparison between some experimental water content data and the predictions of the model. Figure 3 also shows a comparison of the selected nitrogen water content data and predictions of the model. Good agreement is achieved, demonstrating the reliability of techniques and model used in this work.

Conclusions

New experimental data on the solubility of nitrogen in water were generated over a wide temperature range (274.18 to 363.02) K. The new experimental data were employed in tuning the binary interaction parameters between nitrogen and water.

The model predictions on N_2 solubility in the aqueous phase as well as water content of gas phase in water−nitrogen systems have been compared with independent experimental data. The results showed good agreement,

demonstrating the reliability of the experimental techniques and thermodynamic modeling used in this work.

Appendix

Calculation of the Fugacity Coefficient Using an Equation of State. The following general form can be used for expressing any cubic equation of state[33]

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + uv - w^2} \quad (A.1)$$

The fugacity coefficient for component i in a mixture can be expressed as[33]

$$\ln \phi_i = -\ln(Z - B) + \frac{B_i' B}{Z - B} + \frac{A}{(U^2 + 4W^2)^{1/2}} \left[A_i' - \frac{U_i U^2 + 4W_i W^2}{U^2 + 4W^2} \right] \ln\left[\frac{2Z + U - (U^2 + 4W^2)^{1/2}}{2Z + U + (U^2 + 4W^2)^{1/2}} \right] - A\left[\frac{2(2Z + U)W_i W^2 + (UZ - 2W^2)U_i U}{(Z^2 + UZ - W^2)(U^2 + 4W^2)} \right] \quad (A.2)$$

where

$$A = \frac{Pa}{(RT)^2} \qquad B = \frac{Pb}{RT} \quad (A.3, A.4)$$

$$U = \frac{Pu}{RT} \qquad W = \frac{Pw}{RT} \quad (A.5, A.6)$$

$$Z = \frac{Pv}{RT} \quad (A.7)$$

and

$$A_i' = \frac{1}{na}\left[\frac{\partial(n^2 a)}{\partial n_i} \right]_{T, nj \neq i} \qquad B_i' = \frac{1}{b}\left[\frac{\partial(nb)}{\partial n_i} \right]_{T, nj \neq i} \quad (A.8, A.9)$$

$$U_i = \frac{1}{u}\left[\frac{\partial(nu)}{\partial n_i} \right]_{T, nj \neq i} \qquad W_i = \frac{1}{w}\left[\frac{\partial(nw)}{\partial n_i} \right]_{T, nj \neq i} \quad (A.10, A.11)$$

The compressibility factor Z is given by the following dimensionless equation[33]

$$Z^3 - (1 + B - U)Z^2 + (A - BU - U - W^2)Z - (AB - BW^2 - W^2) = 0 \quad (A12)$$

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