mol^{-1} K^{-1}, but both are higher values than given for pure $AlCl_3(l)$.

The negative slope of the X',T curve can have unexpected implications in applications where one is working with $AlCl_3$–NaCl mixtures near the demixing compositions. A temperature rise of a sufficiently $AlCl_3$-rich melt could cause a phase separation which may not reequilibrate into a single phase upon cooling. It is kinetically difficult to transfer $AlCl_3(l)$ into molten $AlCl_3$–NaCl without physically agitating the interface.

Safety

Appropriate precautions should be taken for the containment of liquids considerably above their normal boiling points in glass vessels. An especially dangerous situation can occur when ρ_{av} > ρ_{crit} (see above). The gaseous phase will disappear above a certain temperature and the expansion of liquid $AlCl_3$ will then eventually result in rupture of the tube.

Acknowledgment

We thank Michael J. Dunn and Charles B. Hand for their interest and diligence when making all of the cathetometer readings.

Glossary

a	activity of Al_2Cl_6
C_p	heat capacity at constant pressure, J mol^{-1} K^{-1}
H	enthalpy, kJ mol^{-1}
m	mass, g
P	ideal gas pressure of Al_2Cl_6
t, T	temperature, °C and K, respectively
T_M	triple-point temperature of $AlCl_3$, 466.85 K
v	volume, cm^3
X	mole fraction $AlCl_3$, $AlCl_3$–NaCl scale
y	weight fraction $AlCl_3$, $AlCl_3$–NaCl scale
ρ	density, g cm^{-3}
^{0}, $'$, $''$, $'''$	superscripts denoting overall sample, $AlCl_3$–NaCl phase, $AlCl_3(l)$ phase, and $AlCl_3(g)$ phase, respectively

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Equilibrium Phase Properties of Selected m-Xylene Binary Systems. m-Xylene–Methane and m-Xylene–Carbon Dioxide

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Vapor and liquid equilibrium phase compositions have been measured at 310.9, 394.3, and 477.6 K for the m-xylene–methane binary system and at 310.9, 338.7, 394.3, and 477.6 K for the m-xylene–carbon dioxide system. At each temperature, the pressure ranged from the vapor pressure of m-xylene to about 15 MPa, although in the case of the m-xylene–carbon dioxide system, pressures were extended to the vicinity of the critical region at about 17 MPa. The data were used to calculate equilibrium ratios for each component in the binary system.

Introduction

In order to predict the behavior of typical natural gas condensate and other systems containing heavier undefined fractions of interest to the gas processing industry, it is necessary to have information on the binary pairs making up the mixtures. This is particularly true when the system contains nonparaffinic hydrocarbons and nonhydrocarbons such as carbon dioxide, hydrogen sulfide, or nitrogen. Successful modeling of the behavior of these complex mixtures requires good information on the pure compounds and on the binary interactions that exist between the different molecular species.

The recent work of Ng and Robinson (1, 2) on toluene–carbon dioxide, methylcyclohexane–carbon dioxide, and methylcyclohexane–hydrogen sulfide and Kalra et. al. (3) on n-heptane–carbon dioxide binary systems represented part of a continuing program to measure the properties of typical light hydrocarbons or nonhydrocarbons with C_{7+} binaries. In this study, two systems containing m-xylene were studied. Equilibrium vapor and liquid phase compositions in the m-xylene–methane system were measured at three temperatures ranging from 311 to 478 K and pressures from the vapor pressure of m-xylene to about 15 MPa. In the m-xylene–carbon dioxide system the measurements were made at four temperatures ranging from 311 to 478 K and pressures from the vapor pressure of m-xylene to the vicinity of the critical region at each temperature. This range of temperature overlaps slightly the temperatures studied for this system in the recent work of Sebastian et al. (4), who made experimental phase composition measurements at four temperatures from 463 to 583 K. The measured phase compositions were used to calculate the

equilibrium ratios for each component in the binary system.

