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Liquid−Liquid Equilibria for Methanol + Water + Hexane Ternary Mixtures

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Liquid−liquid equilibria for methanol + water + hexane ternary mixtures were measured at (298.15, 308.15, and 318.15) K under atmospheric pressure. The reliability of the experimental tie-line data was determined through the Othmer−Tobias plots. Such data were essential for the product separation and solvent recycling in the process of methanol synthesis under supercritical conditions using hexane as the solvent.

1. Introduction

Synthesis of methanol from syngas under supercritical conditions was believed to be able to improve the CO equilibrium conversion and enhance the heat- and mass-transfer efficiencies at the same time, and the single-stage conversion can be higher than 90 mol %. The reaction was operated at a temperature of (473 to 483) K and a pressure of (8 to 10) MPa with hexane as a solvent, and the main components in the product mixtures are methanol, hexane, and water.[1,2] Therefore, the problems concerning the product separation and solvent recycling may arise due to the introduction of solvent hexane and it is essential to determine the liquid−liquid equilibria properties of the methanol + water + hexane system.

In this work, the liquid−liquid equilibria for methanol + water + hexane ternary mixtures were measured at (298.15, 308.15, and 318.15) K. The reliability of the experimental tie-line data was determined through the Othmer−Tobias plots.[3] The results show that the introduction of the solvent hexane does not bring much difficulty to the product separation. The methods to separate methanol from the mixture and to recycle the solvent hexane in the process of methanol synthesis under supercritical conditions are suggested on the basis of the equilibria data.

2. Experimental Section

Methanol (>99.5%) from Beijing Chemical Corp. was purified and dried by refluxing with magnesium and iodine, followed by distillation, as described by Letcher et al.[4], Letcher and Deenadayalu,[5] and Furniss et al.[6] Hexane (>97.0%), supplied by Tianjin Tian-Da Chemical Factory, was purified by being passed through columns containing silica gel and basic alumina. Acetone (>99.8%) from Beijing Chemical Agent Corp. and deionized water were further purified by distillation. The purity of all compounds was determined by gas chromatography and was proved to never be <99.5 mol %.

To determine the points on the binodal curve, an equilibrium cell with a volume of about 50 cm^3 was designed. The cell was equipped with a magnetic stirrer and an isothermal water-jacketed beaker to keep the temperature of the liquid mixture constant. The temperature was controlled to within ±0.05 K. Before the experiment, methanol, water, and hexane were added into the cell by mass at certain ratios. After the mixtures were stirred thoroughly for 2 h, they were then kept still for more than 4 h, allowed to separate into two phases, and reach equilibrium. The upper hexane-rich layer and the lower water/methanol-rich layer were sampled with different syringes. To prevent the samples from separating into two phases again during the sampling and analysis, the procedure was done very quickly and the sucked samples were diluted in acetone immediately. The samples solved in acetone (1 cm^3 of sample in 5 cm^3 of acetone) were analyzed by gas chromatography with a thermal conductivity detector and a 3-m Porapak Q column, with helium as the carrier gas. To determine the response factors of each component, a series of the standard solution of water, hexane, and methanol in acetone was prepared with a concentration near that of the test sample. The quantity of each component was then determined by comparison of the chromatograms of both sample solution and standard solution. In this way, the liquid−liquid equilibria data were measured for mixtures of water, methanol, and hexane at (298.15, 308.15, and 318.15) K.

3. Results and Discussion

The compositions of the mixtures on the binodal curve at (298.15, 308.15, and 318.15) K are given in Table 1 and plotted in Figures 1−3, correspondingly. To determine the reliability of the experimental tie-line data, the Othmer−Tobias plots method was employed as shown in Figure 4. The linearity of the plots indicates the reliability and regularity of the tie lines and binodal curves.

