Clathrate Phase Equilibria for the Water–Phenol–Carbon Dioxide System

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Clathrate phase equilibria for the ternary water – phenol – carbon dioxide system containing one-guest and two-host components were studied. Three four-phase equilibrium loci for this ternary system were determined over wide temperature and pressure ranges. A quintuple point, thermodynamically unique, and invariant condition appeared in this type of ternary system, was carefully measured, and were 293.7 K and 57.2 bar. At this quintuple point, five individual phases of water-rich liquid, phenol-rich liquid, carbon dioxide-rich liquid, phenol clathrate, and vapor could coexist in equilibrium. A new experimental technique was used to determine the liquid-phase compositions coexisting with phenol clathrates at the isobaric conditions of 30.0 bar and six temperatures ranging from 278.2 and 303.2 K. A potential applicability of the clathration process to phenol separation from aqueous solutions was demonstrated in terms of phenol concentrations based on carbon dioxide-free concentration. In particular, phenol separation by using high-pressure carbon dioxide as a clathrate-inducing agent could be applied even to multiphase aqueous solutions over an entire range of phenol concentrations.

Introduction

Clathrate compounds are crystalline materials formed by a physical reaction between host molecules and relatively light guest molecules. There are various cavities capable of entrapping guest molecules in an open network of host molecules composing a crystalline framework. Clathrate formation may be classified as a kind of adductive crystallization in that gas molecules lead to the creation of a new solid phase, that is, the clathrate phase (McKetta, 1993).

Depending on the chemical properties of the host species, clathrate compounds can be divided into two categories: aqueous and nonaqueous. Clathrate compounds in which the host molecules are water or deuterium oxide belong to the aqueous clathrates. This kind of inclusion compound is specifically called a clathrate hydrate or gas hydrate. Gas-phase guest molecules generally form nonaqueous clathrates with phenolic compounds such as hydroquinone, phenol, and simple substituted phenols. Two distinct cages are formed in phenolic clathrates that are capable of including suitably sized guest molecules (Atwood et al., 1984). In the case of the carbon dioxide inclusion, one and three molecules of carbon dioxide can be encaged in the small and large cavities, respectively (von Stackelberg et al., 1958).

A large number of research articles related to gas hydrates have been published during the past 40 years, whereas there are far fewer theoretical and experimental studies on the nonaqueous clathrate compounds in the literature. The investigation of the nonaqueous clathrates has focused mainly on their crystalline structures. A variety of research on natural gas hydrate has been carried out since it was recognized that the plugging of gas pipelines in natural gas transportation was primarily due to gas hydrate formation between water and gas composed of methane, ethane, propane, and other light hydrocarbons. A simple desalination process to produce portable water from seawater using hydrate-forming phenomena was proposed in the 1940s (Parker, 1942) and received considerable attention in the 1960s and 1970s.

A large amount of the dissociation equilibrium data for gas hydrates has been reported in the literature and is well summarized by Sloan (1990) and Berecz and Balla-Achs (1983). Significant efforts have also been devoted to the investigation of the phase behavior of multicomponent systems containing the gas hydrates. Especially, the inhibition effect of nonhydrate-forming agents such as methanol, ethylene, glycol, and

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several electrolytes on the hydrate dissociation conditions have been extensively investigated by many workers [Ng and Robinson, 1985; Englezos and Hall, 1994; Kotkoskie et al., 1992; Ng et al., 1987; Englezos and Ngan, 1993; Ross and Toczylkin, 1992; Song and Kobayashi, 1989]. Bakker et al. (1996) recently proposed a general modification in clathrate modeling that gives a complete description of the carbon dioxide hydrate stability field between 253 and 293 K, and 0 and 200 bar, and that can be applied to the carbon dioxide–water system with various salts.

On the other hand, only a few experimental measurements for the phase behavior of the nonaqueous clathrates have been reported in the literature. Most of the past investigations of the nonaqueous clathrates have been limited to crystalline structure, pressure-temperature behavior, and related thermal properties of several phenolic clathrates. Allison and Barrer (1968) measured the dissociation pressures and heats of formation of the clathrates formed from phenol and seven gases (Kr, Xe, CH_4, C_2H_4, C_2H_6, CO_2, and SO_2) at temperatures far below the normal melting point of phenol. Van der Waals and Platteeuw (1959) summarized the dissociation pressures of hydroquinone clathrates at 298.2 K. Trofimov and Kazankin (1968) reported that *p*-cresol forms clathrate compounds with gas species of molecular size smaller than 5.1 Å. They also measured the dissociation pressures of *p*-cresol clathrates produced by suitably sized guest molecules such as HCl, HBr, HI, H_2S, Kr, and Xe.

The objective of this article is thus to thoroughly investigate the highly complicated phase behavior of the binary phenol–carbon dioxide and ternary water–phenol–carbon dioxide systems and the applicability of the clathration process to separation of phenol from an aqueous stream by including carbon dioxide as a clathrate-inducing guest molecule. For the water–phenol–carbon dioxide system containing two hosts and one guest, the four- and five-phase equilibrium conditions were extensively investigated over wide temperature and pressure ranges. In addition, the isobaric equilibrium compositions of this ternary system were carefully measured at 30.0 bar and several temperatures. These results may provide the thermodynamic basis that this clathration process can be used as a new potential separation technology.

A large amount of technological information on the supercritical fluid extraction (SFE) of phenol from aqueous solution has recently been reported by many workers (Ghonasgi et al., 1991a,b; Gupta et al., 1991; Roop and Akgerman, 1989; Roop et al., 1989). SFE of an aqueous solution containing several alcohols has been of interest due to the increased energy costs of conventional processes such as atmospheric distillation. Particularly, SFE of specific materials such as ethanol, lactic acid, and pharmaceuticals from the bioproducts of fermentation has been approved as a powerful recovery process, since it has the ability to break the azeotropic limit of the solutions containing target materials and does not damage fermentation byproducts. Unfortunately, SFE possesses the critical limitation of producing insufficient overall separation yield, although it can obtain comparatively high selectivity. In particular, SFE of phenol from aqueous solution has another limitation that it cannot be applied to the highly concentrated phenol solutions because of the typical liquid–liquid equilibrium behavior of phenol–water mixtures. As previously described, the separation of phenol from aqueous solutions by clathration may overcome these two defects common in the SFE process.

