Vapor-Liquid-Liquid Locus of the System Nitrous Oxide + Water

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This paper presents an investigation of the vapor-liquid-liquid locus of the system nitrous oxide + water. The locus extends from a vapor-liquid-liquid-hydrate quadruple point (12.5 °C and 4.33 MPa) to a three-phase critical end point (36.6 °C and 7.25 MPa). New experimental values for the pressure and temperature along the three-phase locus were obtained, and a comparison was made with a model developed for correlating the solubility of N_2O in water. The agreement between the experiment and the prediction is excellent.

The system nitrous oxide + water is an interesting system. First, it exhibits liquid-liquid immiscibility, which extends from about 12 to 36 °C. At temperatures greater than 36.6 °C, the three-phase critical end point, the second liquid does not form. Second, the system forms a hydrate. Hydrates are solid, icelike crystals that form at conditions where a solid would otherwise not be expected. Villard (*1*) was the first to observe the hydrate in this system. He noted that the hydrate of N_2O persists up to temperatures of about 12 °C. To the best of our knowledge, there has not been a thorough investigation of this hydrate.

In a recent investigation (*2*), experimental measurements of the solubility of nitrous oxide in water under pressure were obtained. In that study, the researchers also proposed a model to correlate the vapor-liquid and liquid-liquid equilibrium using a model based on Henry's law. As an additional test of their model, it was used to predict the liquid-liquid-vapor locus. In this study, experimental points were obtained to check the prediction.

Experimental Work

The experiments were conducted in an apparatus used in this laboratory several times (*2, 3*), and thus only a brief description follows. The basic component of the apparatus was a visual cell. Large windows in the cell made it easy to observe the number and nature of the phases present in the system. This ability was crucial in this study, in particular to find the three-phase critical end point. Attached to the top of the cell was a reservoir to ensure that sufficient mass of vapor was present. The contents of the cell were mixed using a magnetically driven piston pump similar to the one devised by Ruska et al. (*4*). A portion of the vapor was drawn off the reservoir and pumped into the bottom of the cell. The cell-pump system was housed in a large temperature-controlled air bath. The air bath was equipped with a refrigeration unit, in order to study temperatures below room temperature, and heaters for higher temperatures. A Hallikainen Thermotrol controller was used to control the temperature in the air bath.

The temperature of the contents of the cell was measured using a type J (iron/constantan) thermocouple. The thermocouple was calibrated against a platinum resistance thermometer and was determined to be accurate within 0.1 °C over the range of temperatures of interest in this study. The output from the thermocouple was measured using a Hewlett-Packard digital voltmeter. The pressure in the cell was measured with a 0-6.9 MPa (0-1000 psi) Heise bourdon tube gauge for pressures below 6 MPa and a 0-12 MPa gauge for higher pressures. The gauges were calibrated using a dead weight gauge and were found to be accurate within 0.3% of full scale (0.02 and 0.04 MPa, respectively).

The nitrous oxide was supplied by Linde and was specified to be 99+% (by volume) pure. It was used without further purification. The water used was laboratory distilled.

To perform the experiments, water was fed into the system by gravity. A small amount of N_2O was then introduced into the system, and the recirculation pump was turned on. The system was left for several hours, and then the pressure was bled off. The flushing procedure was repeated several times to ensure that no impurities were present in the system. Then, the refrigeration unit was turned on, and the system was cooled to about 15 °C. Nitrous oxide was added to the cell directly from the high-pressure cylinder. The high-pressure gas condensed in the cold apparatus. After a sufficient amount of the second liquid had condensed, the charging procedure was stopped. The amount of the second liquid placed in the cell was determined by experience.

The controller was then set and the mixing pump turned on. The system was allowed to equilibrate for 24 h, after which the temperature and pressure were recorded. The controller was reset such that a point could be obtained at a new temperature. This procedure of resetting the controller and waiting for equilibrium was repeated until the entire locus was obtained.

To determine the vapor-liquid-liquid-hydrate quadruple point, the temperature was slowly reduced until solids were observed to form. Since this apparatus was not designed to investigate the formation of solid phases, this point is less accurate than the remainder of the data. However, it is important to establish the location of this point since it is the coldest temperature at which the three fluid phases can coexist in equilibrium.

The three-phase critical end point was determined twice. First, the temperature was slowly increased until the critical opalescence was observed. The second approach was similar except this time the contents of the cell were heated to a temperature greater than the critical point and then slowly cooled to the critical point. It is believed that these points are less accurate than the rest of the three-phase points, but only slightly so. The establishment of the critical point is important since it is the upper limit to the region where the three fluid phases can coexist in equilibrium.

