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Solubility of Ethane in *N*-Formyl Morpholine

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Measurements of the solubility of ethane in *N*-formyl morpholine have been made over a range of temperatures from (298 to 403) K. Pressures varied between (0.1 and 20.3) MPa. The data were correlated with the Peng−Robinson equation of state.

Introduction

N-formyl morpholine is a physical solvent that is used for the removal of the acid gases, H_2S and CO_2 , from gas streams.[1,2] Physical solvents are polar organic compounds, which have an affinity for hydrogen sulfide and/or carbon dioxide. The solubility of gases in physical solvents is proportional to the partial pressure of the solute gas at low pressures and the enthalpy of solution is small. It is often possible to regenerate the solvent by flashing to a lower pressure; hence, processes using physical solvents require less energy than those using chemical solvents.

Xu et al.[3,4] have measured the solubility and the partial molar volume of the acid gases in a number of physical solvents, including *N*-formyl morpholine.

In this laboratory, we have measured the solubility of H_2S, CO_2, and methane in *N*-formyl morpholine over a range of temperatures and pressures.[5] The solubility of hydrocarbons is important, because the value is a measure of the loss of hydrocarbons in the absorption process. In this work, the solubility of ethane in *N*-formyl morpholine was measured at six temperatures in the range (298.15 to 403.15) K at pressures up to 20.3 MPa.

Experimental Section

The experimental apparatus is similar to that used by Jou et al.[5] The equilibrium cell was mounted in an air bath. The temperature of the contents of the cell was measured by a calibrated iron−constantan thermocouple (Type J), and the pressure in the cell was measured with digital Heise gauges (0−10 MPa and 0−35 MPa). The accuracy of the thermocouple is ±0.1 °C, and the accuracy of the pressure gauges is ±0.1% of full scale.

The *N*-formyl morpholine (NFM, CAS No. 4394-85-8) was obtained from BASF and had a purity of 99%. Ethane was obtained from Matheson and had a purity of 99%. Prior to the introduction of the fluids, the cell was evacuated. About 120 cm^3 of NFM was drawn into the cell. It was heated to 100 °C and evacuated to remove traces of water. The ethane was added to the cell by the cylinder pressure or by means of a spindle press. The circulation pump was started, and the vapor bubbled through the solvent for at least 8 h to ensure that equilibrium was reached.

A sample of the liquid phase, 2 to 20 g, depending on the solubility, was withdrawn from the cell into a 50 cm^3 sample bomb, which had previously been evacuated and weighed. The bomb contained a magnetic stirring bar to help in degassing the sample. The sample bomb was reweighed to determine the mass of the sample and then attached to a vacuum rack. The rack consisted of 6.35 mm OD stainless steel tubing connected to a calibrated Digigauge (0 to 1.0 MPa) and a 50 cm^3 buret. The rack was evacuated and the gas allowed to evolve from the sample bomb into the buret. The moles collected were calculated from the P−V−T data, assuming ideal gas behavior. A correction was made for the residual ethane left in the sample at atmospheric pressure. The accuracy of the liquid-phase analyses is estimated to be ±3%.

Table 1. Solubility of Ethane (2) in *N*-Formyl Morpholine (1)

P/MPa	x_2	P/MPa	x_2	P/MPa	x_2
T = 298.15 K		T = 313.15 K		T = 323.15 K	
20.31	0.114	19.47	0.127	13.39	0.133
16.36	0.111	14.74	0.123	11.06	0.129
11.63	0.106	9.48	0.114	8.50	0.125
6.540	0.0998	5.91	0.104	6.56	0.120
4.250[a]	0.0953	5.33	0.104	5.84	0.111
3.540	0.0875	4.06	0.0887	4.19	0.0873
2.370	0.0619	2.86	0.0659	1.98	0.0449
2.120	0.0566	2.45	0.0577	0.768	0.0185
1.450	0.0403	1.28	0.0323	0.238	0.00559
0.784	0.0227	0.756	0.0187		
0.752	0.0218	0.596	0.0153		
0.372	0.0106	0.236	0.00599		
0.153	0.00475	0.127	0.00340		
0.092	0.00274				
T = 343.15 K		T = 373.15 K		T = 403.15 K	
19.16	0.152	18.32	0.170	18.2	0.189
14.39	0.141	14.60	0.157	14.29	0.166
9.62	0.127	9.96	0.134	9.74	0.132
8.73	0.124	8.16	0.118	9.28	0.130
7.03	0.113	6.65	0.103	6.62	0.101
6.13	0.103	6.49	0.0999	5.56	0.0865
5.20	0.0913	5.23	0.0821	5.47	0.0858
2.11	0.0423	3.76	0.0633	3.98	0.0639
1.29	0.0263	2.83	0.0494	2.72	0.0436
0.794	0.0166	1.46	0.0267	2.50	0.0429
0.703	0.0147	0.747	0.0139	1.51	0.0252
0.205	0.00442	0.562	0.0106	0.696	0.0115
0.119	0.00276	0.236	0.00447	0.671	0.0116
		0.109	0.00210	0.198	0.00332
				0.149	0.00277

[a] Three-phase point (vapor, ethane-rich liquid, NFM-rich liquid).

