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Solubility of Ethane in Diethylene Glycol

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The solubility of ethane in diethylene glycol (DEG) has been determined at temperatures in the range of (298 to 398) K at pressures up to 20.5 MPa. The experimental results were correlated by the Peng−Robinson equation of state, and interaction parameters have been obtained for this system. The parameters in the Krichevsky−Ilinskaya equation were calculated from these interaction parameters.

Introduction

Glycols are widely used in the natural gas industry to dehydrate gas streams and/or inhibit the formation of hydrates. The solubility of the light hydrocarbons in glycols is important, as the dissolved hydrocarbons constitute a loss to the process and result in hydrocarbon emissions to the atmosphere. As such, the estimation of the hydrocarbon content in the glycol is imperative in the design and evaluation phase of these processes. Despite this importance, there are only a limited number of experimental data sets dealing with the solubility of the lighter hydrocarbons in glycols. This paper is a contribution to the continuing effort by this laboratory to measure the solubility of light hydrocarbons in glycols at the temperature and pressures often experienced in these processes. Previously we have measured the solubility of methane in diethylene glycol (DEG).[1] Borodina and Nam[2] measured the solubility of a natural gas (mostly methane) in DEG and its aqueous solutions.

Experimental Section

The apparatus and experimental technique that were used are similar to those described by Jou et al.[3] 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, and the pressure in the cell was measured by digital Heise gauges (0 to10) and (0 to 35) MPa. These gauges had an accuracy of ± 0.1 % of full scale by comparison with a dead-weight gauge. The thermocouple had an accuracy of ± 0.1 °C by comparison with a platinum resistance thermometer. The apparatus was checked by determination of the critical point and vapor pressure of propane, carbon dioxide, and hydrogen sulfide. Differences of ± 0.1 °C and 0.1 % in vapor pressure were found. The diethylene glycol (DEG, CAS Registry No. 111-46-6) was obtained from Aldrich 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 DEG was drawn into the cell. It was heated to 110 °C, and a vacuum was applied to remove traces of water. Chromatographic analysis indicated that the mole fraction of water in the DEG was 0.001. 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 o.d. stainless steel tubing connected to a calibrated Digigauge (range 0 to 1.0 MPa) and a 50 cm^3 buret. The rack was evacuated, and the gas was 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 uncertainty in the liquid-phase analyses is estimated to be ± 3 %.

Results and Discussion

The solubility of ethane in diethylene glycol was determined at temperatures of 298.15 K, 323.15 K, 348.15 K, 373.15 K, and 398.15 K at pressures up to 20.5 MPa. The experimental data are presented in Table 1 and plotted in Figure 1. At the lowest temperature, a sharp transition occurs between (vapor + liquid) and (liquid + liquid) equilibria. At 298.15 K, there is a cusp at 4.22 MPa, which is the three-phase pressure where ethane-rich liquid, vapor, and glycol-rich liquid coexist. At higher pressures a liquid ethane-rich phase is in equilibrium with the liquid glycol phase. At higher temperatures (above the critical temperature of pure ethane), the solubility rises smoothly with pressure.

The equilibrium data were correlated in the manner described by Jou et al.[3] The method requires that an equation of state valid for the solvent and dilute solutions of the solute in the solvent be available. The Peng−Robinson[4] equation of state was used in the calculations. The parameters a_{22} and b_2 of the ethane were obtained from the critical constants. However, DEG decomposes before it reaches its critical temperature and values for the critical temperature and critical pressure are estimated from correlations. For this reason the parameters a_{11} and b_1 for DEG were obtained from the vapor pressure and liquid

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Table 1. Solubility of Ethane (2) in Diethylene Glycol (1)

