Liquid-liquid Equilibria for Hexane in systems composed of Monoethylene glycol + Water + Hexane in the range (283 to 323K)

Flavie REFLOCH

Introduction

In the oil and petroleum industry, gas hydrates cause serious problems with production, distribution, and the storage plants of natural gas. To prevent hydrate formation, glycols are commonly and extensively used as thermodynamic inhibitors. Because of their toxicity, the effects of these hazardous materials on the environment must be taken into account; knowledge of the partitioning behavior of inhibitors, between the aqueous and hydrocarbon phases, is essential. Liquid-liquid equilibria (LLE) data for systems including: glycols, water, and hydrocarbons, are excessively scarce. Hence, the development of methods for calculating inhibition effects, requires experimental data. In this work, the solubility of hexane in aqueous phase was measured in ternary systems of monoethylene glycol (MEG) + water + hexane under atmospheric pressure of 283K, 303K and 323K, for several mole fractions of MEG.

Experimental conditions

Mixtures of known masses of: monoethylene glycol, water, and hydrocarbons, were introduced into the cell, stirred for 6h, and rested within the cell for 4h so as to split the solution into 2 phases. Aqueous phase samples were decanted into a vial, and introduced very quickly into a gas chromatograph (HP 5890 Series II) with a microsyringe. The GC was made up of a split/splitless injector and a FID detector. The column used was a Restek Rtx-35 Amine (30 m long and 0,32mm internal diameter). The injection and detection temperature was 523 K and the oven temperature was programmed as follows: an initial temperature of 323 K was set for 3 min, followed by a temperature change of 15 K/min up to 423 K. The latter temperature was held for 3 min. The gas chromatograph was calibrated for pure components and mixtures of known masses, of different components covering a wide range of compositions. Heptane was used to standardize measurements. In all cases, the calibration curve was linear.

Results and discussion

The experimental LLE data for the hexane from the aqueous phase in a solution composed of: monoethylene glycol, water and hexane, at three temperatures ranging from 283K to 323K are given in Table 1. After several trials, we found that it varied exponentially, similar to the function of molar fraction of water in the aqueous phase, as shown in Figure 1. The solubility of hexane in the aqueous phase, increased with the temperature increase, ranging from 323K to 283K. This was according to the water composition in the organic phase, which varied from around two to three times greater.

Discussion

LLE data for hexane in a ternary system, including monoethylene glycol, have been measured under atmospheric pressures of 283.1 K, 303.1K and 323.1K. All data sets were satisfactorily represented by the IUPAC-NIST solubility data. The experimental results revealed that the organic solubility of hexane in to a solution of monoethylene glycol in water + alkanes mixtures, increased significantly with temperature.
These results allow us to determine the optimal proportion of monoethylene glycol and temperature that can be used by the petroleum industry to inhibit gas hydrate formation.

x1	x3		
	at 283K	at 303K	at 323K
0	3,02E-06	2,98E-06	3,47E-06
0,15	5,31E-06	1,51E-05	1,96E-05
0,3	1,92E-05	9,89E-05	6,35E-05
0,5	5,82E-05	3,85E-04	2,60E-04
0,7	4,66E-04	6,25E-04	7,36E-04
0,85	7,50E-04	1,12E-03	1,54E-03
1	1,39E-03	1,77E-03	2,29E-03

x1 : mole fraction of ethylene glycol in aqueous phase
x3 : mole fraction of hexane in aqueous phase

Table 1 : Results of solubility of hexane for the aqueous phase at three different temperatures different temperatures :

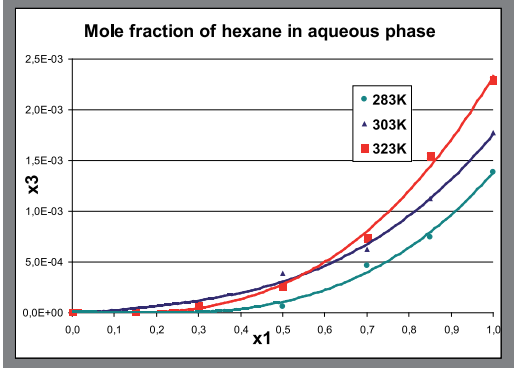

Figure 1 : Distribution of mole fraction of hexane for the aqueous phase in a ternary system made of MEG (1) + water (2) + hexane (3) at three different temperatures :

Université Claude Bernard Lyon 1

Laboratoire des Sciences Analytiques
Equipe THERMALI
43 boulevard du 11 novembre 1918
69622 VILLEURBANNE