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Vapor−Liquid Equilibrium for Four Binary Systems

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Experimental vapor−liquid equilibrium data for cyclohexanone + 2-methylpropan-2-ol, ethyl *tert*-butyl ether + isobutylene, methyl acetate + acetaldehyde, and methyl *tert*-butyl ether + isobutylene are reported. Measurements were made at two temperatures for each system and covered a range from 50 to 175 °C. Corresponding pressures ranged from about 43 kPa to 1838 kPa.

Introduction

The Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers (AIChE) is interested in experimental vapor−liquid equilibrium data on selected binary systems of interest to the chemical process industry. The data obtained from these studies will be useful for improving the reliability of the design and hence the performance and efficiency of industrial plants, primarily those involved in petroleum or petrochemical processing. Another use for the data is to improve the parameters available for use in equations of state or group contribution methods to predict the physical properties and equilibrium phase behavior of multicomponent systems containing selected binary pairs.

The work covered by this DIPPR Project represents experimental vapor−liquid equilibrium phase composition measurements on four binary systems at two temperatures each. The four systems were cyclohexanone + 2-methylpropan-2-ol at 125 °C and 175 °C, ethyl *tert*-butyl ether (ETBE) + isobutylene at 50 °C and 100 °C, methyl acetate + acetaldehyde at 50 °C and 100 °C, and methyl *tert*-butyl ether (MTBE) + isobutylene at 50 °C and 80 °C.

Initially, additional systems were scheduled for measurements, but it was found that chemical reactions occurred for mixtures of 2-methylpropan-2-ol + formic acid at 75 °C and 125 °C and cyclohexanol + valeric acid at 125 ° and 175 °C. In addition, attempts to study methyl *tert*-butyl ether + 2-methyl-2-butene were abandoned because products of polymerization blocked the sample lines.

In each of the experimental studies, equilibrium vapor and liquid compositions were measured at six compositions.

Experimental Section

Materials. The minimum mole percent purity of the materials used for the experimental work were as follows: 2-methylpropan-2-ol, 99.5%; cyclohexanone, 99+ %; isobutylene, 99+ %; methyl acetate, 99+ %; acetaldehyde, 99+ %; MTBE, 99.0%.

The stated purities are those reported by the manufacturer. The ETBE was of unspecified purity. GLC was run for each chemical, and no measurable impurities were detected. Accordingly, the materials were used without further purification.

Equipment. A pistoned sapphire cell was used for the experimental work. This cell consisted of a fully transparent

Table 1. Vapor−Liquid Equlibria for Cyclohexanone + 2-Methylpropan-2-ol, Ethyl *tert*-Butyl Ether + Isobutylene, Methyl Acetate + Acetaldehyde, and Methyl *tert*-Butyl Ether + Isobutylene