Experimental Section

Apparatus and sample analysis

The experimental apparatus used in this work is shown in Figure 1. The apparatus was constructed to measure the clathrate dissociation pressures and the equilibrium compositions of liquid phases that coexist with the clathrate phase. The main components of the apparatus are the equilibrium view cell and sampling compartment. The phase behavior of the systems considered in this work was so complex and diverse that two different types of equilibrium cells were used separately to examine the complete phase behavior. One equilibrium cell is made of 316 stainless steel and has an internal volume of about 50 cm^3. Two windows placed one at the front and one at the back of the cell allow visual observation of phase transitions. The other equilibrium cell is a variable-volume cylinder with a freely moving piston inside. This cell was mainly used to investigate the phase behavior of the mixtures containing only solid, clathrate, and liquid phases with no vapor phase. The variable-volume equilibrium cell is divided into two sections of sample chamber and pressure-generating chamber by the movable piston. Since it is difficult to directly measure the system pressure under specific equilibrium conditions at which the vapor phase cannot exist, an indirect method measuring the pressure of dense gases in the pressure-generating chamber is applied. From preliminary tests, we confirm that the pressure difference between two individual chambers becomes less than 0.2 bar. More detailed descriptions of the equilibrium cells are given elsewhere (Yoon, 1996). The cell contents are agitated by a magnetic spin bar with an external magnet immersed in a water bath. The temperature of the water bath containing a liquid mixture of ethylene glycol and water is controlled by an external circulating refrigerator/heater. The actual temperature in the cell can be measured by a K-type thermocouple with a digital thermometer (Cole-Parmer, 8535-26), with a resolution of ±0.1 K. A Heise gauge (CMM 104957, 0–600-bar range) with a maximum error of ±0.1 bar is used to measure the pressure in the system.

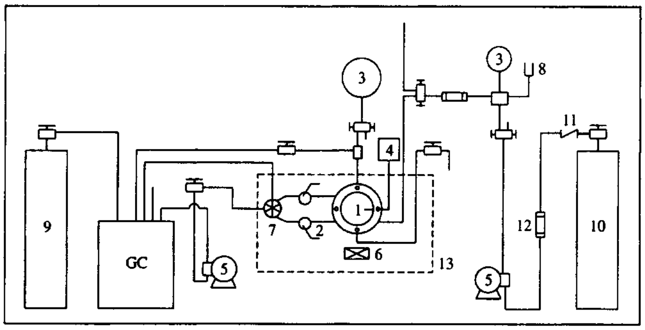

Figure 1. Experimental apparatus used in this work.

1, equilibrium cell; 2, on-off valve; 3, pressure gauge; 4, thermometer; 5, high-pressure pump; 6, magnet; 7, rotary valve; 8, rupture disc; 9, helium gas; 10, CO_2 gas; 11, check valve; 12, line filter; 13, water bath.

For the measurement of liquid compositions at a given equilibrium condition, a sampling valve (Rheodyne, 7413) with a sampling loop of about 0.5 μL was installed and connected to a gas chromatograph (Hewlett-Packard, 5890A) on-line through a high-pressure metering pump (Milton Roy, 2396-31). The gas chromatograph uses a thermal-conductivity detector (TCD) and a 6-ft × 1/8-in.-dia. (1.8-m × 3.2-mm-dia.) column packed with DEGS for analysis of the samples. The conditions of gas chromatography for sample analysis are a carrier-gas flow rate of 30 mL/min, a column temperature programmed from 50°C to 190°C, an injection temperature of 180°C, and a detector temperature of 200°C. Calibration for carbon dioxide gas was performed by using a vapor-sampling valve with a calibrated loop volume of 24.36 μL. After the equilibrium cell was pressurized with pure carbon dioxide at 320 K and a fixed pressure, the carbon dioxide in the sampling loop was transported to the gas chromatograph in order to show the response factors for moles vs. peak areas. The calibration curve constructed was fitted to a third-order polynomial since the response for carbon dioxide in the high-pressure region exhibited an aspect of concavity. Calibration curves for the liquid components were constructed by injecting known amounts of the pure component with the liquid sampling valve and a calibrated microsyringe. These curves were fitted to a linear polynomial for the phenol and a second-order polynomial for the water, which deviated a little from linearity. More detailed descriptions of the calibration procedure are given elsewhere (Yoon et al., 1993a,b).

Experimental procedure

The experiment begins by charging the evacuated equilibrium cell with approximately 30 cm^3 of the solution mixture. After the cell is pressurized to the desired pressure with carbon dioxide, the system was cooled to about 5 K below the anticipated clathrate-forming temperature. Once the temperature becomes constant, clathrate nucleation is induced by agitation of the magnetic spin bar with the immersed magnet in the water bath. When clathrates were formed and the pressure of the system reached a steady state, the cell temperature was then elevated very slowly to dissociate the clathrates formed to a condition where the clathrate phase coexisted with the liquid and vapor phases. The nucleation and dissociation steps were repeated at least two times in order to remove the hysteresis phenomenon. When the amount of minute crystals and the system temperature were kept constant at least for 8 h after the system pressure was stabilized, the pressure was considered as a clathrate dissociation pressure at the specified temperature.