Experimental Method

The experimental equipment used in this work was basically the same as that described in an earlier paper (*1*). The constant-volume equilibrium cell had an internal capacity of about 150 cm³ and was equipped with a Pyrex glass bull's-eye window to observe the interface between phases. Equilibrium was reached by using a rotating stirrer coupled to an externally mounted rotating permanent ceramic magnet.

The cell temperature was maintained by using eight pencil-type 250-W electrical heaters mounted vertically and uniformly spaced in a 1-in. thick alumina shroud surrounding the cell. The temperature was controlled by a Thermac temperature controller. Insulation was provided by a 2-in. thick layer of Cotronic ceramic fiber insulation. The temperature of the cell was obtained by using an iron-constantan thermocouple with signal read out on a Less-Northrup K-3 potentiometer.

Two specially designed valves were inserted directly into the cell body to sample the vapor and liquid phases. The vapor-sampling valve was designed by Kalra and Robinson (*5*), and the detailed design of the liquid-sampling valve has been described by Ng and Robinson (*1*). Both sample valves permitted the removal of micro samples so that the cell conditions were not materially altered during the sampling process.

After removal from the equilibrium cell, the liquid and vapor samples were swept from the valve ports by a stream of hot helium circulated with a stainless-steel, bellows-type diaphragm pump. The sample and helium were circulated through a heated manifold in order to homogenize the mixture before it was injected into the gas chromatograph. The chromatographic sample valve was located in the circulation network which was totally enclosed in the heated manifold.

Materials Used

Chromatoquality *m*-xylene of 99+ mol % purity was supplied by Matheson Coleman and Bell Co. The *m*-xylene was degassed in the equilibrium cell before the introduction of methane or carbon dioxide. Ultrahigh-purity methane containing 99.97+ mol% methane was supplied by the Matheson Co., and 99.9+ mol % purity carbon dioxide was obtained from Linde. These materials were used without further purification.

Experimental Measurements

The temperatures were measured with iron–constantan thermocouples which had been calibrated against a platinum resistance thermometer and were believed to be known to within ±0.06 K. The pressure of the cell contents was measured by using 0–6.89- and 0–20.7-MPa Heise bourdon gauges which had been calibrated against a Ruska dead-weight gauge and were believed to be known to within ±0.1% of the full scale.

The analysis of the liquid and vapor samples was carried out on a Hewlett-Packard Model 5730A gas chromatograph and a 18850A GC terminal. The flame ionization detector was used for the *m*-xylene–methane system, and the thermal conductivity detector was used for the *m*-xylene–carbon dioxide system. Separation for the *m*-xylene–methane system was achieved on a 3.7-m long by 3-mm diameter column using 10% UC W98 on 80–100 mesh Porapak S. For the *m*-xylene–carbon dioxide system, a 3.7-m long by 3-mm diameter column packed with 10% UC W98 on 80–100 mesh Porapak S was used together with a 5.8-m long by 3-mm diameter column packed with 50–80 mesh Porapak QS. This was operated by using a backflush technique. The gas chromatograph was calibrated by using pure components at pressures less than 21 kPa where the

