Vapor−Liquid Equilibria of Benzene and Propylene under Elevated Temperature and Pressure

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To study the alkylation of benzene with propylene under supercritical conditions, high-pressure vapor−liquid equilibria were measured for the benzene + propylene system over the temperature range from 453.15 K to 543.15 K. The Peng−Robinson equation of state was used to calculate the equilibria.

Introduction

Application of supercritical fluids has been attracting more and more interest since the 1980s.[1] In the beginning most researchers focused their attention on physical processes, such as extraction of certain species from food and herbs, and so forth. Recently, supercritical fluid reactions are regarded to be more profitable and significant due to the unique properties of the fluids: high diffusivity, low viscosity, high solubility, and wide variations in density with small changes in pressure or temperature. Since most of the supercritical fluid reaction processes under study are considered to be environmentally benign, they could be called green chemical processes. Supercritical fluid reactions can basically be divided into two kinds: (1) the reactants, together with an inert medium under a supercritical condition such as CO_2, make a reaction system; and (2) the reactant mixture, which contains no inert media, is under a supercritical condition. We have been interested in the second issue, such as alkylation of benzene with propylene. To study reactions of this kind, we need phase equilibria data, as well as the critical points of the binary (or ternary) system at various compositions.

Alkylation of aromatic hydrocarbons is an important process for improving the properties of commercial fuel oil or for providing intermediate products for the chemical industry.[2] However, alkylation of benzene and propylene over a solid acid catalyst is a new process which has some problems. Alkylation under supercritical conditions has been chosen to speed up the reaction, to improve its selectivity, to slow deactivation of catalyst, and to make the process more environmentally benign. Therefore, high-pressure vapor−liquid equilibria of benzene and propylene mixtures are needed to study the reaction carried out in the supercritical or near-critical regions.

Since no vapor−liquid equilibria data of benzene and propylene mixtures under high pressures are currently available, experimental measurements are urgently needed. Two experimental methods are commonly used to study high-pressure phase equilibria, depending on how the composition is determined: the analytical method (or direct sampling method) and the synthetic method (or indirect method).[3] In this paper, the analytical method is used to determine the phase equilibria data for the benzene and propylene system.

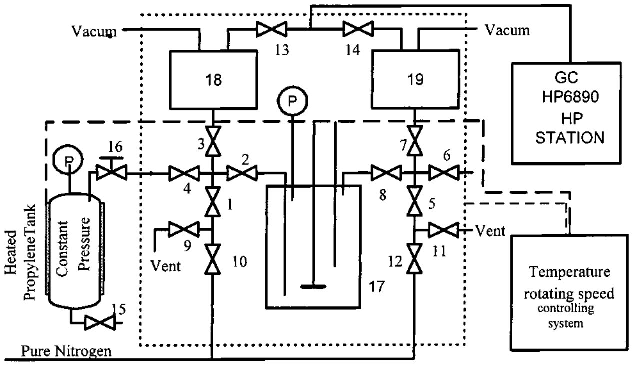

Figure 1. Experimental setup for the high-pressure vapor−liquid equilibria: 1 to 15, valves; 16, pressure regulator; 17, autoclave; 18 and 19, sample vaporizer.

Table 1. Suppliers and Purities of the Chemicals Used in This Study

chemical	supplier	purity/%
benzene	Shanghai Feida Industrial Trade Corporation	>99.95
propylene	Zhenghai	>99.99
nitrogen	Shanghai Chemical Industrial Research Institute	>99.8

Experimental Section

Chemicals. All the chemicals used in this study are commercially available. They were used without further purification. Their suppliers and purities are listed in Table 1.

Apparatus. The experimental setup for the vapor−liquid equilibria measurement is a static-type apparatus composed of three parts: an autoclave of 500 cm^3 in volume with a high-pressure capillary sampling system; the low-pressure sample-vaporizing system; and the on-line analysis device. The high-pressure capillary sampling system is about 0.8 mm in diameter and about 0.35 mL in volume. The apparatus is schematically shown in Figure 1. It is actually a modification of the apparatus applied in the previous study.[4] The system pressure is measured by a precision gauge with an accuracy of ±0.01 MPa. The temperature is measured with a calibrated thermocouple and is controlled to ±0.1 K by an intelligent controller (Shanghai Qisheng Instrument Limited).