In measuring the equilibrium compositions of the ternary carbon dioxide–water–phenol system, the experiment was carried out more carefully. First of all, it is important to properly prepare the liquid mixture of water and phenol in order to obtain the best conditions for the measurement of the liquid-phase compositions, which can be attained only if the amount of the clathrate phase is very small. At the initial nucleation step, the system temperature was maintained slightly below the anticipated clathrate-forming temperature. After the nucleation step ended, the system was slowly heated just above clathrate-dissociating temperature. During this process the clathrate phase gradually dissociated, and then dissolved in the liquid phase. In most of the current experiments, the increase in the total system pressure caused by both the dissociation of the clathrate phase and the slight elevation of the system temperature was found to be minute. When the increase in the system pressure was significant, the system pressure could be maintained by controlling a metering valve. At the end of the experiment, each liquid phase was analyzed at least twice by the gas chromatograph. During sampling, the recirculating pump should be maintained at minimum flow rate to prevent the samples in the loop from being pressurized by the pump stroke. The average of the individual compositions is reported as the equilibrium composition. The equilibrium compositions of the water-rich and phenol-rich liquid phases were generally reproducible to within a mole fraction of 0.0003 and 0.001, respectively.

The carbon dioxide with a minimum purity of 99.9 mol % used in this study was supplied by World Gas Co. The phenol supplied by Sigma-Aldrich Chemical Co. had a purity of 99 mol %. HPLC-grade distilled water supplied by Sigma-Aldrich Chemical Co. was used. These chemicals were used without further purification.

Results and Discussion

Clathrate phase equilibria: pressure – temperature behavior

The hydrate and phenol clathrate equilibrium data of the water–carbon dioxide, phenol–carbon dioxide, and water–phenol–carbon dioxide systems are presented in Table 1 and depicted in Figure 2. In order to establish the validity of the experimental apparatus and procedure the hydrate dissociation pressures of carbon dioxide measured in this work were compared with the data available in the literature (Deaton and Frost, 1946; Unruh and Katz, 1949; Adisasmito et al., 1991), and it was found that our results were in good agreement with the literature values within a maximum deviation of ± 1.5 bar. For the phenol–carbon dioxide clathrate equilibrium results, as seen in Figure 2, a dramatic increase of the dissociation pressures in the vicinity of 319.0 K was observed. It was also found that the experimental phenol-rich liquid–phenol clathrate–vapor (L_p–C–V) equilibrium line of the binary phenol–carbon dioxide system might be linearly extended to the phenol clathrate–solid phenol–vapor (C–S_p–V) equilibrium line (Nikitin and Koval'skaya, 1952). With this extrapolation, a quadruple point at which four individual phases of phenol-rich liquid, phenol clathrate, solid phenol, and vapor coexist in equilibrium might be expected to locate at 313.2 K and 19.0 bar as a first approximation. In general, the three-phase clathrate–solid–vapor equilibrium line is not perfectly linear over the corresponding pressure and temperature ranges, but slightly curved as can be seen in the methane–water system (Sloan, 1990). The curvature shape of the three-phase line changes with the participating host and guest molecules. The exact location of the quadruple point should therefore be determined from the experimental C–S–V and L–C–V equilibrium data, particularly near the quadruple point.

Early, van Leer and Paulaitis (1980) measured and reported the solubilities of phenol and chlorinated phenol in supercritical carbon dioxide at several temperature and pressure conditions by using a flow-type apparatus. Among their

Table 1. Equilibrium Hydrate and Phenol Clathrate Conditions for Water–Carbon Dioxide, Phenol–Carbon Dioxide, and Water–Phenol–Carbon Dioxide Systems

Phase Type*	T/K	P/bar
	Water – carbon dioxide system	
L_w-H-V	275.4	15.6
	277.8	21.0
	280.1	28.2
	282.4	38.9
L_w-L_c-H-V	283.3	45.2
	Phenol – carbon dioxide system	
L_p-C-V	314.2	21.0
	315.6	25.1
	316.7	30.3
	317.8	39.5
	318.8	51.6
	319.1	63.1
	319.2	73.1
	319.3	99.2
	Water – phenol – carbon dioxide system	
L_w-L_p-C-V	290.1	15.0
	291.9	20.8
	293.2	30.0
	293.6	42.5
L_w-H-C-V	279.4	30.0
L_w-L_p-L_c-C-V	293.7	57.2
L_w-L_c-C-V	285.3	47.2
	287.2	49.3
	289.1	51.5
	291.1	54.0
	293.2	56.5
L_w-L_p-L_c-V	295.1	59.0
	297.0	61.7
	299.0	64.4
	300.9	67.2
	302.8	70.0
	304.6	72.7
	307.0	76.6
	307.3*	77.2**

*See in text.
**Measured critical end point.

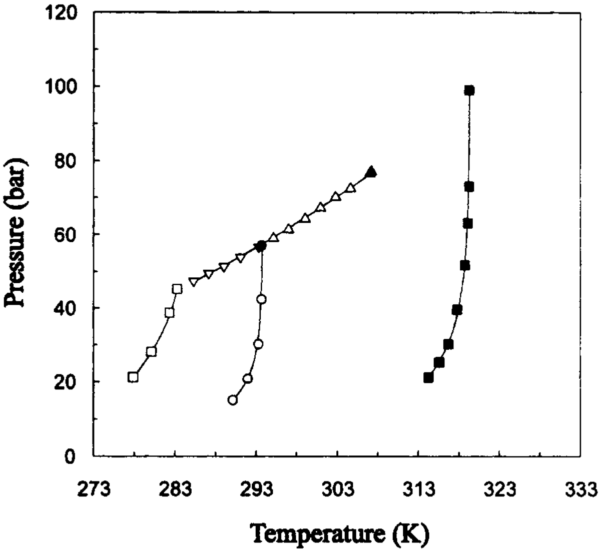

Figure 2. Clathrate phase equilibria for the water–carbon dioxide, phenol–carbon dioxide, and water–phenol–carbon dioxide systems.

