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High-Pressure Vapor−Liquid Equilibrium for Ethylene + Benzene

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High-pressure vapor−liquid equilibrium (VLE) for the ethylene−benzene binary system was measured by the static method at several pressures for temperatures in the range of 513.15−533.15 K. The Peng−Robinson equation of state was used to correlate the data.

Introduction

The alkylation of benzene with ethylene to produce ethylbenzene is of great significance in industry. Since the traditional operation methods have problems of either rapid deactivation of catalyst or pollution to the environment, some new processes have to be developed. Among them, the near critical process may be an important alternative. Thus, the high-pressure vapor−liquid equilibrium data for the ethylene + benzene system are necessary when the operating conditions are to be determined. However, the available VLE data for this system have the highest temperature of 433.15 K (Lyubetskii, 1962), while the newly developing near critical process surpasses this temperature for 70 K or even higher. Thus, the VLE data at high pressure should be measured for the sake of reaction study.

Experimental Section

Method. Benzene was added into a 500 cm^3 autoclave. After it was heated to a required temperature, ethylene was fed into the autoclave by passing through a pressure regulator, which ensured the operating pressure in the whole process to be constant. With 2 h of agitation in the autoclave, the ethylene + benzene equilibrium could be obtained. The sample in the capillary tube between valves V1 to V3 for the vapor phase or valves V4 to V7 for the liquid phase was vaporized into a prevacuumed sample vaporizer and was washed off the tube by heated N$_2$ gas, as shown in Figure 1. The sample vaporizer had a volume large enough to prevent the sample from condensation at room temperature. The compositions of the gas mixture samples were measured by an HP6890 Gas Chromatograph with an FID detector.

Apparatus. The apparatus consisted of a high-pressure autoclave and a vacuum sample vaporizer, as is sketched in Figure 1. Pressure was measured by a pressure gauge with a precision of 0.5 bar. Temperature was measured by a calibrated thermocouple with a precision of 0.1 K.

Table 1. Vapor−Liquid Equilibrium Data for Ethylene (1) + Benzene (2)

T/K	P/bar	x_1	$10^3\sigma$ ($x1$)	y_1	$10^3\sigma$ ($y1$)	$x_{1,\mathrm{cal}}$	$y_{1,\mathrm{cal}}$
513.15	35.0	0.016	2	0.052	4	0.016	0.050
513.15	40.0	0.026	1	0.080	3	0.026	0.080
513.15	45.0	0.038	2	0.119	3	0.039	0.119
513.15	50.0	0.054	3	0.153	5	0.054	0.155
513.15	55.0	0.079	3	0.189	7	0.077	0.187
513.15	60.0	0.115	5	0.223	7	0.105	0.213
513.15	65.0	0.153	6	0.241	9	0.143	0.230
523.15	40.0	0.018	1	0.051	2	0.017	0.050
523.15	45.0	0.025	1	0.085	3	0.027	0.085
523.15	50.0	0.046	2	0.115	5	0.046	0.120
523.15	55.0	0.075	4	0.161	7	0.075	0.153
523.15	60.0	0.112	5	0.191	7	0.106	0.185
533.15	40.0	0.008	2	0.030	3	0.009	0.032
533.15	45.0	0.022	1	0.062	1	0.023	0.062
533.15	50.0	0.042	1	0.093	3	0.040	0.090
533.15	55.0	0.067	2	0.116	4	0.069	0.119

Table 2. Critical Parameters and Accentric Factors Used in the PR EOS

compound	ref	P_c/MPa	T_c/K	ω
ethylene	Reid et al. (1987)	5.040	282.40	0.085
benzene	Reid et al. (1987)	4.890	562.20	0.212

Chemicals. Ethylene was purchased from Shanghai Chemical Industry Research Institute, with its certified purity of 99.95%. Benzene was from Shanghai Feida Industrial Trade Corporation, with a certified purity of 99.5%, and was carefully degassed prior to use.

