J. Chem. Eng. Data **2002,** *47,* 1173−1174

High-Pressure Vapor−Liquid Equilibrium for Nitrogen + Methanol

Torben Laursen* and Simon Ivar Andersen

Engineering Research Center IVC-SEP, Department of Chemical Engineering, The Technical University of Denmark, DK-2800 Lyngby, Denmark

---

A number of authors have reported VLE data for the system nitrogen + methanol, but none of the publications give data for both the liquid and the vapor phases. In this work, experimental data for both the liquid and the vapor phases are presented in the temperature range 25 °C to 45 °C and in the pressure range 7 to 102 bar. The experimental data have been correlated using the Soave−Redlich−Kwong equation of state (SRK) combined with a k_{ij} interaction parameter.

Introduction

In a continuation of a research program involving measurements of VLE and VLLE data, the system nitrogen + methanol was measured. A number of other authors have also measured this system, but none has published data that includes both the liquid and the vapor phases. In this work the VLE system has been measured at 25, 35, and 45 °C in the pressure range 7 to 102 bar, including mole fractions of both the liquid and the vapor phases.

Experimental Section

The measurement appartus, procedures, and uncertainties were previously described in detail.[1] The experimental apparatus is based on a high-pressure autoclave equipped with two windows, a movable sample needle, and valves for performing on-line sampling from the cell. The equipment can be used to measure both VLE and VLLE, but not LLE, for safety reasons. In the method applied, liquid samples are taken by recirculation of liquid through a liquid sampling valve, and gas samples are taken by flushing a vapor sampling valve with heated vapor from the cell.

The composition was measured using a Carlo Erba HRGC 5300 gas chromotograph based on a pure component calibration. The uncertainty of the given mole fractions is estimated to be 0.001 mole fraction.

Chemicals. Methanol with a purity of 99.8% was obtained from J.T.Baker. Nitrogen was supplied by Hede Nielsen with a purity of 99.995%. The purity was verified by GC analysis. The chemicals were used without any further purification.

Results and Discussions

Vapor−liquid equilibrium data for nitrogen + methanol at (25.0, 35.0, and 45.0) °C are presented in Table 1. The values in Table 1 show that the solubility of nitrogen in methanol is small and is only slightly affected by the temperature, while the solubility of methanol in the vapor phase is significantly affected by the temperature, at low pressures.

Figure 1 shows a comparison between experimental data for the liquid phase obtained in this work and literature data.[2−4] The data presented in this work show a slightly smaller solubility of nitrogen, but considering the small measured mole fractions, there is a fair agreement between the data sets.

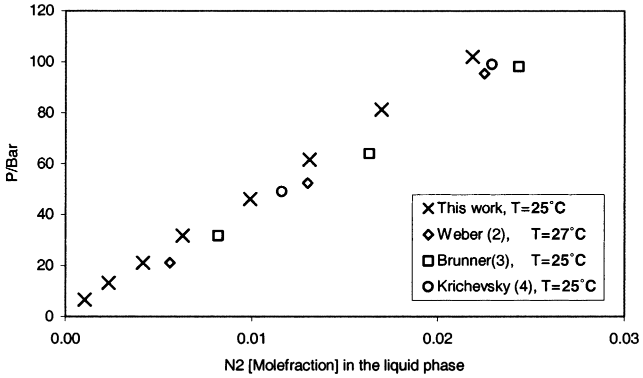

Figure 1. Comparison between three sets of literature data and this work.

Table 1. Composition of the Liquid (x_1) and Vapor (y_1) Phase at the Pressure P for the System N_2 (1) + CH_3OH (2)

x_1	y_1	P/bar	x_1	y_1	P/bar
		T = 25.0 °C			
0.0010	0.9695	6.7	0.0099	0.9944	46.2
0.0023	0.9839	13.2	0.0131	0.9958	61.6
0.0042	0.9906	21.1	0.0170	0.9962	81.3
0.0063	0.9924	31.7	0.0219	0.9963	101.9
		T = 35.0 °C			
0.0012	0.9443	6.8	0.0094	0.9893	43.1
0.0021	0.9685	11.8	0.0143	0.9923	62.1
0.0041	0.9796	20.4	0.0175	0.9926	80.2
0.0065	0.9874	30.8	0.0221	0.9930	101.5
		T = 45.0 °C			
0.0013	0.9201	7.4	0.0101	0.9837	47.0
0.0021	0.9451	11.1	0.0137	0.9866	61.9
0.0040	0.9705	21.4	0.0179	0.9882	81.9
0.0065	0.9763	30.7	0.0221	0.9895	98.5

