Equilibrium Phase Properties of the Toluene–Carbon Dioxide System

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Vapor and liquid equilibrium phase compositions have been determined for the toluene–carbon dioxide binary system at 100.6, 175.0, 249.0, and 399.0 °F over a pressure range from the vapor pressure of toluene to the critical pressure. The data were used to calculate equilibrium ratios for toluene and carbon dioxide in the binary system.

Introduction

Carbon dioxide is frequently found in naturally occurring hydrocarbon reservoirs and in substitute fuel mixtures such as those derived from heavy oils or coal. These mixtures often contain C_{7+} or other undefined fractions which consist of paraffins, aromatics, naphthenes, and sometimes olefins. In modeling the behavior of these complex systems it is often necessary to know the binary interactions that exist between the different molecular species. One such interaction is that between carbon dioxide and toluene in the aromatic fraction. It is largely to obtain information on this type of interaction that the present study was undertaken.

The study consisted of determining the composition of the equilibrium liquid and vapor phases in the carbon dioxide–toluene binary system at four temperatures in the region from 100 to 400 °F and at pressures from the vapor pressure of toluene to the critical pressure at each temperature. The measured phase compositions were used to calculate the equilibrium ratios for carbon dioxide and toluene in the binary system.

Experimental Details

The experimental equipment used in this work was designed to permit the determination of equilibrium phase compositions in a temperature range from about 100 to 600 °F at pressures to 2500 psia. The equilibrium cell was constructed from a 5 in. diameter bar of type 316 stainless steel. The constant-volume cell had an internal capacity of about 150 cm^3 and was equipped with a Pyrex glass bulls-eye window to observe the interface between phases. Equilibrium was attained by using a rotating stirrer coupled to an externally mounted rotating permanent magnet.

A schematic diagram of the equilibrium cell and the associated equipment used is shown in Figure 1. The temperature of the cell and its contents was controlled by using eight pencil-type 250-W electrical heaters mounted vertically and uniformly spaced in a 1 in. thick aluminum shroud surrounding the cell. The temperature control was maintained using a Thermac temperature controller. Insulation was provided by a 2 in. thick layer of Cotronics Ceramic fiber insulation. The temperature of the cell contents was obtained using an iron–constantan thermocouple with signals read out on a Leeds Northrup potentiometer.

In order to sample the vapor and liquid phases two specially designed values were inserted directly into the cell body. The detailed design of the vapor-sample valve has been described by Kalra and Robinson (*3*). The design of the liquid-sampling valve was based on a method used earlier by Fredenslund et al. (*1*). As shown in Figure 2, it consisted of a 0.25-in. diameter steel rod which was mounted through packing along a radius of the equilibrium cell near the bottom. A $^1/_{16}$-in. diameter hole was drilled horizontally along a diameter of the rod near the tip which was immersed in the liquid. A sample of liquid was obtained for analysis by trapping the sample in the nonrotating piston rod and then withdrawing the rod and the trapped sample through the cell wall and subsequently into an evacuated space. Heated helium was circulated through this space and into a heated manifold to prevent condensation of the heavy component prior to injection into the gas chromatograph for analysis.

The heated manifold was controlled at a temperature of about 240 °F. Its operation and use are described in detail by Kalra et al. (*2*).