□, L_w-H-V phase boundary for water–carbon dioxide; ■, L_p-C-V phase boundary for phenol–carbon dioxide; ○, L_w-L_p-C-V phase boundary for water–phenol–carbon dioxide; ▽, L_w-L_c-C-V phase boundary for water–phenol–carbon dioxide; △, L_w-L_p-L_c-V phase boundary for water–phenol–carbon dioxide; ▲, critical end point for water–phenol–carbon dioxide; ●, quintuple point for water–phenol–carbon dioxide.

results, it may be necessary to consider the solubility data of phenol in supercritical carbon dioxide for a pressure range of 79.29–249.43 bar at 309.2 K as the equilibrium solubilities of phenol clathrate rather than pure solid phenol, since the temperature and pressure conditions belong to a region in which the carbon dioxide cannot be in equilibrium with pure solid phenol, but rather with the phenol clathrates formed by a coupling with the guest carbon dioxide molecules. Before the experiment you should therefore check carefully to see whether or not the solution mixtures form clathrate within the specified temperature and pressure ranges.

For the water–phenol–carbon dioxide system, several interesting phenomena were observed. As shown in Figure 2, the four-phase, water-rich liquid–phenol-rich liquid–phenol clathrate–vapor (L_w-L_p-C-V), dissociation pressures were measured at several temperatures near 293.0 K. Like the phenol–carbon dioxide clathrate equilibrium results given earlier, the dramatic increase in the four-phase dissociation pressures was observed in the vicinity of 293.0 K. One of the most interesting results observed in this work is that a quintuple point at which the five phases of water-rich liquid, phenol-rich liquid, carbon dioxide-rich liquid, phenol clathrate, and vapor coexist in equilibrium was carefully measured and found to be 293.7 K and 57.2 bar. Although the existence of the quintuple points for the ternary system containing the clathrate (or hydrate) has been referred to by earlier workers (van der Waals and Platteeuw, 1959), this study is the first systematic approach for accurately measuring the exact location of quintuple points. For five phases to be in equilibrium at the quintuple point, five neighboring four-phase loci must intersect at the quintuple point. Three distinguishable four-phase loci identified as the water-rich liquid–phenol-rich liquid–phenol clathrate–vapor (L_w-L_p-C-V), water-rich liquid–carbon dioxide-rich liquid–phenol clathrate–vapor (L_w-L_c-C-V), and water-rich liquid–phenol-rich liquid–carbon dioxide-rich liquid–vapor (L_w-L_p-L_c-V), were measured. In particular, a critical end point at which critical opalescence occurs during the phase transition was also measured visually and found to be 307.3 K and 77.2 bar. The three-phase region appears again beyond this critical end point. The general trend for the remaining two four-phase loci specified as the water-rich liquid–phenol-rich liquid–carbon dioxide-rich liquid–phenol clathrate (L_w-L_p-L_c-C) and phenol-rich liquid–carbon dioxide-rich liquid–phenol clathrate–vapor (L_p-L_c-C-V) can be determined easily, but its detailed description will be presented in the final subsection of this part.

Isobaric clathrate phase equilibria: temperature-composition behavior

Isobaric three- and four-phase equilibrium results for the water–phenol–carbon dioxide system at 30.0 bar are summa-

Table 2. Isobaric Three- and Four-Phase Equilibrium Results for Water (1)–Phenol (2)–Carbon Dioxide (3) at 30.0 bar

		L_w-Phase			L_p-Phase		
T (K)	Phase Type*	x_1	x_2	x_3	x_1	x_2	x_3
279.4	L_w-H-C-V	0.9770	0.0060	0.0170			
279.7	L_w-C-V	0.9734	0.0061	0.0206			
282.0		0.9714	0.0066	0.0220			
284.0		0.9750	0.0072	0.0178			
285.6		0.9742	0.0076	0.0182			
287.9		0.9731	0.0085	0.0184			
289.8		0.9731	0.0091	0.0178			
278.2	L_w-H-C	0.9763	0.0060	0.0177			
293.2	L_w-L_p-C-V	0.9633	0.0134	0.0233	0.611	0.294	0.095
303.2	L_w-L_p-V	0.9672	0.0141	0.0187	0.638	0.283	0.079
313.2		0.9686	0.0154	0.0160	0.671	0.264	0.065
278.2	L_w-L_p-C	0.9814	0.0146	0.0040	0.627	0.361	0.012
279.4		0.9807	0.0148	0.0045	0.630	0.356	0.014
284.0		0.9791	0.0145	0.0064	0.633	0.345	0.022
289.8		0.9740	0.0143	0.0117	0.630	0.327	0.043
303.2	L_P-C-V				0.402	0.464	0.134

*See in text.

rized in Table 2. The isobaric ternary equilibrium compositions at 30.0 bar and temperatures of 278.2, 279.4, 284.0, 289.8, 293.2, and 303.2 K are plotted in the triangular diagrams, respectively, as shown in Figures 3–8. Carbon dioxide molecules can stably occupy the large cavities in the type I hydrate structure with a carbon dioxide/water mole ratio of 6/46 (Sloan, 1990). The composition of carbon dioxide in the hydrate phase thus becomes 0.115 in mole fraction. The small cavities in the type I hydrate structure may also be occupied to some extent by carbon dioxide molecules, even though the size of guest molecules is a little larger than that of the small cavities. The composition of carbon dioxide in the phenol clathrate phase has a value of 0.250 in mole fraction, since the carbon dioxide/phenol mole ratio is known as 4/12 in the unit crystal structure (Palin and Powell, 1945, 1947, 1948; Powell, 1948; von Stackelberg et al., 1958). In this case the small and larger cavities existing in the phenol clathrates were assumed to be fully occupied by carbon dioxide molecules. This ideal full-occupancy of the cavities in the clathrate (or hydrate) phase by guest molecules cannot, however, be attained in real systems. This concept of ideal occupancy was chosen in this study only to fix the reference state.