T/K									
298.15 K		323.15 K		348.15 K		373.15 K		398.15 K	
P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$
0.030	0.518	0.025	0.350	0.039	0.425	0.043	0.409	0.029	0.266
0.116	1.99	0.125	1.627	0.167	1.77	0.116	1.08	0.125	1.065
0.312	5.35	0.242	3.13	0.126	1.38	0.220	2.12	0.284	2.50
0.544	9.05	0.636	8.19	0.263	2.84	0.256	2.42	0.814	6.82
0.890	15.1	1.62	20.4	0.672	7.11	0.338	3.14	1.38	11.7
1.74	27.0	3.12	35.1	1.64	17.0	0.643	5.89	2.34	19.0
2.63	38.9	5.54	53.9	2.79	27.2	2.17	19.0	3.87	30.2
3.75	51.0	6.65	56.4	3.45	32.7	3.79	32.6	4.45	34.6
4.22[a]	55.1	9.15	60.4	4.49	41.1	4.13	34.4	6.57	46.8
5.46	56.1	11.93	63.7	6.38	51.8	6.50	49.6	8.98	58.0
7.72	57.2	14.59	65.5	8.16	58.0	8.93	59.1	11.40	68.9
9.68	59.7	17.05	67.6	10.58	64.6	11.65	68.3	13.97	77.0
11.84	60.2	19.58	69.8	12.68	67.4	14.30	74.1	16.35	84.4
14.70	60.9			14.78	70.6	16.98	78.4	18.89	87.7
17.46	61.6			17.37	73.2	19.48	82.5		
20.45	61.1			20.04	76.9				

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

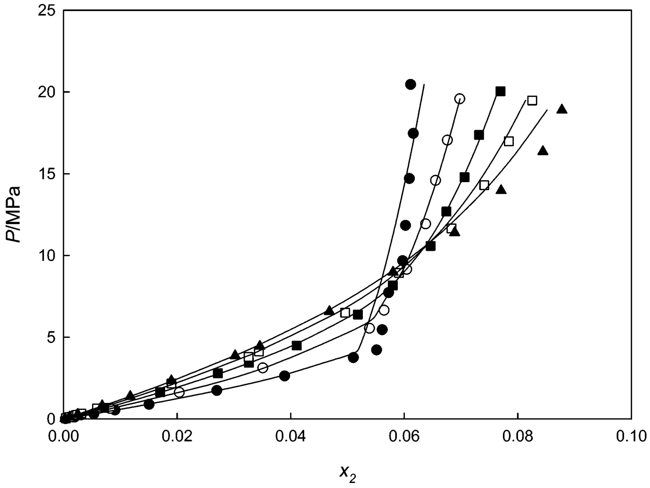

Figure 1. Experimental solubility of ethane (x_2) in diethylene glycol: ●, 298.15 K; ○, 323.15 K; ■, 348.15 K; □, 373.15 K; ▲, 398.15 K; —, Peng−Robinson correlation.

Table 2. Equation of State Parameters

	diethylene glycol (1)		ethane (2)		
T/K	a_{11}[a]	b_1[b]	a_{22}[a]	b_2[b]	k_{12}
298.15	7.41	89.2	0.612	40.5	0.077
323.15	7.05	89.7	0.587	40.5	0.097
348.15	6.71	90.2	0.562	40.5	0.117
373.15	6.40	90.6	0.540	40.5	0.138
398.15	6.11	91.0	0.518	40.5	0.158

[a] Units of a are Pa·m^6·mol^{-2}. [b] Units of b are cm^3·mol^{-1}.

density. The critical constants and acentric factors of the ethane and the equations for the vapor pressure and density of pure DEG were taken from the compilation of Rowley et al.[5] The resulting values of a_{11} and b_1 for DEG and a_{22} and b_2 for ethane are given in Table 2. The values of a_{11} and b_1 are slightly different from those presented earlier[1] because of small differences between the data compilation that was used[5] and that used in the earlier work.[6] The experimental solubility data were used to obtain the binary interaction parameter (k_{12}), which appears in the mixing rule of the equation of state:

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

Values of k_{12} were found to be dependent on temperature and can be fitted by a linear relationship:

$$k_{12} = 8.17 \times 10^{-4}T/\mathrm{K} - 0.167 \tag{2}$$

The correlation reproduces the experimental data with an overall average percent deviation in the mole fraction of 2.2 %, about the same as the experimental uncertainty. However, the correlation does not represent the three-phase point well. At 4.22 MPa and 298.15 K, the calculated value of x_2 is 5.21×10^{-3}, compared with the measured value of 5.51×10^{-3}, an error of 5.6 %, the maximum in the whole data set. Since the correlation misses the cusp, it is a compromise at higher pressures. As well, the calculated isotherm at 398.15 K is not in good agreement with the experimental data above about 10 MPa. This may be the result of choosing a linear correlation for the temperature dependence of k_{12}, and perhaps a higher order polynomial is needed