Table I. Equilibrium Phase Properties of the Toluene-Carbon Dioxide System

pressure, psia	composition		equilibrium constant	
	liquid	vapor	K_{CO_2}	$K_{toluene}$
		100.6 °F		
48.4	0.0300	0.978	32.6	0.0230
216	0.133	0.993	7.50	0.0079
414	0.264	0.997	3.78	0.0045
590	0.406	0.996	2.45	0.0067
809	0.603	0.994	1.65	0.0143
1006	0.869	0.992	1.14	0.0594
1064	0.931	0.993	1.07	0.101
1123	0.971	0.993	1.02	0.230
		175.0 °F		
54.6	0.0206	0.886	43.0	0.116
203	0.0765	0.963	12.6	0.0398
446	0.172	0.978	5.68	0.0263
830	0.328	0.981	2.99	0.0281
1213	0.491	0.978	1.99	0.0442
1386	0.588	0.973	1.65	0.0614
1626	0.720	0.961	1.34	0.141
1683	0.749	0.954	1.27	0.184
1729	0.787	0.946	1.20	0.256
1785	0.843	0.931	1.11	0.440
		249.0 °F		
58.4	0.0172	0.660	38.4	0.346
143.5	0.0396	0.847	21.4	0.160
354	0.106	0.926	8.76	0.0823
758	0.231	0.953	4.13	0.0615
1222	0.368	0.953	2.59	0.0742
1635	0.495	0.943	1.90	0.114
2004	0.621	0.921	1.48	0.208
2218	0.715	0.879	1.23	0.423
		399.0 °F		
171	0.0127	0.266	21.0	0.743
426	0.0722	0.638	8.84	0.390
722	0.140	0.749	5.37	0.292
1021	0.209	0.785	3.76	0.272
1330	0.276	0.793	2.87	0.286
1727	0.378	0.787	2.08	0.342
1976	0.445	0.770	1.73	0.415
2208	0.569	0.716	1.38	0.658

Material Used

Research-grade toluene of 99.94 mol % purity was supplied by the Phillips Petroleum Co. The most probable impurities were

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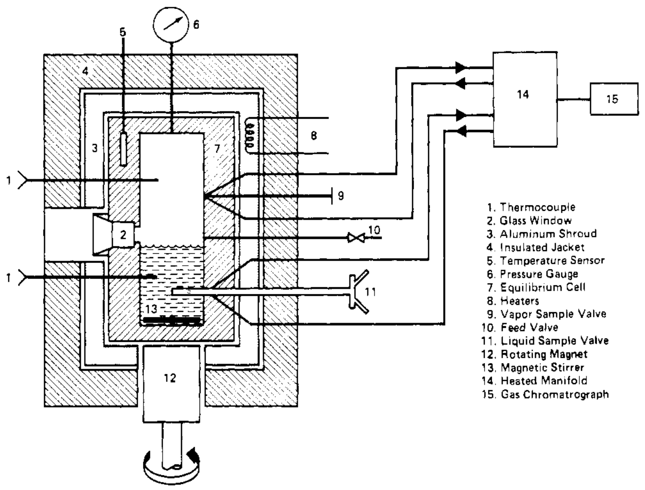

Figure 1. Schematic diagram of experimental equilibrium cell and auxilliary equipment.

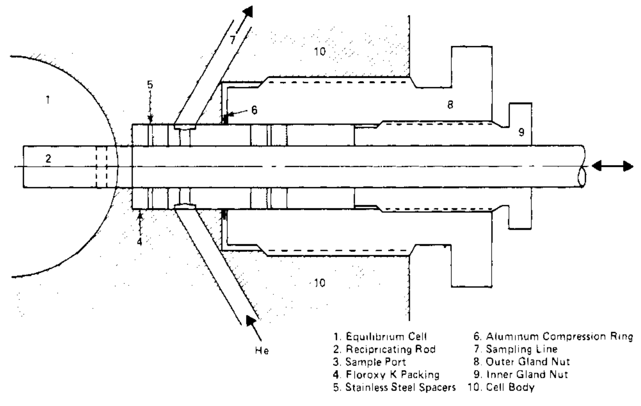

Figure 2. Liquid-sampling valve.

benzene and ethylbenzene. Carbon dioxide gas having a purity of 99.9+ mol % was supplied from Linde. Both were used without further purification.