Results

The points along the liquid-liquid-vapor locus obtained in this study are tabulated in Table I. As noted above, there are two points reported for the critical end point, one from each method. The results are plotted in Figure 1. Because

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Table I. Liquid–Liquid–Vapor Locus and Three-Phase Pressure for the System Nitrous Oxide + Water

	P/MPa			P/MPa	
t/°C	exptl	correlatn[a] (2)	t/°C	exptl	correlatn[a] (2)
12.5 ± 0.1	4.33 ± 0.02[b]	4.28	27.0 ± 0.1	5.93 ± 0.02	5.93
13.0 ± 0.1	4.33 ± 0.02	4.33	28.1 ± 0.1	6.04 ± 0.04	6.07
14.0 ± 0.1	4.44 ± 0.02	4.44	28.6 ± 0.1	6.14 ± 0.04	6.13
14.9 ± 0.1	4.54 ± 0.02	4.53	29.7 ± 0.1	6.26 ± 0.04	6.27
16.4 ± 0.1	4.69 ± 0.02	4.69	30.6 ± 0.1	6.38 ± 0.04	6.39
16.5 ± 0.1	4.66 ± 0.02	4.70	31.4 ± 0.1	6.50 ± 0.04	6.50
17.0 ± 0.1	4.77 ± 0.02	4.75	33.5 ± 0.1	6.77 ± 0.04	6.79
18.2 ± 0.1	4.85 ± 0.02	4.88	33.6 ± 0.1	6.80 ± 0.04	6.81
21.8 ± 0.1	5.27 ± 0.02	5.29	34.4 ± 0.1	6.92 ± 0.04	6.92
22.2 ± 0.1	5.28 ± 0.02	5.34	35.5 ± 0.1	7.04 ± 0.04	7.08
22.7 ± 0.1	5.40 ± 0.02	5.40	35.7 ± 0.1	7.16 ± 0.04	DNC
23.3 ± 0.1	5.42 ± 0.02	5.47	36.0 ± 0.1	7.21 ± 0.04	DNC
24.1 ± 0.1	5.52 ± 0.02	5.57	36.6 ± 0.1	7.25 ± 0.06[c]	DNC
25.1 ± 0.1	5.69 ± 0.02	5.69	36.7 ± 0.1	7.25 ± 0.06[c]	DNC

[a] DNC = did not converge. [b] Vapor–liquid–liquid–hydrate quadruple point. [c] Three-phase critical end point.

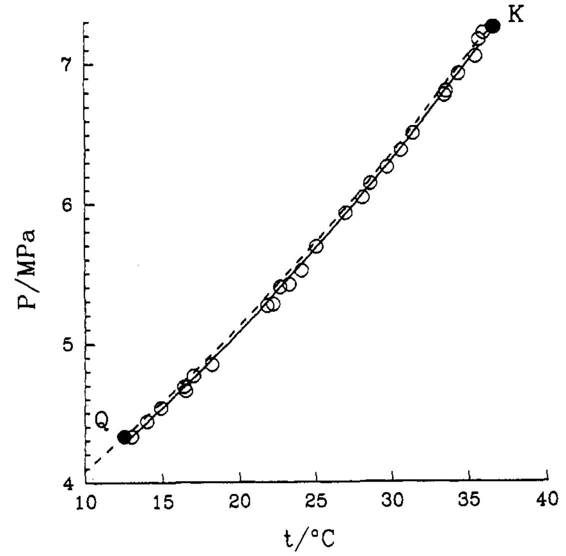

Figure 1. Vapor–liquid–liquid locus for the system N_2O + H_2O: ○, ●, this work; —, from the correlation of Jou et al. (2); - - -, the vapor pressure of nitrous oxide from Daubert and Danner (5); K, three-phase critical end point; Q, vapor–liquid–liquid–hydrate quadruple point.

of its proximity, the vapor pressure of nitrous oxide is also plotted in Figure 1. The vapor pressure plotted is the correlation from Daubert and Danner (5).

The experimental data were correlated using a Clausius–Clapeyron-type equation. A least-squares fit of all of the data (including the quadruple point and both measured critical points) resulted in the following equation:

$$\ln(P/\mathrm{MPa}) = 8.206 - 1929.1/(T/\mathrm{K}) \qquad (1)$$

The average absolute deviation between the data and this equation is 0.02 MPa, and the maximum deviation is 0.07 MPa.

A model for the solubility of vapor and liquid nitrous oxide in water was developed by Jou et al. (2). Details of the model will not be repeated here. However, the model uses the Peng–Robinson equation of state (6) to calculate the fugacities of the components in the nonaqueous phases. Interestingly, when Peng and Robinson (7) attempted to apply their equation of state to aqueous systems (the equation was used to calculate the fugacity in all phases), they found that good results could not be obtained. The predictions for the nonaqueous phases were good, but those for the aqueous phase were very poor. To overcome this problem in the model used here, the fugacities for the aqueous phase were calculated using a Henry's law approach for nitrous oxide and a Raoult's law approach for water. A three-phase algorithm (7) was used to perform the calculations. The model predictions are plotted in Figure 1 and tabulated in Table I. As the temperature approaches the critical temperature (within about 1 °C), converged solutions could not be obtained. Hence, the last three points in Table I are marked DNC. Notwithstanding, it is clear from Figure 1 and Table I that the predictions from the model of Jou et al. (2) are in excellent agreement with the experimental data.

Conclusions

New experimental data for the three-phase locus of the system nitrous oxide + water were obtained. A comparison was made with a solubility model based on Henry's law. Although Henry's law is not often used to correlate this type of equilibrium, this prediction is excellent.

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