Phase Equilibria of Carbon Dioxide Hydrate System in the Presence of Sucrose, Glucose, and Fructose

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The three-phase (H−L_w−V) equilibria of the carbon dioxide hydrate formation system in aqueous solutions containing sucrose, glucose, and fructose were experimentally determined at pressures ranging from 1.580 to 4.355 MPa and at temperatures between 273.6 and 281.7 K. The upper quadruple points (H−L_w−L_{CO_2}−V) were also measured at concentrations of 10, 20, and 30 mass % sucrose, glucose, and fructose. The addition of carbohydrates exhibited a similar inhibition effect as that observed for electrolytes and alcohols. A thermodynamic model predicting the three- and four-phase hydrate equilibria while accounting for the inhibition effect of carbohydrates was developed on the basis of the van der Waals−Platteeuw model and the Redlich−Kwong−Soave equation of state with a modified version of the Huron−Vidal mixing rule. The calculated results were found to be in good agreement with the experimental data.

Introduction

Clathrate hydrates (or gas hydrates) are a kind of inclusion compound and are formed by physically stable interactions between water and relatively small guest molecules entrapped in the cavities of a three-dimensional lattice-like structure built by water molecules. They are divided into three distinct structures, I, II, and H, which differ in cavity size and shape. Especially the H hydrate needs both large and small guest molecules to stabilize the structure. Some of the dissolved solutes in water such as alcohols, electrolytes, and water-soluble polymers change the energy of intermolecular interaction in the liquid phase and inhibit hydrate formation. The chemical potential of water molecules decreases because of hydrogen bond formation between water molecules and inhibitors, and therefore the equilibrium hydrate formation conditions are depressed by adding inhibitors. The inhibition of hydrate formation has been used to prevent the plugging problem during production and processing in the oil and gas industries. On the other hand, hydrate formation could be used for the development of seawater desalination, gas storage, and separation processes (Sloan, 1990; Englezos, 1993). In particular, aqueous organic solutions may be concentrated using hydrate formation; this might be adapted as a more economical and efficient method than freeze concentration because the hydrate easily forms at temperatures above the normal freezing point of water. Huang et al. (1965, 1966) reported the characteristics of CH_3Br and CCl_3F hydrates in a variety of aqueous solutions containing carbohydrates, proteins, and lipids. They also attempted to concentrate apple, orange, and tomato juices using hydrate formation and successfully removed approximately 80% of the water content.

The hydrate phase equilibria of the binary water + carbon dioxide system have been extensively investigated in detail (Larson, 1955; Unruh and Katz, 1949; Chun et al., 1996). Inhibition effects of alcohols, electrolytes, and polymers have been also reported in the carbon dioxide hydrate formation system (Ng and Robinson, 1985; Englezos and Hall, 1994; Dholabhai et al., 1993; Kang et al., 1998). On the other hand, the phase equilibria of hydrate-forming systems in aqueous carbohydrate solutions have been rarely investigated. Bond and Russell (1949) reported the hydrate-forming conditions of hydrogen sulfide in aqueous solutions containing 50 wt % dextrose and sucrose. Recently, Chun and Lee (1998) have investigated the phase equilibria of the R22 ($CHClF_2$) hydrate formation system containing sucrose, glucose, and lactic acid and developed a thermodynamic model for considering the inhibition behavior. Several predictive methods have been developed to compute the phase equilibria of hydrate-forming systems (van der Waals and Platteeuw, 1959; Parrish and Prausnitz, 1972; Holder et al., 1980). Anderson and Prausnitz (1986) suggested a simple approach for calculating the inhibition effect of methanol on hydrate formation. Englezos (1992) and Englezos and Hall (1994) also proposed predictive methods to compute the hydrate-forming conditions in aqueous electrolyte and polymer solutions.

The objective of this work was to test the applicability of hydrate phenomenon to the concentration of dilute aqueous carbohydrate solutions. As the first attempt of this research, three-phase (hydrate−aqueous solution−vapor) equilibria for the carbon dioxide hydrate-forming system in the presence of three carbohydrates (sucrose, glucose, and fructose) were measured together with the upper quadruple points, at which four phases (H−L_w−L_{CO_2}−V) coexist.

Experimental Section

Materials. The carbon dioxide used for the present study was supplied by World Gas Co. and had a stated purity of 99.9 mol %. The water was supplied from Sigma-Aldrich Chemical Co. with a purity of 99.1 mol %. Sucrose and D-(+)-glucose with a minimum purity of 99.5 mol % and D-(−)-fructose with 99 mol % purity were supplied by Sigma Chemical Co. All chemicals were used without further purification.