Figure 3 indicates that a tie-line representing the two-phase equilibrium compositions of the hydrate and phenol clathrate phases exists as a boundary to divide two individual three-phase regions of the hydrate–phenol clathrate–vapor (H–C–V) and water-rich liquid–hydrate–phenol clathrate (L_w–H–C). This tie-line can be considered to be an ideal equilibrium condition where all carbon dioxide, water, and phenol molecules are converted into the hydrates and phenol

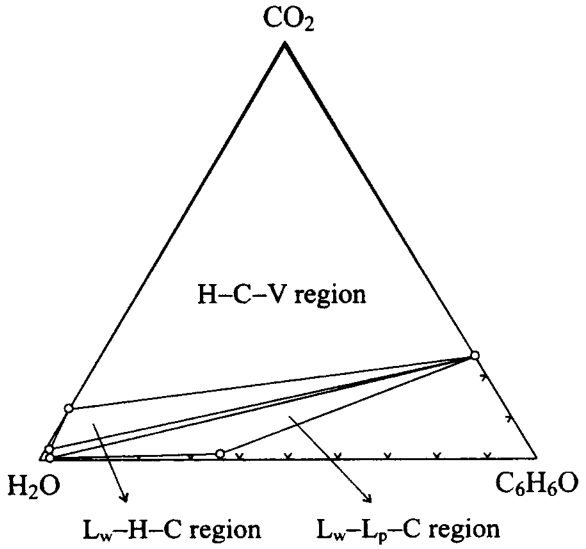

Figure 3. Phase equilibria of water–phenol–carbon dioxide at 278.2 K and 30 bar; ○, this work.

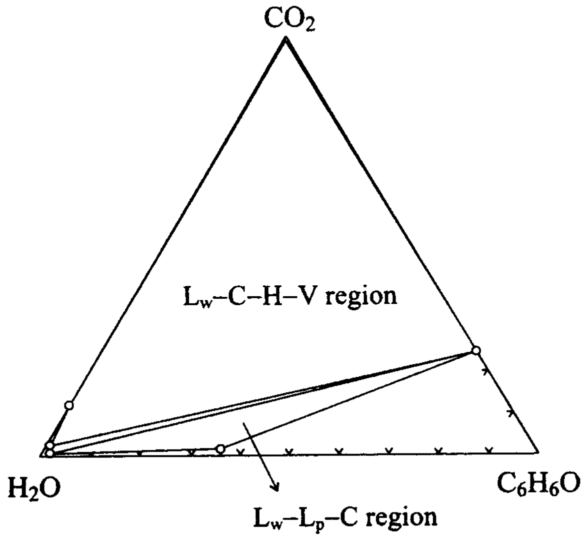

Figure 4. Phase equilibria of water–phenol–carbon dioxide at 279.4 K and 30 bar; ○, this work.

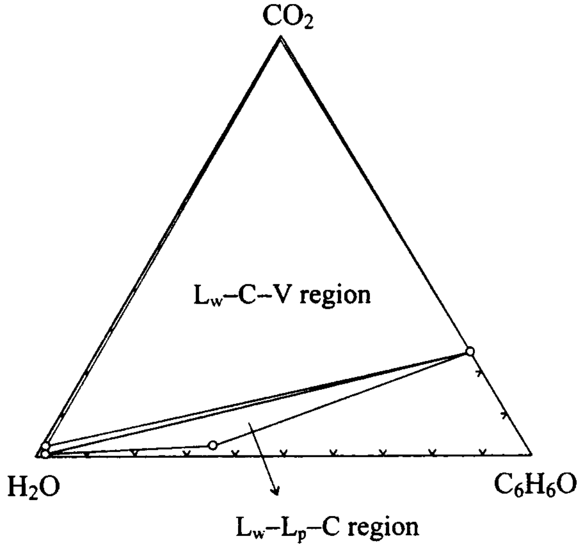

Figure 5. Phase equilibria of water-phenol-carbon dioxide at 284.0 K and 30 bar; ○, this work.

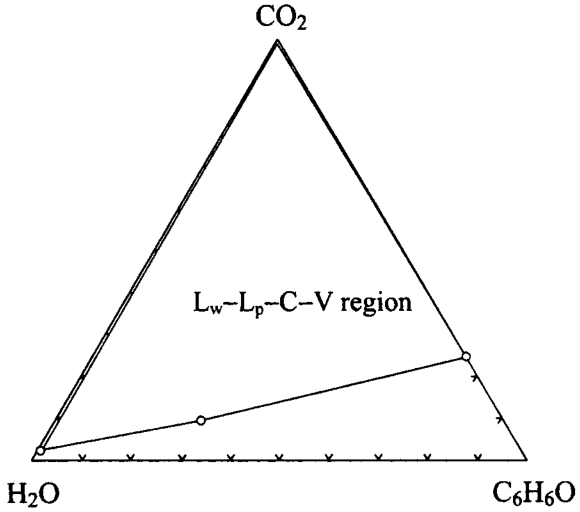

Figure 7. Phase equilibria of water-phenol-carbon dioxide at 293.2 K and 30 bar; ○, this work.

clathrates. The relative amounts of the hydrate and phenol clathrate are determined from the initial feed composition. The L_w–H–C and H–C–V equilibrium regions represented by two different triangles shapes can be obtained by controlling the feed compositions. The L_w–H–C region is generally formed when the relative amount of carbon dioxide in the ternary mixture becomes small. Since the vapor phase cannot exist in this region, the variable-volume cell was used to maintain the isobaric equilibrium condition of 30.0 bar. The formation of the water-rich liquid–phenol-rich liquid–phenol clathrate (L_w–L_p–C) region requires less carbon dioxide than does the L_w–H–C region. In this region only the phenol clathrate phase can coexist with two liquid phases. However, the formation of the H–C–V region requires a sufficient amount of carbon dioxide. In this region all the water and phenol molecules combine with the gas phase carbon dioxide molecules to make the hydrates and phenol clathrates that are in equilibrium with the carbon dioxide gas phase.