P/kPa	x_2	y_2	P/kPa	x_2	y_2
Cyclohexanone (1) + 2-Methylpropan-2-ol (2)					
t = 125.0 °C					
43 (42.9)	0.0	0.0	290	0.6619	0.9427
84	0.1101	0.5408	328	0.7761	0.9631
170	0.3402	0.8240	382	0.9051	0.9871
229	0.5004	0.9001	423 (423.7)	1.0	1.0
t = 175.0 °C					
163 (161.4)	0.0	0.0	1046	0.7389	0.9406
363	0.1727	0.6031	1214	0.8654	0.9709
626	0.3961	0.8140	1358	0.9652	0.9925
818	0.5567	0.8863	1412 (1422.9)	1.0	1.0
Ethyl *tert*-Butyl Ether (1) + Isobutylene (2)					
t = 50.0 °C					
46 (46.1)	0.0	0.0	370	0.6024	0.9402
120	0.1452	0.6608	458	0.7597	0.9709
208	0.3114	0.8339	521	0.8612	0.9846
290	0.4607	0.9021	607 (608.2)	1.0	1.0
t = 100.0 °C					
222 (222.9)	0.0	0.0	1160	0.6402	0.9015
481	0.1922	0.5907	1393	0.7747	0.9433
692	0.3411	0.7487	1591	0.8796	0.9709
949	0.5098	0.8496	1838 (1827.6)	1.0	1.0
Methyl Acetate (1) + Acetaldehyde (2)					
t = 50.0 °C					
78 (78.7)	0.0	0.0	203	0.6893	0.8749
101	0.1257	0.3148	229	0.8297	0.9387
143	0.3606	0.6420	243	0.9023	0.9666
173	0.5258	0.7783	261 (260.1)	1.0	1.0
t = 100.0 °C					
368 (370.8)	0.0	0.0	730	0.6605	0.8132
452	0.1591	0.3018	793	0.7692	0.8813
544	0.3298	0.5276	879	0.9156	0.9601
653	0.5254	0.7136	930 (927.9)	1.0	1.0
Methyl *tert*-Butyl Ether (1) + Isobutylene (2)					
t = 50.0 °C					
86 (85.4)	0.0	0.0	379	0.5887	0.8963
147	0.1331	0.4911	456	0.7326	0.9409
224	0.2839	0.7121	542	0.8825	0.9786
309	0.4534	0.8349	608 (608.2)	1.0	1.0
t = 80.0 °C					
212 (215.1)	0.0	0.0	853	0.6701	0.8985
353	0.1591	0.4723	1051	0.8524	0.9593
483	0.2988	0.6619	1171	0.9564	0.9891
628	0.4496	0.7865	1224 (1220.8)	1.0	1.0

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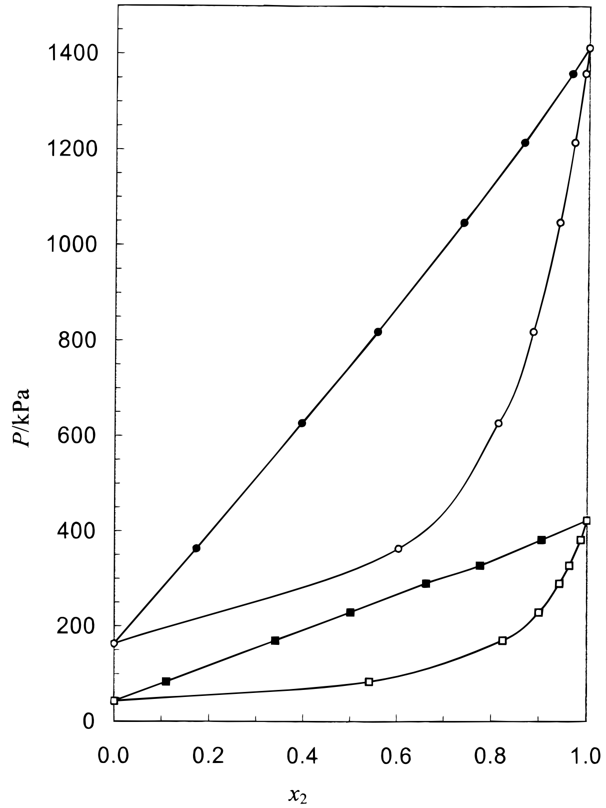

Figure 1. Equilibrium phase compositions for cyclohexanone (1) + *tert*-methylpropan-2-ol (2): ●, liquid, 175 °C; ○, vapor, 175 °C; ■, liquid, 125 °C; □, vapor, 125 °C.