Table 2. Critical Properties, Acentric Factors, and Molar Masses Used

	T_c/K	P_c/MPa	W	M/g·mol^{-1}
N_2	126.20	3.400	0.0377	28.014
CH_3OH	512.64	8.097	0.5640	32.042

---

* Corresponding author. E-mail: tl@kt.dtu.dk.

10.1021/je020006z CCC: $22.00

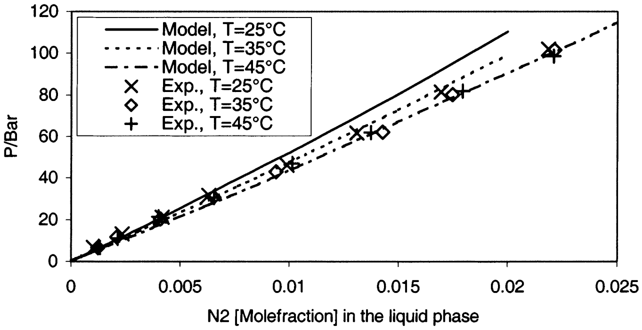

Figure 2. Pressure−composition data for nitrogen (1) + methanol (2), comparing the experimental results with model results for the liquid phases.

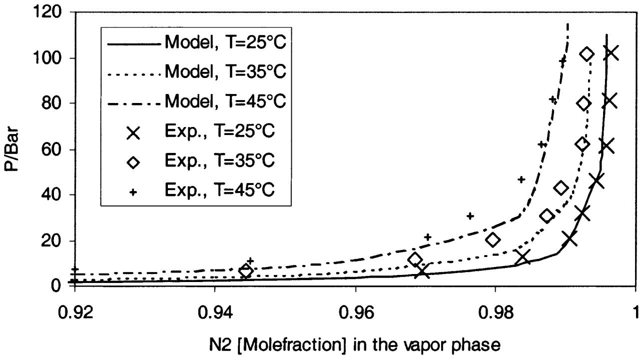

Figure 3. Pressure−composition data for nitrogen (1) + methanol (2), comparing the experimental results with model results for the vapor phases.

The data were correlated using the Soave−Redlich−Kwong (SRK) equation of state[5] combined with the k_{ij} interaction parameter. The critical constants and the acentric factors were taken from the DIPPR[6] database, and are given in Table 2. The parameters were fitted using equal fugacity as the object function. The parameters obtained were $K_{12} = K_{21} = -0.1418$. Comparisons of the correlations with the measured data are shown in Figures 2 and 3. It is seen that the data are well correlated.

Acknowledgment

The authors appreciate the help from Peter Rasmussen to prepare this manuscript.

Literature Cited

(1) Laursen, T.; Rasmussen, P.; Andersen, S. I. VLE and VLLE measurements of dimethyl ether containing systems. *J. Chem. Eng. Data.* **2002**, *47* (2), 198−202.

(2) Weber, W.; Zeck, S.; Knapp, H. Gas Solubilities in Liquid Solvents at High Pressures: Apparatus and Results for Binary and Ternary Systems of N_2, CO_2 and CH_3OH. *Fluid Phase Equilib.* **1984**, *18*, 253−278.

(3) Brunner, E.; Hultenschmidt, W.; Schlichthärle, G. Fluid Mixtures at High Pressures IV. Isothermal Phase Equilibria in Binary Mixtures Consisting of (Methanol + Hydrogen or Nitrogen or Methane or Carbon Monoxide or Carbon Dioxide). *J. Chem. Thermodyn.* **1987**, *19*, 273−291.

(4) Krichevsky, I. R.; Lebedeva, E. S. *Zh. Fiz. Khim.* **1947**, *21*, 715.

(5) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(6) Daubert, T. E.; Danner, R. P. *DIPPR. Physical and thermodynamic properties of pure compounds, Data compilation*; Hemisphere: New York, 1989.

Received for review January 14, 2002. Accepted June 3, 2002.

JE020006Z