At temperatures greater than 279.4 K—the water-rich liquid–phenol clathrate–hydrate–vapor (L_w–C–H–V) equilibrium temperature at 30.0 bar—the hydrate phase does not coexist with the phenol clathrate phase in equilibrium, as shown in Figures 5–8. The hydrate phase can also exist just up to 280.3 K, which represents the dissociation temperature of the carbon dioxide hydrate in pure water at 30.0 bar. The three-phase equilibrium region of the water-rich liquid–hydrate–vapor (L_w–H–V) must therefore exist in the narrow temperature range of 279.4–280.3 K. The L_w–H–V equilibrium compositions are very hard to detect, since the phenol concentrations in the L_w phase were too small to be in the calibration range. However, the existence of the L_w–H–V three-phase region could be confirmed by several trials using visual observation of the variation of initial concentrations of the water–phenol mixture. It has been commonly known that

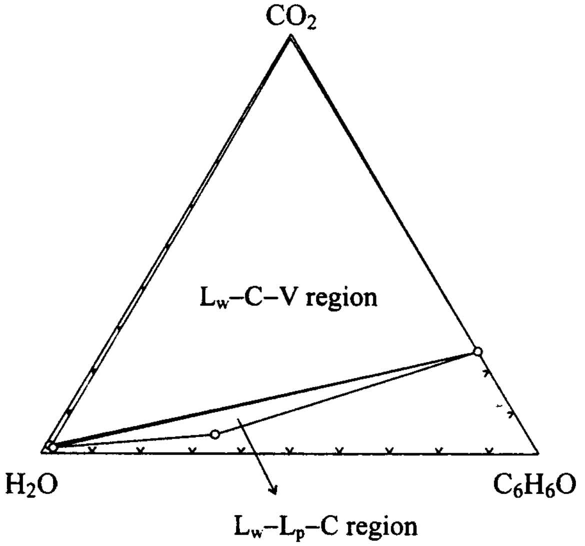

Figure 6. Phase equilibria of water-phenol-carbon dioxide at 289.8 K and 30 bar; ○, this work.

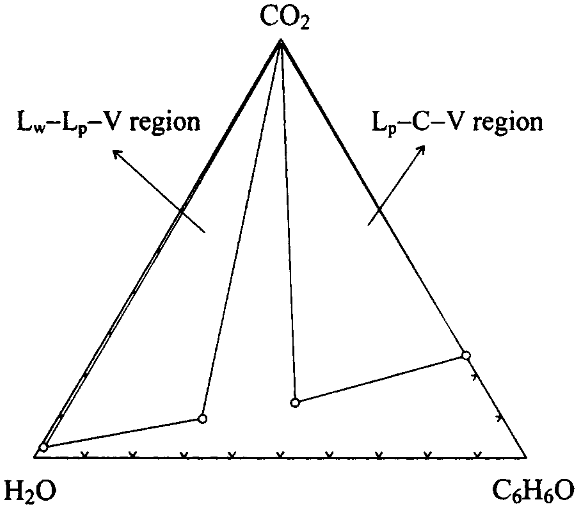

Figure 8. Phase equilibria of water-phenol-carbon dioxide at 303.2 K and 30 bar; ○, this work.

the hydrate dissociation pressures can be inhibited by the addition of a small amount of some organic compounds, such as methanol and ethylene glycol. It is quite reasonable, however, to suppose that, in the 279.4–280.3 K temperature range, the hydrate phase was inhibited by a small amount of phenol dissolved in the L_w phase. Consequently, the occurrence of the L_w–H–V three-phase region can be attributed to this inhibition effect of phenol in the hydrate phase. The minimum temperature at which the L_w–H–V three-phase region can exist has to be 279.4 K, and the hydrate phase was inhibited by a phenol concentration of 0.006 in mole fraction at this condition. The four-phase L_w–L_p–C–V equilibria of the ternary water–phenol–carbon dioxide system at 293.2 K and 30.0 bar are presented in Figure 7. The phenol clathrate phase coexists with the L_p phase as well as with both the L_w and vapor phases. It should be noted that the two three-phase regions appearing at 284.0 and 289.8 K merged at 293.2 K to generate one four-phase region. By this merging step, the carbon dioxide concentration in the L_p phase at 293.2 K increased about a factor of 2 more than that at 289.8 K. At a higher temperature than 293.2 K, the phenol clathrate phase equilibrated only with the vapor and L_p phases, but did not coexist with the L_w phase as shown in Figure 8.

Figure 9 shows the experimental phenol concentrations in the L_w and L_p phases on the basis of the carbon dioxide-free concentration at 30.0 bar and several of the temperatures that have been considered. The liquid–liquid equilibrium (LLE) data (Sorensen and Arlt, 1979) and stable solid–liquid equilibria (Rhodes and Markley, 1921) for the binary water–phenol system at atmospheric pressure are simultaneously depicted for reference in Figure 9. Monotectic and eutectic points exist, as can be seen in Figure 9, with the one located at $x_{\text{phenol}} = 0.325$ and $T = 293.2$ K, and the other at $x_{\text{phenol}} = 0.0061$ and $T = 279.4$ K. The phenol concentration in the L_w phase increased up to 0.0137 in mole fraction in the temperature interval between the monotectic and eutectic points. Further, it is interesting to note that the phenol concentration increased remarkably only in the very narrow temperature range of 289.8–293.2 K. At the monotectic temperature, 293.2 K, the phenol concentrations in the L_w and L_p phases of the ternary water–phenol–carbon dioxide system almost correspond to those of the binary water–phenol system. However, below 293.2 K the deviation of phenol concentrations in the L_w phase from both systems increases with decreasing temperature and has a maximum at the eutectic temperature, 279.4 K. At 279.4 K the phenol concentration in the L_w phase of the ternary system is diluted to a half the concentration of the binary system. On the other hand, above 293.2 K, the phenol concentration deviations of the L_w and L_p phases in both systems increase slightly with temperature. At temperatures just above the eutectic temperature, 279.4 K, the large amount of phenol dissolved in water can be separated with great success into the phenol clathrate (C) and water-rich liquid (L_w). The pure solid phenol is easily obtained by the spontaneous dissociation of the phenol clathrate under atmospheric conditions. Moreover, the phenol concentrations in the L_w phase can also be reduced to 0.006 in mole fraction. This result offers as big an advantage as the new potential separation method in that the phenol clathration overcomes the binary water–phenol LLE limitation and, in particular, makes it possible to produce pure solid phenol. In addition, Figure 9 shows the peculiar inhibition behavior of the dissociation temperature, which is quite different from the common inhibition effect explained in the literature. In the isobaric condition of 30.0 bar, the dissociation temperature of pure phenol clathrates coupled with carbon dioxide is 316.5 K. The dissociation temperature of phenol clathrates drops from 316.5 K to 293.2 K as the water mole fraction in the liquid phase is increased from 0% to 67.5%. As the liquid-phase mole fraction of water increases from 67.5% to 98.6%, the dissociation temperature of phenol clathrates remains constant at 293.2 K. This phenomenon occurs because the further addition of water beyond 67.5 mol % merely results in a change in the relative amount of the two L_w and L_p phases, the compositions of each phase remaining constant, and thus does not affect the dissociation temperature of phenol clathrates. When the water mole fraction is increased more than 98.6%, the L_p phase disappears, and only the L_w phase can coexist with phenol clathrates and vapor phases. In this range the dissociation temperature of phenol clathrates drops from 293.2 K to 279.4 K, the eutectic temperature, as the water mole fraction in liquid phase is increased from 98.6% to 99.4%. Consequently, this discontinuous inhibition effect of water on the phenol clathrate dissociation temperature is mainly due to the monotectic and eutectic behaviors of the ternary water–phenol–carbon dioxide mixture.