Although the equation of state (EOS) is useful for calculations in the range of temperatures and pressures where the data were obtained, it is unwise to extrapolate to conditions outside the range of the experimental data. However, the Krichevsky−Ilinskaya equation has a sound theoretical basis and, if the solubility of the solute is relatively low, allows reasonable calculations to be made at conditions outside the range of the experimental data. Bender et al.[7] have shown the connection between the Peng−Robinson EOS, the binary interaction parameter, and the three parameters in the Krichevsky−Ilinskaya equation. This equation is discussed in the book by Prausnitz et al.[8] and is given by

$$\ln(\hat{f}_2/x_2) = \ln H_{21} + \frac{\bar{v}_2^{\infty}(P - P_1^{\mathrm{s}})}{RT} + \frac{A}{RT}(x_1^2 - 1) \tag{3}$$

where $\hat{f}_2$ is the fugacity of the solute in the solution, x_2 is the mole fraction of the solute in the liquid phase, P is the total pressure, P_1^{s} is the vapor pressure of the solvent, R is the gas constant, T is the absolute temperature, and x_1 is the mole fraction of the solvent in the liquid phase. The three parameters are the Henry's constant (H_{21}), the partial molar volume at infinite dilution ($\bar{v}_2^{\infty}$), and the Margules parameter (A). Recently, Schmidt[9] has corrected the equations that relate these parameters to the binary interaction parameter in the Peng−Robinson EOS. The equations were used to obtain the three parameters, and

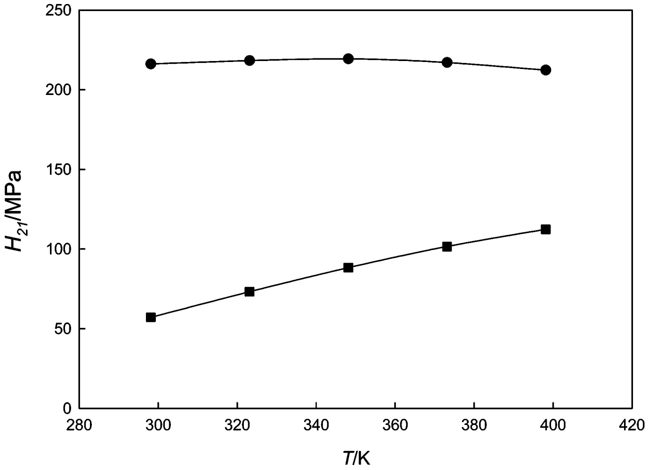

Figure 2. Temperature dependence of the Henry's constants of methane and ethane (H_{21}) in DEG; ●, methane;[1] ■, ethane.

Table 3. Parameters of the Krichevsky−Ilinskaya Equation

T/K	H_{12}/MPa	$\bar{v}_2^\infty$/cm^3·mol^{-1}	A/RT
298.15	57.1	49.7	1.29
323.15	73.2	51.5	1.25
348.15	88.3	53.6	1.21
373.15	101.6	56.2	1.19
398.15	112.4	59.2	1.17

they are given in Table 3. The Henry's constant for ethane in diethylene glycol is plotted in Figure 2 for comparison with that for methane. The Henry's constant for methane appears to be near a maximum (minimum solubility), and it will decrease with further increasing temperature. All solutes behave in this fashion, but often temperatures are not high enough for the maximum to be observed. The Henry's constant for ethane increases with temperature (indicating that the solubility is decreasing with increasing temperature). The values in Figure 2 indicate that the solubility of ethane (at the vapor pressure of the solvent) is about five times that of methane in DEG. The partial molar volume at infinite dilution is somewhat proportional to the "size" of the solute and values for ethane in glycols are typically[3] between 50 and 60 cm^3/mol. The Margules parameters (A) are a measure of the intermolecular forces in the solutions and may be positive or negative. It is typically a weak function of temperature.

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