Experimental Measurements

The iron-constant thermocouples used in this study were calibrated against a platinum resistance thermometer. Temperatures are believed known to within ±0.1 °F. The pressure of the cell contents was measured using 0-2000 and 0-3000 psi Heise bourdon gauges, which had been calibrated against a Ruska dead-weight gauge. The pressures are believed known to within ±0.1% of the full scale. A Hewlett-Packard Model 5830A chromatograph with thermconductivity detector was used for composition analysis. A 6 ft by $^1/_8$ in. diameter column packed with Porapak QS was used. The gas chromatograph was calibrated using pure components only and the response factor of toluene relative to carbon dioxide was found to be 0.467. The repeatability of the analyses was generally within 0.2 mol % and their accuracy is believed to be within 0.3 mol %. At least two samples of each phase were taken at each equilibrium condition, and four analyses were run on each sample. The average of the resulting eight analyses was recorded as the equilibrium value.

Results

The results of the direct experimental measurements of equilibrium liquid- and vapor-phases compositions are tabulated in Table I and represented graphically in Figure 3 for four isotherms at 100.0, 175.0, 249.0, and 399.0 °F. The equilibrium ratios for the components of the binary systems were calculated from the measured phase compositions. The resulting equi-

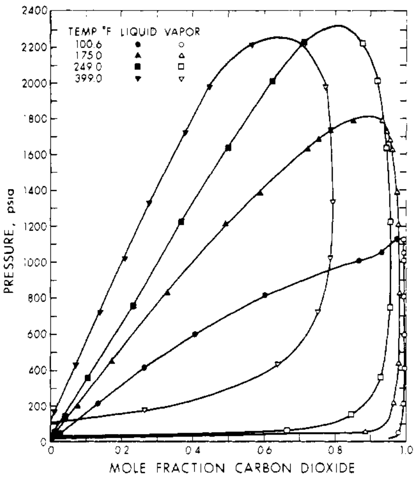

Figure 3. Pressure-equilibrium phase composition diagram for the toluene-carbon dioxide binary system.

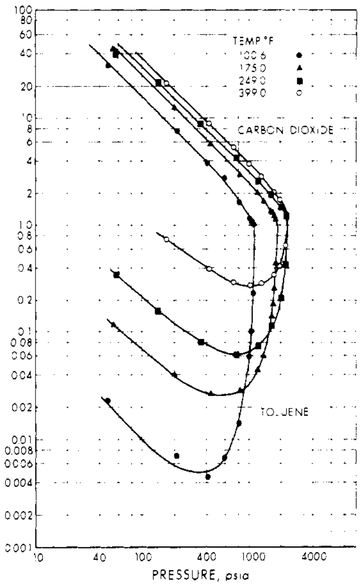

Figure 4. Equilibrium ratios for toluene and carbon dioxide in the toluene-carbon dioxide binary system.

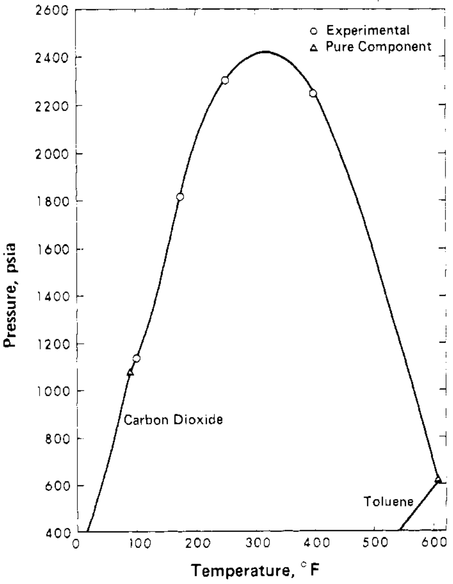

Figure 5. Critical locus for the toluene-carbon dioxide binary system.

librium ratios are also tabulated in Table I and shown in Figure 4.

Discussion

The four temperatures chosen for studying this binary system all lie between the critical temperatures for the two pure components. 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 is possible to obtain the critical pressure corresponding to each experimental temperature from the K–P plot. These values are presented graphically in Figure 5.