Table I. Equilibrium Phase Properties of the *m*-Xylene-Methane Binary System

| press., MPa	x_{CH_4}	y_{CH_4}	K_{CH_4}	$K_{m\text{-xylene}}$
		T = 310.9 K		
0.407	0.0136	0.9864	72.5	0.0138
2.13	0.0583	0.9953	17.1	0.0050
4.69	0.1299	0.9960	7.67	0.0046
6.92	0.1699	0.9966	5.87	0.0041
9.12	0.2214	0.9960	4.50	0.0051
11.58	0.2514	0.9952	3.92	0.0064
13.74	0.2954	0.9946	3.37	0.0077
		T = 394.3 K		
0.517	0.0118	0.8816	74.7	0.120
1.83	0.0407	0.9581	23.5	0.0437
3.86	0.0866	0.9740	11.2	0.0285
5.98	0.1431	0.9778	6.83	0.0259
8.36	0.1774	0.9789	5.52	0.0257
11.2	0.2301	0.9772	4.25	0.0296
14.48	0.2951	0.9750	3.30	0.0355
		T = 477.6 K		
1.06	0.0156	0.526	33.7	0.482
2.50	0.0482	0.768	15.9	0.244
4.48	0.0930	0.848	9.11	0.168
7.02	0.148	0.871	5.90	0.152
9.44	0.204	0.886	4.34	0.143
11.78	0.252	0.889	3.53	0.149
13.91	0.295	0.879	2.99	0.171
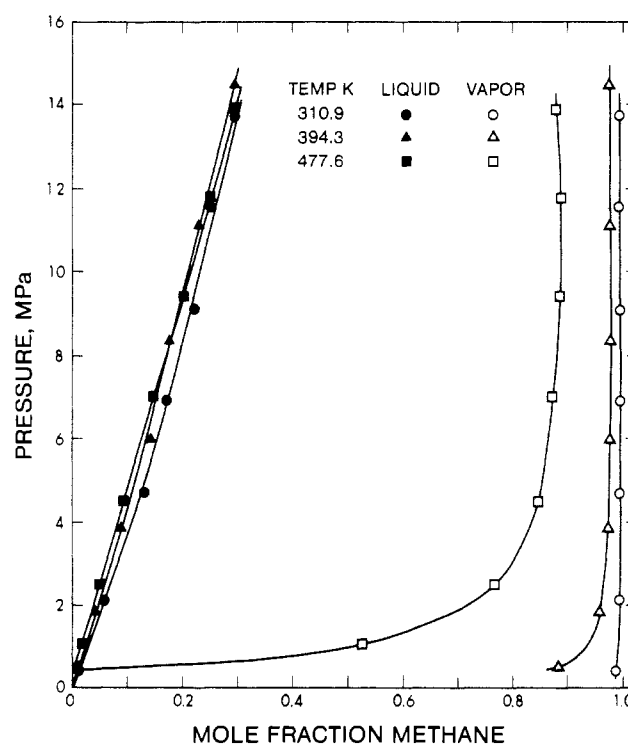
Figure 1. Pressure–equilibrium phase composition diagram for the methane–*m*-xylene system.

response was linear. The response factor of *m*-xylene relative to methane was found to be 0.132, and that of *m*-xylene to carbon dioxide was found to be 0.419.

At least two samples of each phase were taken for analysis, and at least three chromatograms were run on each sample. Thus, the reported compositions are the result of averaging at least six determinations. The repeatability of the analyses was generally within 0.2 mol %.

Results

The experimental values of the equilibrium liquid and vapor phase compositions for the *m*-xylene–methane system are
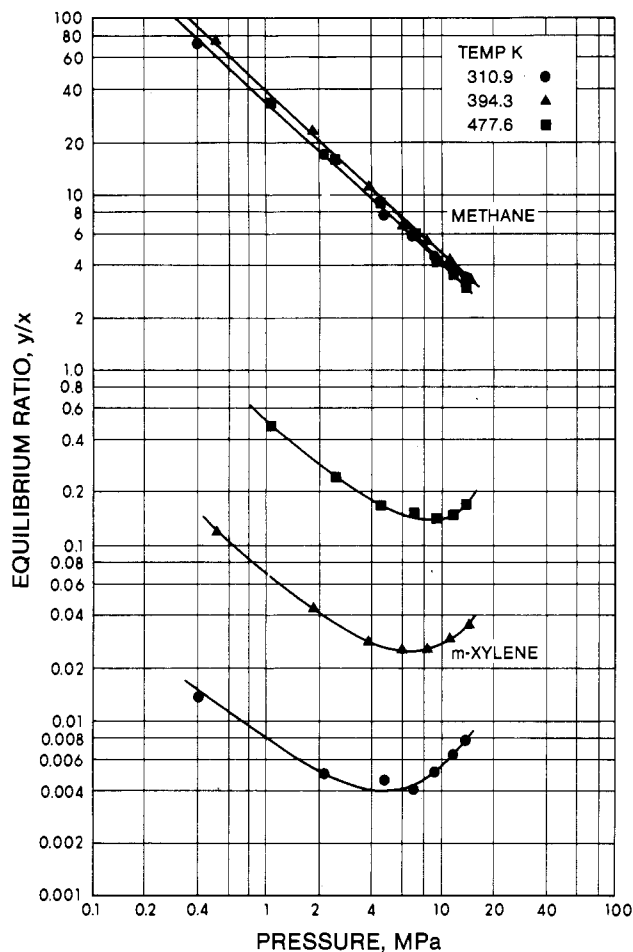
Figure 2. Equilibrium ratios for methane and m-xylene in the methane-m-xylene system.