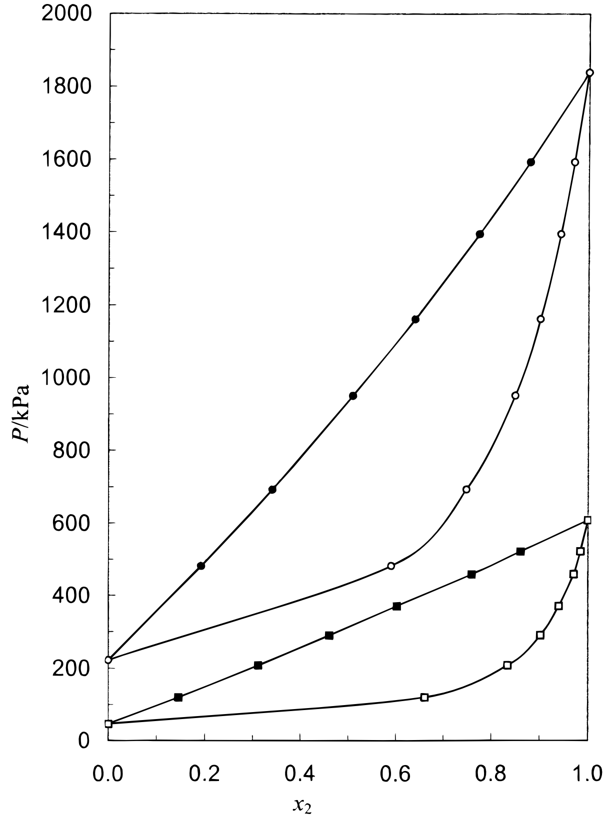

Figure 2. Equilibrium phase compositions for ethyl butyl ether (1) + isobutylene (2): ●, liquid, 100 °C; ○, vapor, 100 °C; ■, liquid, 50 °C; □, vapor, 50 °C.

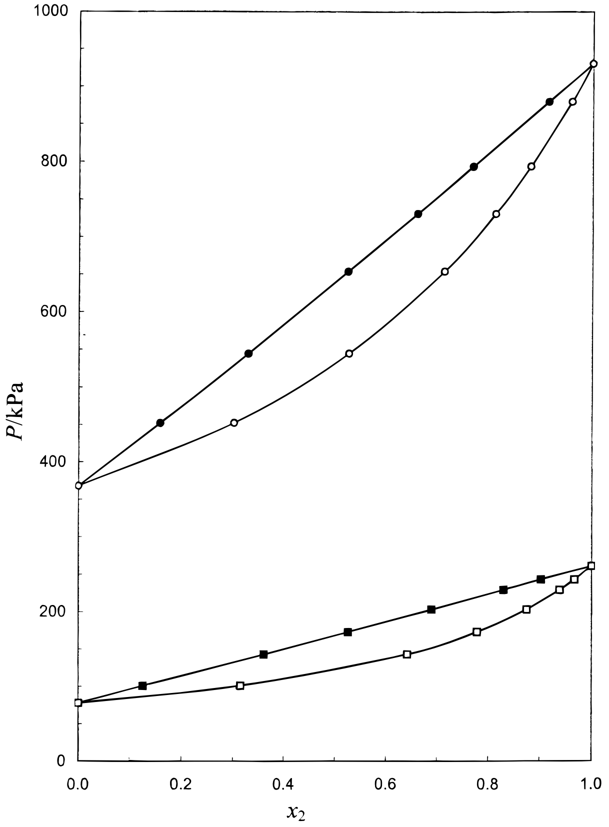

Figure 3. Equilibrium phase compositions for methyl acetate (1) + acetaldehyde (2): ●, liquid, 100 °C; ○, vapor, 100 °C; ■, liquid, 50 °C; □, vapor, 50 °C.

sapphire cylinder mounted firmly between two steel headers. The top header contained the necessary openings and valves for charging the components to the cell, for measuring the cell pressure, and for removing samples for analysis. The bottom header provided access for mercury, which was added to or removed from the cell by a hand-operated mercury pump to adjust the pressure. The body of the cell was 2.5 cm i.d. with a length of 15.2 cm. The working volume of the cell was about 45 cm^3.

The main cell and all the necessary lead lines and valves were mounted inside a controlled temperature air bath. The entire assembly including the cell and bath were rocked about a horizontal axis to equilibrate the cell contents. This cell and its auxiliary equipment have been described in some detail by Huang et al. (1985).

Measurements. Temperatures were measured using iron−constantan thermocouples that had been calibrated against a platinum resistance thermometer. Each temperature was read out on a Hewlett-Packard 3455A digital voltmeter. Temperature accuracy was estimated at 0.1 K.

