High-Pressure Solubility of Hydrogen in Dimethyl Ether

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Isothermal vapor−liquid equilibrium data have been measured for the system hydrogen (1) + dimethyl ether (2) at three temperatures, 15.00, 33.00, and 43.00 °C. Two cubic equations of state have been used to correlate the results, the Soave−Redlich−Kwong (SRK) and the Peng−Robinson (PR) equations. For the SRK equation, the MHV2 mixing rule was used in combination with the modified UNIFAC model, and for the PR equation, the MHV2 mixing rule was used in combination with the original UNIQUAC model.

Introduction

This paper is the second in a series containing phase equilibrium data for binary systems of dimethyl ether. The systems carbon dioxide + dimethyl ether and carbon monoxide + dimethyl ether have been presented previously (Jónasson et al., 1995).

Dimethyl ether is a colorless gas that can be produced from natural gas, coal, or biomass. Today dimethyl ether is primarily used as a propellant for spray cans. Recently it has been found that dimethyl ether can also be used as a fuel in engines, replacing diesel oil. An advantage is that it gives considerably less pollution than diesel oil (Hansen et al., 1995).

Phase equilibrium data for binary systems containing dimethyl ether are needed for proper use of dimethyl ether and for the design of dimethyl ether plants.

Apparatus and Procedures

The measurements were made in a 700 cm^3 cell made of steel as previously described (Jónasson et al., 1995). The composition of the gas phase and the liquid phase is measured using a Hewlett-Packard 5840A gas chromatograph. Argon is now being used as a carrier gas. This was due to the fact that the thermal conductivity of hydrogen is similar to the thermal conductivity of helium. As the sensor of the gas chromatograph is based on thermal conductivity, there would be difficulties in using helium as a carrier gas. Argon has a reasonably lower thermal conductivity than both helium and hydrogen.

Materials

The dimethyl ether used in this work was supplied by Fluka with a minimum guarantied purity of 99.2%, and the hydrogen was supplied by Hede Nielsen with a minimum guarantied purity of 99.0%. The compounds were all used without further purification.

Results and Discussion

In order to measure compositions for mixtures of hydrogen and dimethyl ether, a calibration curve for the gas chromatograph was prepared. A fourth-order polynomial was drawn to fit the points, and this gave a standard deviation of 0.011. The polynomial was found suitable for calculation of the vapor and the liquid compositions.

The system hydrogen (1) + dimethyl ether (2) was measured at three isotherms at 15.00, 33.00, and 43.00 °C. The results are shown in Table 1 and in Figures 1−3.

Table 1. Composition of the Liquid (x_1) and Vapor (y_1) Phases at the Pressure P for the System Hydrogen (1) + Dimethyl Ether (2)

x_1	y_1	P/MPa	x_1	y_1	P/MPa
t = 15.00 °C					
0.000	0.000	0.43	0.015	0.769	2.56
0.001	0.156	0.51	0.020	0.803	3.09
0.001	0.260	0.63	0.025	0.829	3.69
0.002	0.366	0.77	0.032	0.850	4.35
0.003	0.457	0.93	0.038	0.865	5.04
0.004	0.535	1.12	0.043	0.878	5.74
0.006	0.605	1.17	0.047	0.885	6.44
0.008	0.672	1.69	0.058	0.898	7.14
0.011	0.726	2.09			
t = 33.00 °C					
0.000	0.000	0.73	0.024	0.684	3.22
0.001	0.123	0.85	0.030	0.722	3.87
0.002	0.199	0.96	0.039	0.757	4.55
0.003	0.328	1.18	0.046	0.781	5.21
0.005	0.395	1.40	0.052	0.799	5.87
0.007	0.460	1.65	0.060	0.809	6.56
0.010	0.530	1.96	0.063	0.825	7.21
0.013	0.587	2.32	0.072	0.843	7.99
0.018	0.647	2.73			
t = 43.00 °C					
0.000	0.000	0.94	0.021	0.614	3.09
0.001	0.098	1.03	0.028	0.666	3.62
0.001	0.164	1.15	0.037	0.699	4.19
0.003	0.238	1.34	0.042	0.733	4.84
0.005	0.330	1.59	0.052	0.750	5.48
0.007	0.415	1.88	0.061	0.764	6.14
0.011	0.495	2.24	0.068	0.781	6.84
0.016	0.553	2.64			

Two cubic equations of state have been used to correlate the results, the Soave−Redlich−Kwong (SRK) and Peng−Robinson (PR) equations. The SRK equation has been used with the MHV2 mixing rule in combination with the modified UNIFAC model, and the PR equation has been used with the MHV2 mixing rule in combination with the original UNIQUAC model. The mixing rule combines the cubic equation with a model for the excess Gibbs energy (Dahl et al., 1991; Dahl and Michelsen, 1990; Larsen et al., 1987).

In the MHV2/UNIFAC model, the interaction parameters between the ether group (CH_3O) and the hydrogen group (H_2) were calculated (numbers 10 and 22 in the UNIFAC model). In the MHV2/UNIQUAC model the interaction parameters between the hydrogen molecule (1) and the dimethyl ether molecule (2) were calculated. The estimated parameters are shown in Table 2.