Apparatus. A schematic diagram of the experimental apparatus used in this work was presented in a previous

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study (Chun et al., 1996). The apparatus was constructed to measure the clathrate hydrate dissociation pressures through the visual observation of phase transitions. The equilibrium cell was made of type 316 stainless steel and had an internal volume of about 50 cm^3. Two sight glasses equipped at the front and back of the cell allowed the visual observation of phase transitions that occurred inside the equilibrium cell. The cell was immersed in a water bath, and its contents were vigorously stirred by a magnetic spin bar with an external magnet. The temperature of the water bath was controlled by an externally circulating refrigerator/heater. The temperature in the cell was measured by a K-type thermocouple with a digital temperature readout (Cole-Parmer, 8535-26) having a resolution of ±0.1 K. This thermometer was calibrated with an ASTM 63C mercury thermometer ranging from −8 to 32 °C with a resolution of ±0.1 °C. A Heise gauge (CMM 44307) with a range of 0 to 20 MPa with a maximum error of ±0.01 MPa was used to measure the relatively high dissociation pressures. A high-pressure metering pump (Milton Roy, 2396-31) was used to pressurize the system up to pressures greater than the pressure in the gas cylinder.

Procedures. The experiment was begun by charging the equilibrium cell with about 20 cm^3 of an aqueous solution containing sucrose, glucose, or fructose. The air that may enter the system during the charging process was eliminated from the cell by flushing with carbon dioxide gas several times. After the cell was pressurized to a desired pressure with carbon dioxide, the system was then cooled to about 5 K or more below the anticipated clathrate-forming temperature. Once the system temperature became constant, clathrate hydrate nucleation was induced by agitating the magnetic spin bar. When the whole content of water was transformed into the clathrate hydrates and the system pressure reached a steady-state condition, the cell temperature increased at a rate of about 1 K·h^{-1} until the clathrate phase was in coexistence with the liquid and vapor phases. The system temperature was then slowly increased at a rate of 0.2 K·h^{-1}, and the system was maintained for a sufficient time to stabilize the cell pressure. The nucleation and dissociation steps were repeated at least two times in order to reduce the hysteresis phenomenon. When it was determined by visual observation that a very small amount of crystals existed without significantly increasing or decreasing its size and the system temperature was maintained constant for at least 8 h after the system pressure stabilized, this constant pressure was considered to be the equilibrium pressure of the $H-L_w-V$ phase region at the corresponding temperature.

The upper quadruple point ($H-L_w-L_{CO_2}-V$) measurement was initiated by charging CO_2 to the state at which three phases, aqueous solution, liquid CO_2, and vapor, coexisted. Because the liquid CO_2 was immiscible with water and the density of liquid CO_2 was lower than that of water, the liquid CO_2 layer was located just above the aqueous solution phase. The system temperature was lowered to transform water completely into hydrates and was kept constant until the system pressure became stable. Then, the temperature was slowly increased to dissociate hydrates into aqueous solution and liquid CO_2 phases. Until the amount of hydrate particles remained very small, the temperature was increased slowly. When four phases were clearly observed, the temperature and pressure at that point were determined to be the upper quadruple point.

Table 1. Hydrate Phase Equilibrium Data of the Systems Containing Three Different Carbohydrates

system	concn	T/K	P/MPa
water + CO_2 + sucrose	20 mass % sucrose	281.6[a]	4.34[a]
		280.5	3.58
		279.3	3.03
		278.1	2.53
		276.4	2.06
		274.4	1.63
	30 mass % sucrose	280.6[a]	4.25[a]
		279.7	3.63
		279.5	3.03
		277.3	2.58
		275.6	2.08
		274.0	1.73
water + CO_2 + glucose	10 mass % glucose	281.7[a]	4.36[a]
		280.8	3.73
		279.6	3.10
		278.2	2.58
		275.7	1.87
		274.3	1.58
	20 mass % glucose	280.6[a]	4.25[a]
		279.6	3.55
		278.6	3.05
		277.1	2.52
		275.2	1.98
		274.0	1.73
	30 mass % glucose	278.8[a]	4.05
		278.0	3.57
		277.0	3.07
		276.1	2.71
		275.3	2.43
		274.1	2.08
water + CO_2 + fructose	20 mass % fructose	280.6[a]	4.24[a]
		279.3	3.46
		278.4	3.00
		276.6	2.36
		274.4	1.80
	30 mass % fructose	278.9[a]	4.07[a]
		277.3	3.11
		276.5	2.73
		274.9	2.21
		273.6	1.88

[a] Upper quadruple point ($H-L_w-L_{CO_2}-V$).

Results and Discussion

The phase equilibria of carbon dioxide hydrate mixtures which were determined in aqueous sucrose, glucose, and fructose solutions having 10, 20, and 30 carbohydrate mass % are tabulated in Table 1. Three phase equilibrium lines ($H-L_w-V$) and quadruple points ($H-L_w-L_{CO_2}-V$) were presented in Figures 1−3 along with the corresponding compositions. The hydrate equilibria of the binary carbon dioxide and water system (Chun et al., 1996) are also given for comparison. Undoubtedly, the addition of carbohydrates showed the inhibition effect on the $H-L_w-V$ three-phase equilibrium conditions of the carbon dioxide hydrate system.