Figure 3. Pressure-equilibrium phase composition diagram for the carbon dioxide-m-xylene system.

tabulated in Table I and represented graphically in Figure 1 for three isotherms at 310.9, 394.3, and 477.6 K. The equilibrium ratios for each component in this binary system were calculated from the measured phase compositions and are shown in Table I and Figure 2.

Similarly, the experimentally measured equilibrium phase compositions for the m-xylene-carbon dioxide system are presented in Table II and shown in Figure 3 for four isotherms at 310.9, 338.7, 394.3, and 477.6 K. The equilibrium ratios are also given in Table II and shown in Figure 4.

The equilibrium ratios for m-xylene at each temperature and for carbon dioxide at two temperatures obtained from the work of Sebastian et al. are also plotted in Figure 4. Agreement between the two sets of data in the area where the temperatures overlap appears to be good. The equilibrium ratio for carbon dioxide in this binary system passes through a maximum at approximately 500 K.

In this study, all of the temperatures used for the two binary systems lie between the critical temperatures for the two pure components for each system. Since the equilibrium ratios for the two components converge to unity at the critical pressure of the binary mixture that has the experimental temperature as its critical temperature, it allows us to obtain the critical pressure corresponding to each experimental temperature from the K-P plot. This method was used to obtain the critical locus for the m-xylene-carbon dioxide system which is shown graphically in Figure 5. The numerical values are tabulated in Table III.

This procedure was not used for the m-xylene-methane system because the highest experimental pressures were several megapascals below the critical pressure. It was felt that the relatively long extrapolation left too much uncertainty in the critical pressure values.
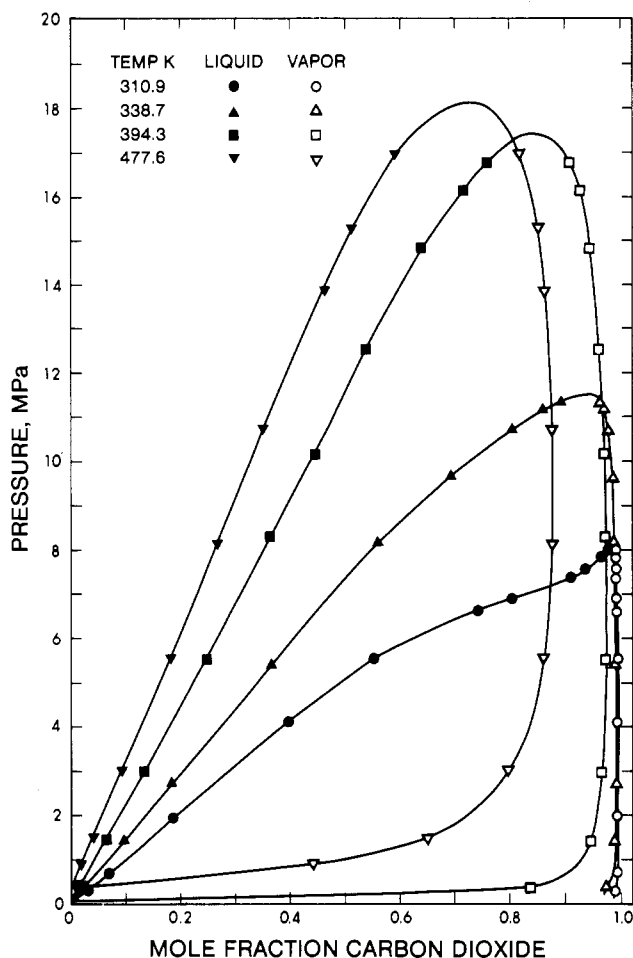
Discussion