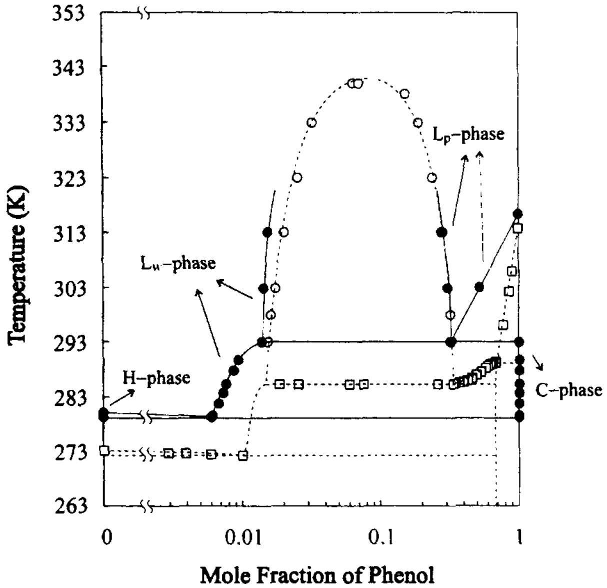

Figure 9. Isobaric temperature-composition diagram of water–phenol–carbon dioxide on the basis of carbon dioxide-free concentration at 30 bar.

●, this work; ○, liquid–liquid equilibrium data of water–phenol by Sørensen and Arlt (1979); □, solid–liquid equilibrium data of water–phenol by Rhodes and Markley (1921).

On the other hand, Figure 10 shows the three-phase L_w–L_p–C equilibrium behavior of the ternary water–phenol–carbon dioxide system. While all phases appearing in Figure 9 coexisted with the carbon dioxide vapor phase, no vapor phase coexisted at all with all phases appearing in Figure 10. In spite of the existence of the phenol clathrate phase, the compositions of the L_w and L_p phases for the ternary system almost coincide with those of the corresponding phases

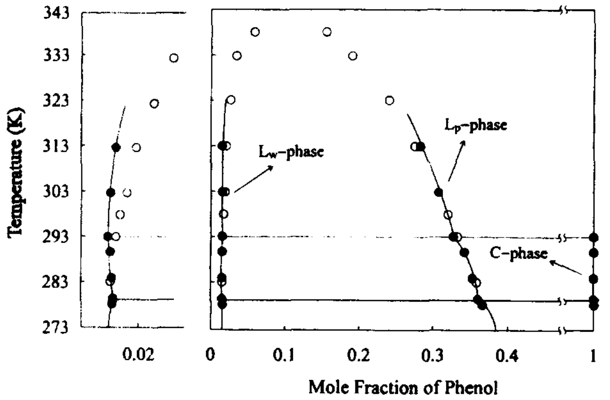

Figure 10. Isobaric temperature-composition diagram of water-phenol-carbon dioxide in three-phase equilibrium regions without vapor phase on the basis of carbon dioxide-free concentration at 30 bar.

●, this work; ○, liquid-liquid equilibrium data of water-phenol by Sørensen and Arlt (1979).

of the binary LLE system. It is therefore concluded that the phenol separation and purification process by using clathration is only successful if a sufficient amount of carbon dioxide can be supplied to the process units.

Complete pressure-temperature diagram

A complete pressure-temperature ($p-T$) diagram for the ternary phenol-water-carbon dioxide system is presented in Figure 11. The binary $p-T$ diagram is also included in this figure for comparison. An arbitrary scale was used, otherwise the location of all phase boundaries, including the quadruple and quintuple points, cannot be provided in one diagram. The phase boundary loci in the low-temperature and -pressure ranges were eliminated from Figure 11 to avoid too much complexity. The $p-T$ behavior of pure components was not plotted, since it is easy to understand. A plot of this type seems to resemble those of the ternary systems containing gas hydrates (von Stackelberg and Frühbuss, 1954; Carroll and Mather, 1991; Harmens and Sloan, 1990). It should be noted that previous works dealt with the ternary systems containing one host and two guest components, whereas this study was focused on the phase behavior of the ternary system containing two hosts and one guest. The overall $p-T$ behavior of the ternary system can be qualitatively described from the phase-equilibrium information of the binary water-carbon dioxide, phenol-carbon dioxide, and water-phenol systems. Eight individual phases of the water-rich liquid, phenol-rich liquid, carbon dioxide-rich liquid, hydrate, clathrate, ice, solid phenol, and vapor shown in Figure 11 were designated by L_w, L_p, L_c, H, C, I, S_p, and V, respectively. Five quintuple points that appeared in the ternary phenol-water-carbon dioxide system were also designated by Q_{n1}, Q_{n2}, Q_{n3}, Q_{n4}, and Q_{n5} in Figure 11.