The binary subsystem methanol + hexane exhibits a miscibility gap with a upper critical solution temperature (UCST) of 306.8 K.[7,8] The methanol compositions in the upper hexane-rich layer and in the lower methanol-rich layer at 298.15 K are 0.270 and 0.791 in Savini et al.'s work;[7] Skrzecz's recommended values are 0.2487 and 0.7911, respectively.[8] As suggested by Savini et al.,[7] the small differences between the present data and those in the literature are most probably the result of the differences in the purities of the hexane used. For comparison, the mutual solubility data for water + methanol + hexane

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Table 1. Composition of Points on the Binodal Solubility Curve for Mixtures H_2O (1) + C_6H_{14} (2) + CH_3OH (3)

water/methanol-rich phase			hexane-rich phase			water/methanol-rich phase			hexane-rich phase		
x_1^w	x_2^w	x_3^w	x_1^h	x_2^h	x_3^h	x_1^w	x_2^w	x_3^w	x_1^h	x_2^h	x_3^h
298.15 K											
1.0000	0.0000	0	0.0178	0.9822	0	0.2873	0.0105	0.7022	0.0124	0.9636	0.0240
0.9435	0.0000	0.0565	0.0080	0.9779	0.0141	0.2578	0.0145	0.7277	0.0096	0.9726	0.0178
0.8440	0.0000	0.1560	0.0093	0.9810	0.0097	0.2337	0.0162	0.7501	0.0065	0.9656	0.0279
0.6806	0.0000	0.3194	0.0107	0.9840	0.0053	0.2056	0.0217	0.7727	0.0162	0.9226	0.0612
0.6352	0.0000	0.3648	0.0166	0.9693	0.0141	0.1717	0.0262	0.8021	0.0074	0.9491	0.0435
0.5566	0.0000	0.4434	0.0115	0.9767	0.0118	0.1455	0.0307	0.8238	0.0155	0.9177	0.0668
0.5276	0.0000	0.4724	0.0130	0.9805	0.0065	0.1205	0.0368	0.8427	0.0127	0.9321	0.0552
0.4953	0.0009	0.5038	0.0100	0.9827	0.0073	0.0936	0.0481	0.8583	0.0073	0.9246	0.0681
0.4462	0.0017	0.5521	0.0117	0.9767	0.0116	0.0509	0.0754	0.8737	0.0124	0.8885	0.0991
0.4143	0.0032	0.5825	0.0090	0.9821	0.0089	0.0177	0.1143	0.8680	0.0069	0.8362	0.1569
0.3606	0.0057	0.6337	0.0108	0.9812	0.0080	0.0109	0.1550	0.8341	0.0060	0.7825	0.2115
0.3210	0.0080	0.6710	0.0189	0.9584	0.0227	0	0.2323	0.7677	0	0.7278	0.2722
308.15 K											
1.0000	0.0000	0	0.0174	0.9826	0	0.2216	0.0175	0.7609	0.0036	0.9629	0.0335
0.8065	0.0000	0.1935	0.0193	0.9705	0.0102	0.1899	0.0212	0.7889	0.0035	0.9533	0.0432
0.7205	0.0000	0.2795	0.0178	0.9709	0.0113	0.1407	0.0369	0.8224	0.0061	0.9215	0.0724
0.6199	0.0000	0.3801	0.0152	0.9736	0.0112	0.1011	0.0582	0.8407	0.0134	0.8936	0.0930
0.5526	0.0000	0.4474	0.0119	0.9764	0.0117	0.0743	0.0835	0.8422	0.0085	0.8629	0.1286
0.4757	0.0024	0.5219	0.0105	0.9788	0.0107	0.0605	0.0962	0.8433	0.0061	0.8981	0.0958
0.4071	0.0047	0.5882	0.0045	0.9700	0.0255	0.0396	0.1149	0.8455	0.0125	0.8164	0.1711
0.3532	0.0108	0.6360	0.0039	0.9774	0.0187	0.0242	0.1390	0.8368	0.0137	0.7946	0.1917
0.3041	0.0106	0.6853	0.0037	0.9717	0.0246	0.0174	0.1744	0.8082	0.0059	0.6747	0.3194
0.2559	0.0141	0.7300	0.0039	0.9670	0.0291						
318.15 K											
1.0000	0.0000	0	0.0170	0.9830	0	0.2908	0.0138	0.6954	0.0097	0.9529	0.0374
0.9343	0.0000	0.0657	0.0059	0.9824	0.0117	0.2357	0.0143	0.7500	0.0121	0.9208	0.0671
0.7361	0.0000	0.2639	0.0088	0.9704	0.0208	0.1805	0.0260	0.7935	0.0041	0.9327	0.0632
0.6369	0.0000	0.3631	0.0127	0.9660	0.0213	0.1492	0.0369	0.8139	0.0066	0.8996	0.0938
0.5986	0.0000	0.4014	0.0101	0.9676	0.0223	0.1202	0.0434	0.8364	0.0054	0.9038	0.0908
0.5379	0.0000	0.4621	0.0167	0.9615	0.0218	0.0796	0.0742	0.8462	0.0151	0.8638	0.1211
0.5129	0.0000	0.4871	0.0132	0.9675	0.0193	0.0463	0.1219	0.8318	0.0137	0.8075	0.1788
0.4206	0.0085	0.5709	0.0125	0.9584	0.0291	0.0323	0.1715	0.7962	0.0158	0.7093	0.2749
0.3818	0.0098	0.6084	0.0061	0.9575	0.0364	0.0179	0.2191	0.7630	0.0182	0.6109	0.3709
0.3425	0.0130	0.6445	0.0067	0.9543	0.0390						