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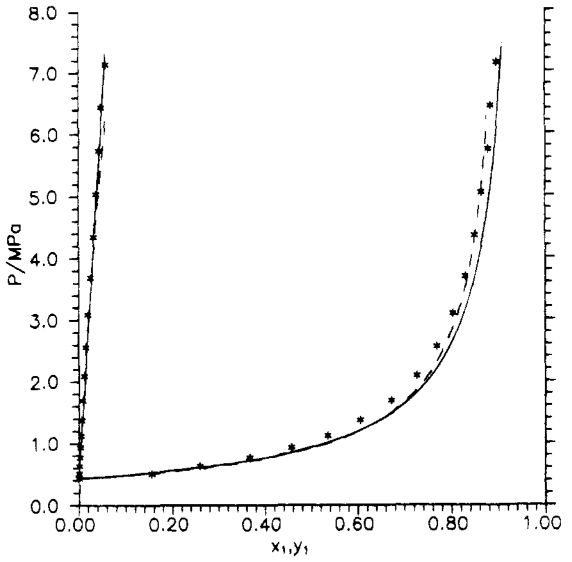

Figure 1. Isothermal pressure–composition data for hydrogen (1) + dimethyl ether (2) at 15.00 °C: (*) experimental data, (—) SRK/MHV2/UNIFAC, (- - -) PR/MHV2/UNIQUAC.

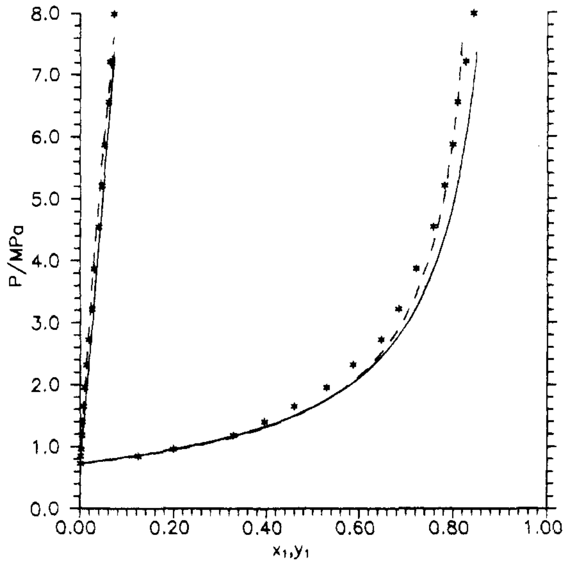

Figure 2. Isothermal pressure–composition data for hydrogen (1) + dimethyl ether (2) at 33.00 °C: (*) experimental data, (—) SRK/MHV2/UNIFAC, (- - -) PR/MHV2/UNIQUAC.

The results of the correlations of the two models are shown in Figures 1–3. In Figure 1 at 15.00 °C both models are seen to correlate the results well. The MHV2/UNIFAC model correlates the liquid phase slightly better, but the MHV2/UNIQUAC model correlates the vapor phase better. In Figure 2 at 33.00 °C both models correlate the liquid phase well, but again, MHV2/UNIQUAC correlates the vapor phase better than the MHV2/UNIFAC model. In Figure 3 at 43.00 °C both models correlate the results equally well.

Conclusions

Three isotherms have been measured for the system hydrogen + dimethyl ether at 15.00, 33.00, and 43.00 °C. This system has not been measured previously.

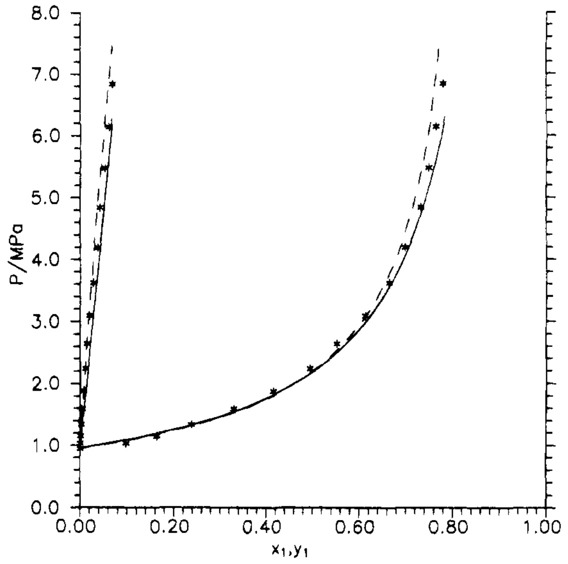

Figure 3. Isothermal pressure–composition data for hydrogen (1) + dimethyl ether (2) at 43.00 °C: (*) experimental data, (—) SRK/MHV2/UNIFAC, (- - -) PR/MHV2/UNIQUAC.

Table 2. Interaction Parameters for the Hydrogen (1) + Dimethyl Ether (2) System

model	interaction parameters
SRK/MHV2/UNIFAC	$A_{10,22,1} = 293.378$ K, $A_{10,22,2} = -4.196$ $A_{22,10,1} = 261.095$ K, $A_{22,10,2} = -2.030$
PR/MHV2/UNIQUAC	$a(1,2) = -282.310$ K $a(2,1) = 1059.973$ K

Two models have been used to correlate the experimental data, SRK in combination with the MHV2/UNIFAC model and PR in combination with the MHV2/UNIQUAC model. Both models are seen to correlate the liquid phase well, but the PR/MHV2/UNIQUAC model correlates the vapor phase slightly better than the SRK/MHV2/UNIFAC model.

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