As indicated earlier, one of the primary objectives of this work was to obtain the binary interaction parameter for systems containing carbon dioxide and toluene. 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 value determined this way normally gives a good prediction of the dew point locus as well. As an example, the interaction parameter δ_{ij} in the relationship

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

for evaluating the parameter a_m for the Peng–Robinson (*4*) equation of state was found to be 0.09 for the toluene–carbon dioxide binary. Within a range of pressures up to 90% of the critical, the average absolute difference between the experimental and predicted bubble point pressure is 20.3 psi, and the average arithmetic difference is −7.8 psi.

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Ionization Constant of Mandelic Acid and Some of Its Derivatives†

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The ionization constants of mandelic acid and 16 of its derivatives were measured in aqueous solution at 25 °C using the potentiometric method described by Albert and Serjeant.

Ionization constants have been determined for only a relatively small number of mandelic acid derivatives. Prior to 1966 values had been reported only for mandelic acid (*7*) and *m*-halo (*7*), *o*-, *m*-, and *p*-nitro (*3*), and *p*-bromo (*2*) derivatives of mandelic acid. In 1966 Klingenberg, Thole, and Lingg (*5*) published ionization constant values for 13 mandelic acid derivatives. Table I is a summary of the values reported. The ionization constants of nine additional derivatives have been determined. Results obtained for mandelic acid and seven of the previously reported derivatives are also given.

Experimental Section

The acids used in this work (Table II) were synthesized by methods appearing in the literature except for mandelic acid and *m*-hydroxy- and 4-hydroxy-3-methoxymandelic acids which were purchased from commercial sources.

Ionization constants were measured potentiometrically by the procedure given in Albert and Serjeant (*1*). This consists essentially in the measurement of the pH of a solution of a known concentration of the test acid after addition of successive increments of standard base until the equivalence point is reached. The ionization constant is calculated from the equation

$$pK_a^M = pH + \log \frac{[HA] - \{H^+\}}{[A^-] + \{H^+\}}$$

where [HA] is the stoichiometric concentration of the undissociated acid molecular, [A⁻] is the stoichiometric concentration of the anion, and {H⁺} is the activity of the hydrogen ion as calculated from the measured pH. The constant so obtained is a "mixed" constant since both concentration and activity terms are used. The thermodynamic constant can be obtained from the equation

$$pK_a^T = pK_a^M \pm \frac{0.507\sqrt{I}}{1 + 1.6\sqrt{I}}$$

Table I. Previously Reported Ionization Constants of Mandelic Acid and Its Derivatives at 25 °C

acid[a]	method[b]	pK_a	type[c]	ref
p-nitromandelic	con.	2.98	T	3
m-nitromandelic	con.	3.03	T	3
p-iodomandelic	pot.	3.14	M	5
o-nitromandelic	con.	3.15	T	3
p-chloromandelic	pot.	3.15	M	5
p-bromomandelic[d]	pot.	3.15	M	5
p-fluoromandelic	pot.	3.19	M	5
m-bromomandelic	con.	3.23	T	7
m-chloromandelic	con.	3.24	T	7
m-fluoromandelic	con.	3.24	T	7
m-iodomandelic	con.	3.26	T	7
o-fluoromandelic	pot.	3.30	M	5
o-chloromandelic	pot.	3.31	M	5
o-bromomandelic	pot.	3.32	M	5
mandelic[e]	con.	3.41	T	7
p-methoxymandelic	pot.	3.42	M	5
p-ethylmandelic	pot.	3.55	M	5
2,5-dimethylmandelic	pot.	3.57	M	5
p-*n*-butylmandelic	pot.	3.58	M	5
p-isopropylmandelic	pot.	3.64	M	5
o-methoxymandelic	pot.	3.64	M	5

[a] Concentration 0.01 M. [b] Key: con. = conductometric, pot. = potentiometric. [c] Key: T = thermodynamic, M = mixed. [d] A pK_a of 3.39 reported at 18 °C (*7*). [e] A pK_a of 3.06 reported at 18 °C (*2*).

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