Results and Discussion

Measurements were made at (298.15, 313.15, 323.15, 343.15, 373.15, and 403.15) K at pressures up to 20.3 MPa. The data are presented in Table 1. The experimental data

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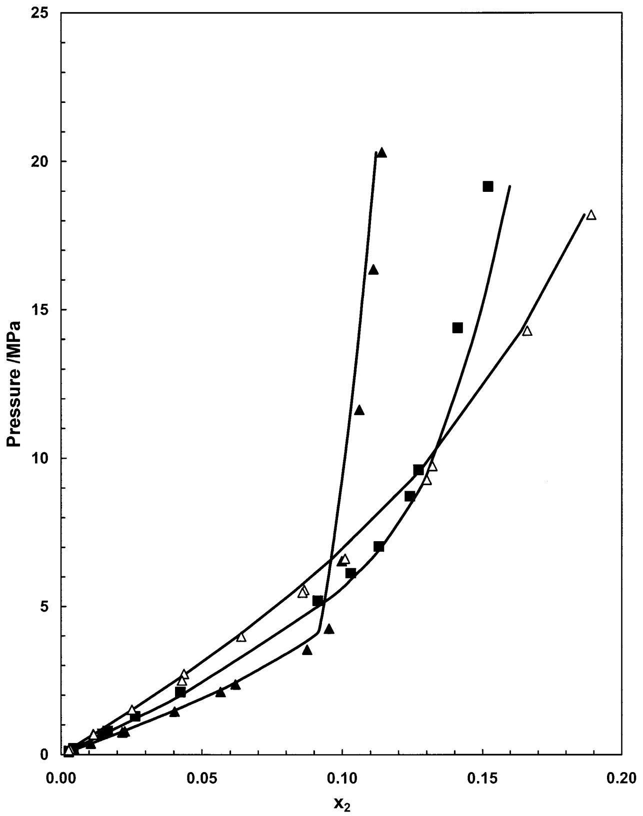

Figure 1. Solubility of ethane in NFM: ▲, 298.15 K; ■, 343.15 K; △, 403.15 K; —, Peng−Robinson correlation.

were correlated with the Peng−Robinson[6] equation of state. The procedure followed was similar to that used by Jou et al.[5] The *a* and *b* parameters for NFM were taken from Jou et al.,[5] and the critical constants and acentric factor for ethane were taken from Daubert and Danner.[7] The experimental solubility data were used to obtain the binary interaction parameter which appears in the mixing rule of the equation of state:

$$a_{12} = (a_{11}a_{22})^{1/2}(1 - \delta_{12}) \tag{1}$$

Values of δ_{12} were found to be dependent on the temperature and were fit by a linear relationship

$$\delta_{12} = 1.412 \times 10^{-4}T + 0.056 \tag{2}$$

Table 2. Parameters for the Krichevsky−Ilinskaya Equation

T/K	H_{21}/MPa	v_2^∞/cm^3 mol^{-1}	A/RT
298.15	34.4	51.3	1.054
313.15	37.4	52.6	0.995
323.15	39.8	53.4	0.966
343.15	44.0	55.3	0.913
373.15	50.9	58.5	0.862
403.15	57.6	62.1	0.834

Using the values of δ_{12}, calculations of the vapor−liquid equilibria were made using the Peng−Robinson equation. The results of the calculation are shown in Figure 1 for three of the isotherms. The correlation reproduces the experimental data with an overall average percent deviation in the mole fraction of 3%, about the same as the experimental uncertainty. At 298.15 K, there is a cusp at 4.25 MPa, which is the three-phase pressure where vapor, ethane-rich liquid, and NFM-rich liquid are present. At higher pressures, the two liquid phases are in equilibrium. The equation of state is able to represent both vapor−liquid and liquid−liquid equilibria well. There is a connection between the binary interaction parameter and the three parameters in the Krichevsky−Ilinskaya equation: the Henry's constant, the partial molar volume of the solute at infinite dilution, and the Margules parameter. These parameters are presented in Table 2.

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