The gas and the vaporized liquid samples are analyzed using a HP6890 gas chromatograph which is connected to a computer for data processing. An HPOV-PEG20 type

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10.1021/je0002179 CCC: $20.00

Table 2. Experimental and Calculated $p-x-y$ Data for the Propylene (1) + Benzene (2) System

T/K	P/MPa	$x_{1,\mathrm{exp}}$	$x_{1,\mathrm{cal}}$	$10^3\lvert\Delta x\rvert$	$y_{1,\mathrm{exp}}$	$y_{1,\mathrm{cal}}$	$10^3\lvert\Delta y\rvert$
453.15	1.5	0.0318	0.0318	0.0	0.2589	0.2613	2.4
453.15	2.0	0.0654	0.0686	3.2	0.4092	0.4185	9.3
453.15	2.5	0.1131	0.1068	6.3	0.5087	0.5125	3.8
453.15	3.0	0.1423	0.1464	4.1	0.5725	0.5741	1.6
453.15	3.5	0.1862	0.1879	1.7	0.6198	0.6166	3.2
453.15	4.0	0.2268	0.2315	4.7	0.6536	0.6468	6.8
453.15	4.5	0.2831	0.2779	5.2	0.6748	0.6682	6.6
453.15	5.0	0.3256	0.3279	2.3	0.6917	0.6827	9.0
453.15	5.5	0.3925	0.3830	9.5	0.7022	0.6914	10.8
453.15	6.0	0.4565	0.4461	10.4	0.7011	0.6938	7.3
473.15	2.0	0.0357	0.0342	1.5	0.2192	0.2230	3.8
473.15	2.5	0.0715	0.0691	2.4	0.3465	0.3475	1.0
473.15	3.0	0.0976	0.1030	5.4	0.4358	0.4290	6.8
473.15	3.5	0.1387	0.1413	2.6	0.4937	0.4884	5.3
473.15	4.0	0.1896	0.1798	9.8	0.5377	0.5300	7.7
473.15	4.5	0.2247	0.2205	4.2	0.5693	0.5603	9.0
473.15	5.0	0.2695	0.2630	6.5	0.5868	0.5810	5.8
473.15	5.5	0.3172	0.3109	6.3	0.6065	0.5964	10.1
473.15	6.0	0.3721	0.3641	8.0	0.6137	0.6042	9.5
523.15	4.0	0.0629	0.0638	0.9	0.1683	0.1706	2.3
523.15	4.5	0.0985	0.1011	2.6	0.2257	0.2285	2.8
523.15	5.0	0.1451	0.1394	5.7	0.2673	0.2712	3.9
523.15	5.5	0.1847	0.1826	2.1	0.3051	0.3009	4.2
523.15	6.0	0.2396	0.2362	3.4	0.3268	0.3222	4.6
533.15	4.0	0.0345	0.0350	0.5	0.0896	0.0920	2.4
533.15	4.5	0.0729	0.0708	2.1	0.1537	0.1543	0.6
533.15	5.0	0.1079	0.1106	2.7	0.1987	0.2014	2.7
533.15	5.5	0.1581	0.1560	2.1	0.2396	0.2340	5.6
543.15	4.5	0.0396	0.0401	0.5	0.0792	0.0810	1.8
543.15	5.0	0.0799	0.0803	0.4	0.1285	0.1308	2.3
543.15	5.5	0.1315	0.1280	3.5	0.1706	0.1670	3.6

column and a flame ionization detector (FID) are used for determination of the composition.

Method. During the experiments, benzene is initially fed into the autoclave. Then, the high-pressure part enveloped by the dotted line (Figure 1) is heated to the desired temperature and propylene is added slowly into the autoclave through a pressure regulator. The desired pressure is approached. The equilibrium is finally reached in about 2.5 h. The liquid sample in the capillary between valves 1 and 3 and the gas sample in the capillary between valves 5 and 7 are guaranteed to be completely vaporized into the two evacuated sample containers. Then, heated nitrogen is used to sweep the sampling capillaries and to pressurize the sampling containers slightly higher than atmospheric pressure. Finally, the samples are introduced through a six-way valve into the gas chromatograph and the compositions are determined. Every point was measured two times.

Results and Discussion

Results. Alkylation of benzene and propylene over β-zeolite has been suggested to be carried out in industry at temperatures ranging from 160 °C to 200 °C and pressures from 1.5 MPa to 3.0 MPa. The benzene-to-propylene ratio is to be maintained from 3 to 6. However, to realize the alkylation under supercritical conditions, it is estimated that the temperature should range from 240 °C to 270 °C. This is why the temperatures listed in Table 2 were selected for the vapor−liquid equilibria determination, though the investigated temperature range is somewhat broader than the estimated range.