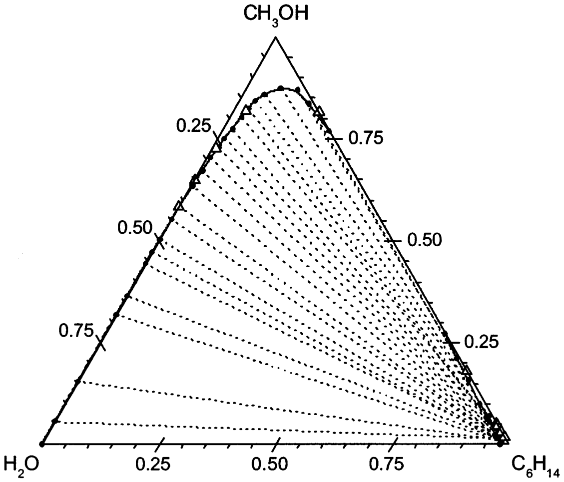

Figure 1. Coexistence curves and tie lines for H_2O + C_6H_{14} + CH_3OH at 298.15 K (the data of Kogan et al.[9] at 293.15 K are showed as △).

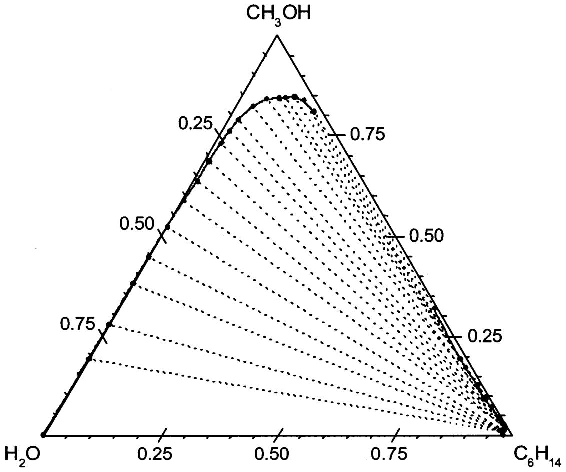

Figure 2. Coexistence curves and tie lines for H_2O + C_6H_{14} + CH_3OH at 308.15 K.

at 293.15 K by Kogan et al.[9] are also shown in Figure 1. As the influence of temperature on the mutual solubility of the ternary system is insignificant, the authors' results show good agreement with those in the literature.