As indicated earlier, one of the primary objectives of this work was to obtain the binary interaction parameter for systems containing methane, carbon dioxide, and m-xylene. The usual method for determining the interaction parameter is to find the value which will give the minimum deviation between the experimental bubble-point locus and the bubble-point locus predicted by an equation of state. The values determined this way normally give a good prediction of the dew-point locus as well. As an example, the Peng-Robinson equation of state (6) has the form

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)}$$

and an interaction parameter δ_{ij} in the relationship

$$a_m(t) = (1 - \delta_{ij})(a_i a_j)^{1/2}$$

The optimum values for the interaction parameters δ_{ij} were found to be 0.05 for the m-xylene-methane system and 0.09 for the m-xylene-carbon dioxide system for the above relationships.

Glossary

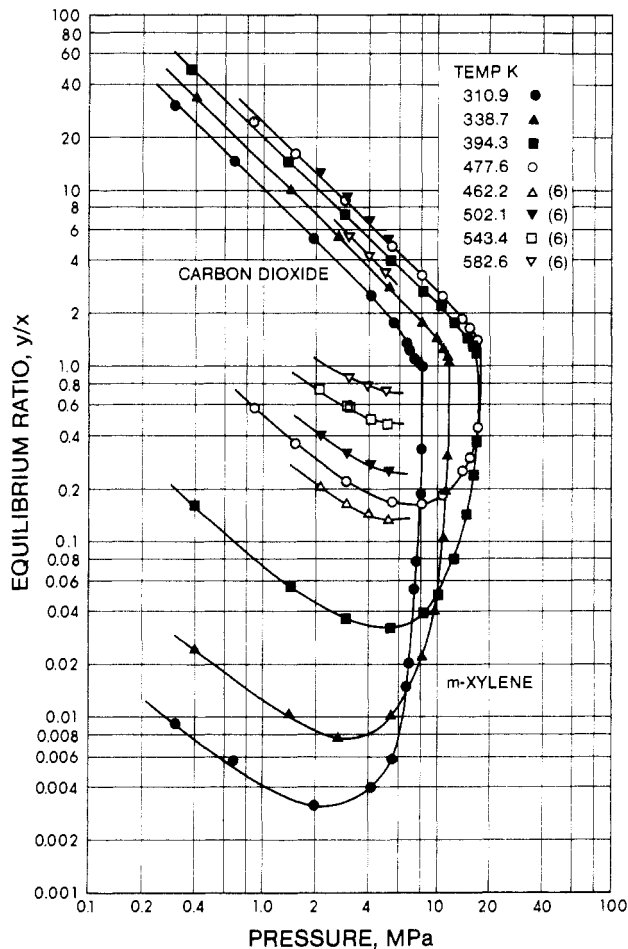|	
P	pressure
R	universal gas constant
T	temperature
v	molal volume
a, b	constants in equation of state
δ	binary interaction parameter

Figure 4. Equilibrium ratios for carbon dioxide and m-xylene in the carbon dioxide–m-xylene system.