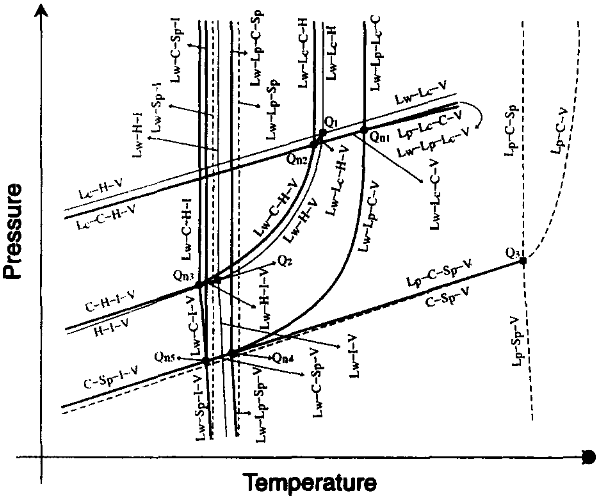

Figure 11. Complete pressure-temperature diagram for the water-phenol-carbon dioxide system.

The univariant equilibria of the binary water-carbon dioxide system have been indicated by thin lines; those of the binary phenol-carbon dioxide system by dashed lines; those of water-phenol system by dashed and dotted lines; and those of the ternary water-phenol-carbon dioxide system by heavy lines.

As previously explained, the quintuple point Q_{n1} at which five L_w, L_p, L_c, C, and V phases coexist was measured and found to be 293.7 K and 57.2 bar. The exact locations of the remaining four quintuple points are carefully presented in the following description. The main consideration used for the complete construction of the $p-T$ diagram is that the five four-phase boundary loci must meet at one quintuple point. Two four-phase L_p-L_c-C-V and L_w-L_p-L_c-C boundaries must therefore start from the Q_{n1}. The almost vertical L_w-L_p-L_c-C line serves as a temperature limitation under which the L_w phase is capable of coexisting with the phenol clathrate phase in equilibrium. The L_p-L_c-C-V line may lie below the L_w-L_p-L_c-V line because phenol is less volatile than water. This interpretation is consistent with our experimental result that the L_w-L_p-L_c-V line always lies below the three-phase L_w-L_c-V line of the binary water-carbon dioxide system. The five four-phase loci also branch at the second quintuple point, Q_{n2}. It can be easily anticipated that the four-phase L_w-L_c-H-V line, starting at the quadruple point Q_1 of the binary water-carbon dioxide system, only appears in the narrow temperature and pressure ranges. The ternary four-phase L_w-C-H-V line perhaps lies above the three-phase L_w-H-V dissociation line of the binary water-carbon dioxide system. As previously stated, this is mainly due to the fact that the carbon dioxide hydrate dissociation pressures are inhibited by small amounts of phenol dissolved in the L_w phase. In addition, the ternary four-phase L_w-L_c-C-V and L_c-C-H-V lines should be located below the binary three-phase L_w-L_c-V and L_c-H-V lines, respectively, because of the carbon dioxide vapor-pressure decrease resulting from adding phenol to the liquid phases.

Like Q_{n2}, the quintuple point Q_{n3} is located near the binary quadruple point Q_2. The ternary four-phase L_w-H-I-V line between Q_2 and Q_{n3} only covers the narrow temperature and pressure ranges. The ternary four-phase C-H-I-V line is found to be located a little above the binary three-phase H-I-V line. It is interesting to note here that the two quintuple points Q_{n4} and Q_{n5} result from the existence of a monotectic and an eutectic point, respectively, of the binary water-phenol system at atmospheric pressure. Stephen and

Stephen (1964) reported earlier that the eutectic point of the binary water–phenol system was determined at 272.0 K and the monotectic point at 274.9 K. As can be seen in Figure 11, the two three-phase L_w-S_p-I and $L_w-L_p-S_p$ lines of the binary water–phenol system represent the extension of these eutectic and monotectic points along the pressure increase. Therefore, the ternary four-phase $L_w-L_p-S_p-V$ and L_w-S_p-I-V lines must necessarily start from two quadruple points of the binary water–phenol system, which may be located at very low pressures. Then they terminate at Q_{n4} and Q_{n5}, respectively.

Conclusion

A new experimental apparatus was built to measure clathrate dissociation pressures and equilibrium compositions of liquid phases that coexist with the clathrate phase. The apparatus could even be applied to the measurement of the multiphase equilibria with no vapor phase by using a variable-volume equilibrium cell. The $p-T$ behavior of the binary phenol–carbon dioxide and the ternary water–phenol–carbon dioxide systems was measured over wide temperature and pressure ranges. For the binary phenol–carbon dioxide system, a dramatic increase in the dissociation pressures was observed in the vicinity of 319.0 K. Three four-phase equilibrium lines of the ternary water–phenol–carbon dioxide system were also measured. In particular, the quintuple point at which five individual phases can coexist in equilibrium was carefully measured and found to be 293.7 K and 57.2 bar. A possible application of the clathration process to the separation of phenol from aqueous solution was demonstrated by measuring the isobaric three- and four-phase equilibrium compositions of the ternary system at 30.0 bar and six temperatures ranging from 278.2 K to 303.2 K. The clathration process for separating phenol from the aqueous solution has considerable advantage in that it can be applied even to multiphase solutions over an entire range of phenol concentrations. A complete $p-T$ diagram of the binary and ternary systems was constructed qualitatively with the aid of both the experimentally determined phase boundaries and the related phase behavior information. In this diagram, the locations of the five quintuple points and four phase-equilibrium boundaries were also represented and their thermodynamic validity was thoroughly investigated. These $p-T$ diagram and isobaric phase-equilibrium results of the water–phenol–carbon dioxide system may provide a basis for the design of a phenol purification process by clathration. A kinetic study of phenol clathrate formation with a newly designed apparatus is in progress in our laboratory to confirm the process feasibility of the process as a new potential separation method. Our research related to clathration should be further extended to more complex systems containing multihost and multiguest components in order to understand the overall phase behavior.

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