Experimental Results

Experimental results are given in Table 1 along with the normal distribution limits of error in the mean value of GC tested concentration.

The phase envelope for the system is shown in Figure 2.

Data Treatment

The Peng−Robinson equation of state (Peng and Robinson, 1976) was used for the correlation of experimental data, and a special AM method (Eubank, 1992) was used

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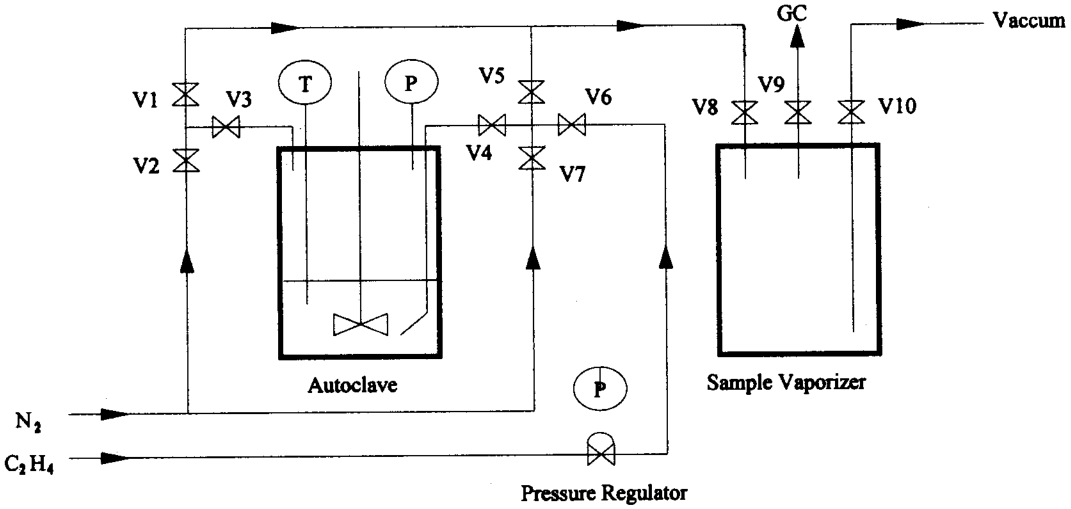

Figure 1. Experimental setup: (V1−V10) valves.

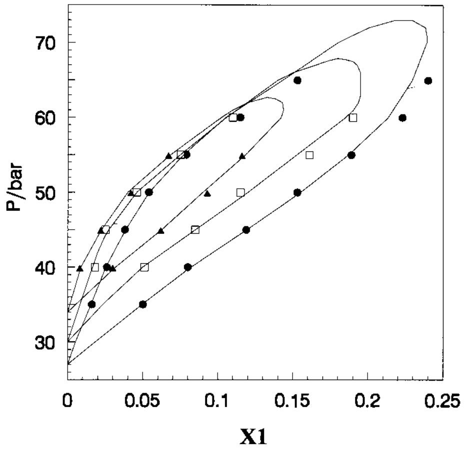

Figure 2. Pressure as a function of ethylene mole fraction in the ethylene (1) + benzene (2) system at different temperatures: 513.15 K (●); 523.15 K (□); 533.15 K (▲); solid lines were obtained by connecting lines of calculated results with the PR EOS.

to maintain the convergence of calculation near the critical region so that the phase envelope could be closed. The critical parameters and accentric factors are listed in Table 2.

The binary interaction parameter was adjusted using the following objective function

$$Q = \sum_{j=1}^{n}\left[\left(\frac{x_{j,exp} - x_{j,cal}}{x_{j,exp}}\right)^2 + \left(\frac{y_{j,exp} - y_{j,cal}}{y_{j,exp}}\right)^2\right]$$

where n is the number of experimental data points; the subscript exp stands for an experimental quantity, and cal stands for a calculated one. The interaction parameter for ethylene + benzene was found to be 0.0311 by the present authors with the most conventional mixing rule.

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