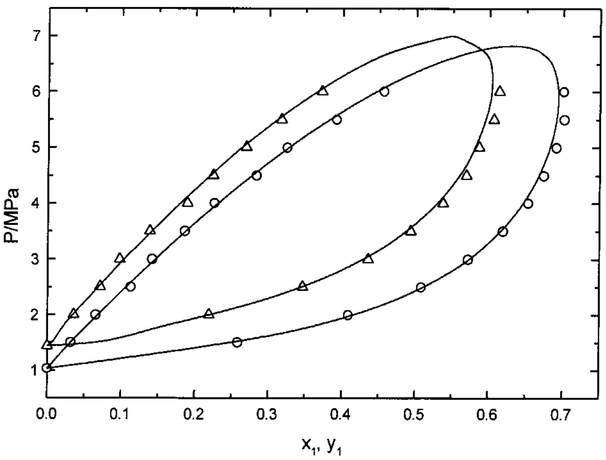

Figure 2. Comparison between the experimentally determined vapor−liquid equilibria for the propylene (1) + benzene (2) system and the calculated results: ○, 453.15 K; △, 473.15 K; curve, calculated with the PR EOS.

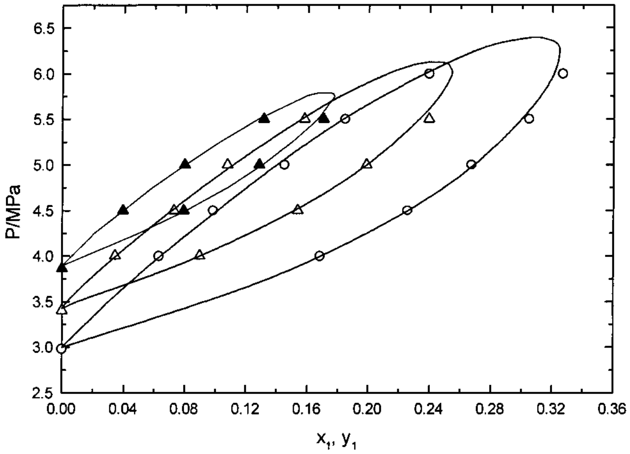

Figure 3. Comparison between the experimentally determined vapor−liquid equilibria for the propylene (1) + benzene (2) system and the calculated results: ○, 523.15 K; △, 533.15 K; ▲, 543.15 K; curve, calculated with the PR EOS.

Table 3. Pure Compound Properties[6] Used in the Study

component	T_c/K	P_c/MPa	ω
benzene	562.2	4.89	0.212
propylene	364.9	4.60	0.144

Table 4. Interaction Coefficient k_{ij} and Objective Function F

	453.15 K	473.15 K	523.15 K	533.15 K	543.15 K
k_{ij}	0.0863	0.0847	0.0582	0.0597	0.0588
10^3F	9.79	12.50	3.87	3.31	2.18

Data Correlation. In this paper, the Peng−Robinson equation of state[5] is used to correlate the experimental data using the conventional mixing rule. The properties of benzene and propylene are given in Table 3. The area method,[7] indicated as AM, is used to calculate the equilibrium compositions; with this method a convergence near the critical point is obtained. The following objective function F is used to estimate the interaction constant k_{ij} in Table 4

$$F = \sum_{i=1}^{N_{\mathrm{exp}}} \sum_{j=1}^{N_{\mathrm{comp}}} \left[\left(\frac{x_{ij,\mathrm{exp}} - x_{ij,\mathrm{cal}}}{x_{ij,\mathrm{exp}}}\right)^2 + \left(\frac{y_{ij,\mathrm{exp}} - y_{ij,\mathrm{cal}}}{y_{ij,\mathrm{exp}}}\right)^2\right]$$

where the subscripts exp and cal represent the experimental and calculated value, respectively, and comp stands for the component. The experimental results and calculations are shown in Table 2 and in Figures 2 and 3. Satisfactory agreement between the experimental data and calculated results was observed. To check the extrapolation of the PR

EOS, the pure benzene saturated vapor pressures were calculated and shown in Figures 2 and 3. They have little difference from the data from the literature.[8]

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Received for review July 21, 2000. Accepted February 1, 2001. This work is supported by the National Natural Science Foundation of China and the China Petrochemical Corporation (Contract No. 29792077).

JE0002179