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Short communication

Vapor–liquid equilibrium in the system ethane + ethylene glycol

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Abstract

The solubility of ethane in ethylene glycol (EG) has been determined at temperatures in the range 298–398 K at pressures up to 20 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.

Keywords: Solubility; Ethane; Ethylene glycol; Equation of state; Gas dehydration

1. 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 results 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 in the continuing effort by this laboratory to measure the solubility of light hydrocarbons in glycols at the temperatures and pressures often experienced in these processes. Previously we have measured the solubility of methane in ethylene glycol (EG) [1] and the solubility of propane in ethylene glycol [2].

2. Experimental

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 (0–10, 0–35 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 ethylene glycol (EG, CAS No. 107-21-1) 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 EG was drawn into the cell. It was heated to 110 °C and a vacuum applied to remove traces of water. Chromatographic analysis indicated that the water content of the EG was 0.1 mol%. 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, 2–20 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 (0–1.0 MPa) and a 50 cm^3 burette. The rack was evacuated and the gas allowed to evolve from the sample bomb into the burette. 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%.

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Table 1
Solubility of ethane (2) in ethylene glycol (1)

298.15 K		323.15 K		348.15 K		373.15 K		398.15 K	
P (MPa)	$x_2 \times 10^3$	P (MPa)	$x_2 \times 10^3$	P (MPa)	$x_2 \times 10^3$	P (MPa)	$x_2 \times 10^3$	P (MPa)	$x_2 \times 10^3$
0.0996	0.583	0.0972	0.458	0.133	0.487	0.100	0.334	0.135	0.407
0.577	3.12	0.816	3.43	0.919	3.24	0.784	2.59	0.666	2.14
2.51	11.7	2.69	10.2	3.53	11.1	2.54	7.97	5.60	14.9
4.21[a]	16.4	6.40	18.0	7.54	18.3	6.58	17.1	9.27	21.4
5.53	16.8	10.34	19.4	13.65	22.2	10.94	22.5	13.95	28.8
9.50	17.7	15.11	20.5	19.23	24.3	14.81	25.8	18.25	30.8
15.17	19.2	19.50	22.1			18.25	28.0		
20.34	20.3								

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

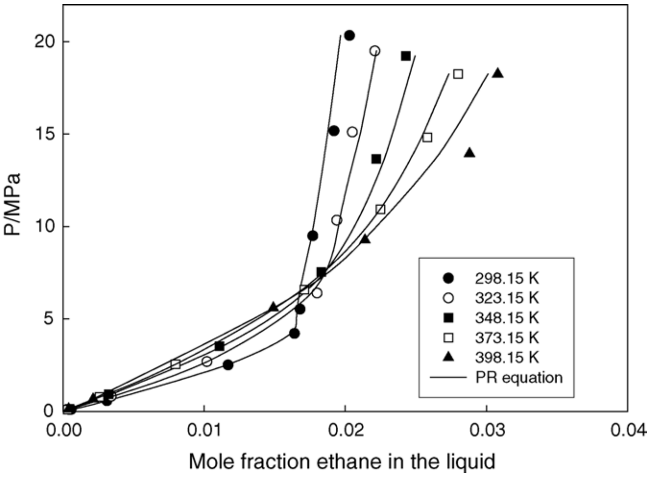

Fig. 1. Experimental data for the EG (1) + ethane (2) system compared with correlated values using the Peng–Robinson equation.

3. Results

The solubility of ethane in ethylene glycol was determined at the temperatures of 298.15, 323.15, 348.15, 373.15, and 398.15 K at pressures up to 20.3 MPa. The experimental data are presented in Table 1 and plotted in Fig. 1. At the lowest temperature, a sharp transition occurs between (vapor + liquid) and (liquid + liquid) equilibria. At higher pressures a liquid ethane-rich phase is in equilibrium with the liquid glycol phase. At 298.15 K, there is a cusp at 4.21 MPa, which is the three-phase pressure where ethane-rich liquid, vapor and glycol-rich liquid coexist.

4. Discussion

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. The parameters a_{11} and b_1 for EG were obtained from the vapor pressure and liquid density, as EG decomposes before reaching its critical temperature. The critical constants and acentric factors of the ethane and the equations for the vapor pressure and density of EG were taken from the compilation of Rowley et al. [5]. The resulting values of a_{11} and b_1 for EG, and a_{22} and b_2 for ethane are given in Table 2. 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:

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

In two-phase regions, the isothermal flash routine algorithm presented by Whitson and Brulé [6] was used. The binary interaction parameter was iteratively modified until the difference in the calculated and experimental liquid mole fractions was less than the set tolerance. Values of k_{12} were found to be dependent on the temperature and can be fitted by a linear relationship:

$$k_{12} = 9.22 \times 10^{-4}\, T(K) - 0.264 \tag{2}$$

The correlation reproduces the experimental data with an overall average per cent deviation in the mole fraction of 2.1%, about the same as the experimental uncertainty.

Table 2
Equation of state parameters

T (K)	Ethylene glycol (1)		Ethane (2)		k_{12}
	a_{11} (Pa m^6 mol^{-2})	b_1 (cm^3 mol^{-1})	a_{22} (Pa m^6 mol^{-2})	b_2 (cm^3 mol^{-1})	
298.15	3.66	51.7	0.612	40.5	0.011
323.15	3.51	51.9	0.587	40.5	0.034
348.15	3.37	52.1	0.562	40.5	0.057
373.15	3.24	52.3	0.540	40.5	0.080
398.15	3.11	52.4	0.518	40.5	0.103