Pressures were measured using various pressure transducers depending on the range and magnitude of the pressures encountered during the experiment. They were as follows: (A) Druck Pressure Transmitter, model PTX 110/w, range 0 to 0.1 MPa, accuracy ±0.13 kPa; (B) Statham Absolute Pressure Transducer, model PA208TC-100-350, range 0 to 0.7 MPa, accuracy ±0.07 kPa; (C) Statham Universal Transducing Cell, model UC3-UC3-UGP4-200, range 0 to 1.4 MPa, accuracy ±2 kPa; and (D) Statham Universal Transducing Cell, model UC3-UGP4-500, range 0 to 3.5 MPa, accuracy ±5 kPa.

All analytical work was carried out on a Hewlett-Packard model 7620A Gas Chromatograph (GC) coupled with an HP-3353 Data Acquisition System. A thermal conductivity detector was used to analyze all compounds. Calibrations were made for each component, and the relative response factors were obtained from peak areas against sample size.

At least six samples of each phase were taken for analysis so that the reported compositions are the result of averaging

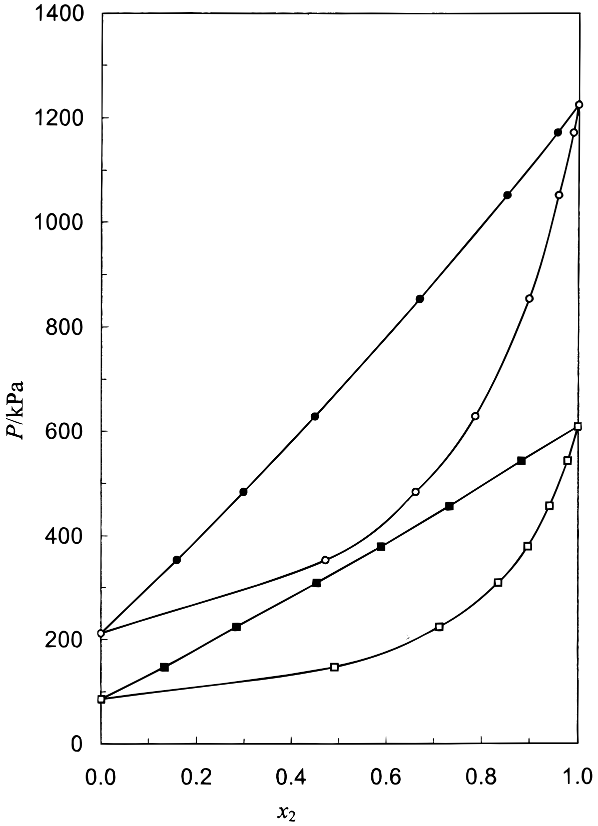

Figure 4. Equilibrium phase compositions for methyl *tert*-butyl ether (1) + isobutylene(2): ●, liquid, 80 °C; ○, vapor, 80 °C; ■, liquid, 50 °C; □, vapor, 50 °C.

six measurements. The repeatability of the analyses was generally within ±3% of the relative standard deviation.

Procedures

Prior to commencing an experiment, the equipment was thoroughly cleaned and evacuated. A suitable amount of the less volatile component was then added to the cell, followed by a predetermined quantity of the more volatile component. The contents of the cell were mixed by rocking the cell assembly, and the cell was simultaneously brought to the desired temperature and pressure. When equilibrium had been established, the rocking motion was stopped and the sampling process commenced.

The gas phase was sampled by continuously drawing off a vapor stream through the sample valve under isobaric isothermal conditions. It was mixed with a stream of helium and circulated through the chromatographic valve. Several samples were taken for analysis at periodic intervals.

After the vapor phase had been analyzed, the remainder of the vapor phase plus a small interface portion of the liquid were removed from the cell. The liquid phase was then sampled and analyzed by using a similar procedure.

At the completion of each measurement, a new set of conditions was established by adjusting the pressure and/or adding more material. The equilibration and sampling sequence was then repeated.

Results

The experimental results are presented in Table 1 and are shown graphically in Figures 1 to 4. The vapor pressures of the pure components at each experimental temperature are compared with the values calculated by Danner and Daubert (1988) given in parentheses.

Literature Cited

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