It was found that the ternary mixtures of the methanol + water + hexane system separate into two phases over a wide range of temperature and composition. Below the UCST of the binary system methanol + hexane, the solubility curves for hexane in the water/methanol-rich layer emerge from the methanol−water side and then approach the methanol−hexane side. When the temperature is higher than the UCST of the binary system methanol + hexane, the miscibility gap at the methanol−hexane side disappears, although the binodal curves are still closed to the hexane−methanol axis and it is very difficult to determine the accurate critical point.

The methanol content in the upper layer and the hexane content in the lower layer decrease rapidly with increasing water content in the system. The water/methanol-rich phase contains little hexane while the hexane-rich phase contains little water and methanol when the water content in the system exceeds 0.45; the compositions of the upper layer lie practically on the methanol−hexane side of the concentration triangle near the hexane apex and the

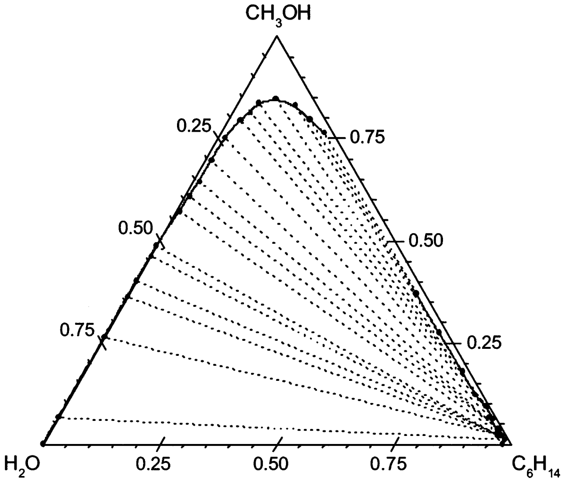

Figure 3. Coexistence curves and tie lines for H_2O + C_6H_{14} + CH_3OH at 318.15 K.

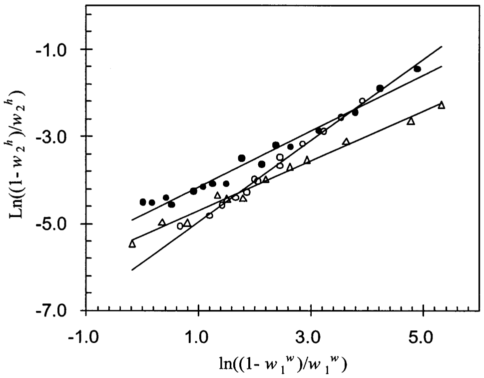

Figure 4. Othmer−Tobias plots for H_2O + C_6H_{14} + CH_3OH: 298.15 K (△), 308.15 K (○), and 318.15 K (●).

compositions of the lower layer lie on the methanol−water side near the axis. Moreover, the influence of temperature on mutual solubility is limited and diminishes with increasing water content in the system. The results reveal that the separation of methanol−hexane mixtures can be easily achieved by dilution with a relatively small amount of water at ordinary temperatures.

In the process of the methanol synthesis under supercritical conditions, the initial mole fraction of hexane in the reactants mixture is 0.2 to 0.3; the liquid product mainly consists of mole fractions of methanol 0.3 to 0.4, water 0.1 to 0.2, and hexane 0.3 to 0.4. When the water content in the product mixture is adjusted, two phases could be formed; in a wide range of temperature and composition, the mole fraction of hexane in the upper hexane-rich phase is >0.98, while <0.015 in the lower water/methanol-rich phase. Therefore, hexane could be reclaimed in the hexane-rich phase for recycling without further treatment; the water/methanol-rich phase would be refined by distillation. The liquid−liquid equilibria data suggested that lower temperature is more favorable for the separation, although such separation could be achieved in a wide range of temperatures from (298 to 318) K.

4. Conclusions

The liquid−liquid equilibria for methanol + water + hexane ternary mixtures were measured at (298.15, 308.15, and 318.15) K. The reliability of the experimental tie-line data was determined through the Othmer−Tobias plots. The results reveal that the separation of methanol−hexane mixtures can be easily achieved by dilution with a relatively small amount of water at ordinary temperatures. The influence of temperature on mutual solubility is limited and diminishes with increasing water content in the system.

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