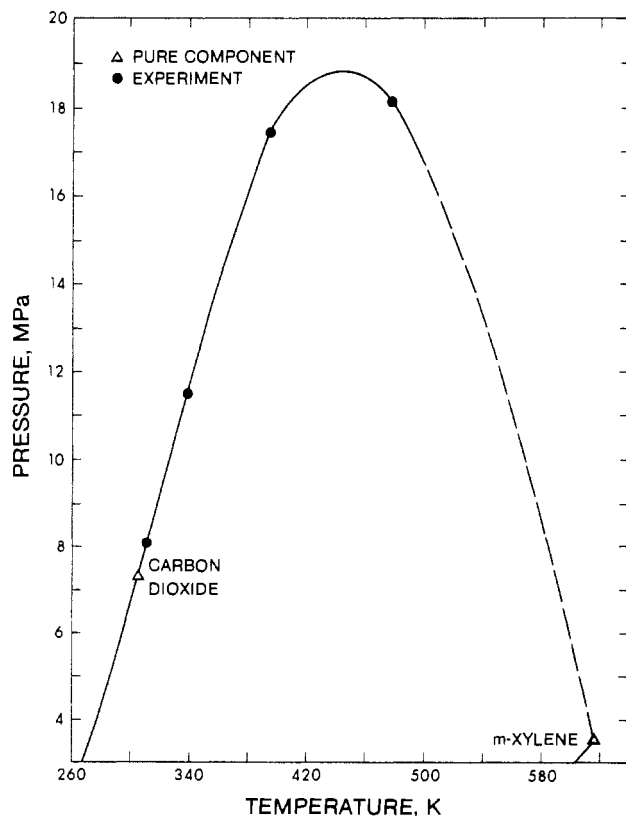**Figure 5.** Critical locus for the carbon dioxide–m-xylene binary system.

y   mole fraction in vapor phase
x   mole fraction in liquid phase

Table II. Equilibrium Phase Properties of the m-Xylene–Carbon Dioxide Binary System

press., MPa	x_{CO_2}	y_{CO_2}	K_{CO_2}	$K_{m\text{-xylene}}$
		$T = 310.9$ K		
0.310	0.0330	0.9911	30.0	0.00920
0.687	0.0678	0.9947	14.7	0.00569
1.94	0.1882	0.9975	5.30	0.00308
4.10	0.3985	0.9976	2.50	0.00399
5.54	0.5532	0.9974	1.80	0.00582
6.61	0.7429	0.9962	1.34	0.0148
6.89	0.8047	0.9960	1.24	0.0205
7.37	0.9124	0.9953	1.09	0.0537
7.55	0.9374	0.9951	1.06	0.0783
7.85	0.9690	0.9943	1.03	0.184
8.00	0.9812	0.9936	1.01	0.340
		$T = 338.7$ K		
0.400	0.0290	0.9759	33.6	0.0248
1.42	0.0958	0.9906	10.3	0.0104
2.71	0.1861	0.9938	5.34	0.00762
5.37	0.3661	0.9936	2.71	0.0101
8.15	0.5615	0.9902	1.76	0.0223
9.67	0.6935	0.9872	1.42	0.0418
10.71	0.8062	0.9794	1.21	0.106
11.16	0.8631	0.9728	1.13	0.199
11.33	0.8938	0.9664	1.08	0.316
		$T = 394.3$ K		
0.394	0.0180	0.8387	46.7	0.164
1.44	0.0653	0.9480	14.5	0.0556
2.98	0.1353	0.9686	7.16	0.0363
5.54	0.2479	0.9757	3.94	0.0323
8.31	0.3666	0.9755	2.66	0.0387
10.16	0.4453	0.9721	2.18	0.0503
12.53	0.5387	0.9627	1.79	0.0809
14.81	0.6422	0.9480	1.48	0.145
16.12	0.7162	0.9292	1.30	0.249
16.75	0.7594	0.9093	1.20	0.377
		$T = 477.6$ K		
0.889	0.0185	0.4412	23.9	0.569
1.52	0.0414	0.6513	15.7	0.364
3.00	0.0936	0.7986	8.53	0.222
5.54	0.1839	0.8617	4.69	0.169
8.12	0.2674	0.8783	3.28	0.166
10.71	0.3531	0.8792	2.49	0.187
13.89	0.4655	0.8648	1.86	0.253
15.30	0.5117	0.8516	1.66	0.304
16.97	0.5937	0.8183	1.38	0.447

Table III. Critical Temperatures and Corresponding Critical Pressures on the Critical Locus of the m-Xylene–Carbon Dioxide System

temp, K	critical press., MPa	temp, K	critical press., MPa
310.9	8.09	394.3	17.44
338.7	11.51	477.6	18.13

K   equilibrium ratio y/x

Subscripts

m   pertaining to mixture
i, j   molecular species

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