The equilibrium criteria of the hydrate-forming system are based on the equality of the fugacity of water and carbon dioxide in all phases which coexist simultaneously

$$\hat{f}_i^{H} = \hat{f}_i^{L} = \hat{f}_i^{V} \; (=f_w^{I}) \qquad (1)$$

where H stands for the hydrate phase such as structure I or II hydrates, L for the liquid phase such as the water-rich or guest-rich liquid phases, V for the vapor phase, and I for the ice phase. However, it should be noted that carbohydrates cannot participate in the formation of hydrates and therefore their hydrate phases do not exist. The fugacities of a specific component in the vapor and liquid phases were calculated using the Redlich−Kwong−

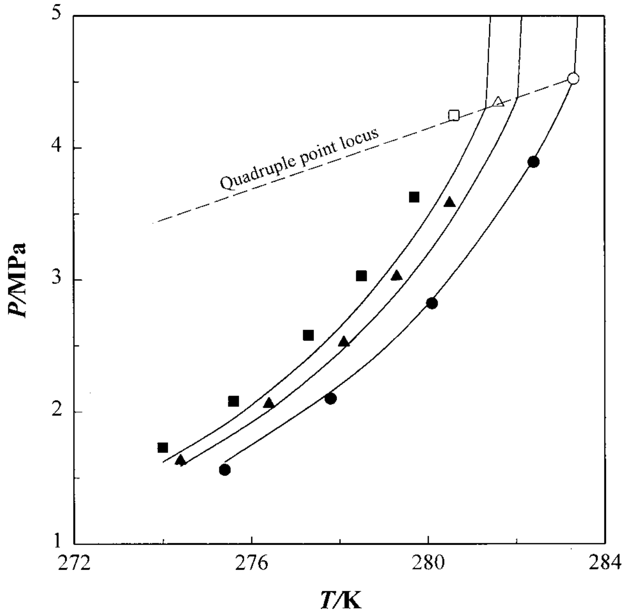

Figure 1. Hydrate phase equilibria of the ternary water + sucrose + carbon dioxide system: (●) 0 mass % sucrose; (▲) 20 mass % sucrose; (■) 30 mass % sucrose; (empty symbols) upper quadruple points; (—) calculated results.

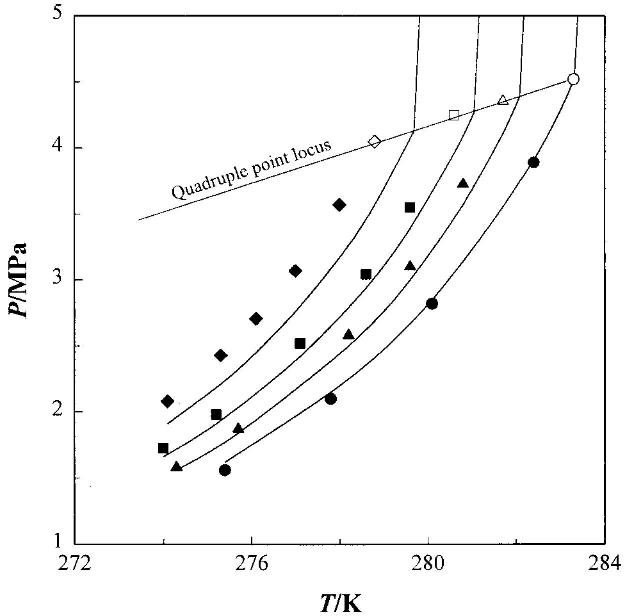

Figure 2. Hydrate phase equilibria of the ternary water + glucose + carbon dioxide system: (●) 0 mass % glucose; (▲) 10 mass % glucose; (■) 20 mass % glucose; (◆) 30 mass % glucose; (empty symbols) upper quadruple points; (—) calculated results.

Soave equation of state (Soave, 1972) incorporated with a modified version of the Huron−Vidal mixing rule (Michelsen, 1990). The UNIFAC group-contribution model (Fredenslund and Sørensen, 1993) was used as the excess Gibbs energy model of the Huron−Vidal mixing rule. The fugacity of water in the hydrate phase, $\hat{f}_w^H$ based on the van der Waals and Platteeuw model (1959) is given by the equation

$$\hat{f}_w^H = f_w^{MT}\exp\left(\frac{-\Delta\mu_w^{MT-H}}{RT}\right) = f_w^{MT}\exp(-\sum_m v_m \ln(1 + \sum_j C_{mj}\hat{f}_i^V)) \quad (2)$$

where v_m is the number of cavities of type m per water

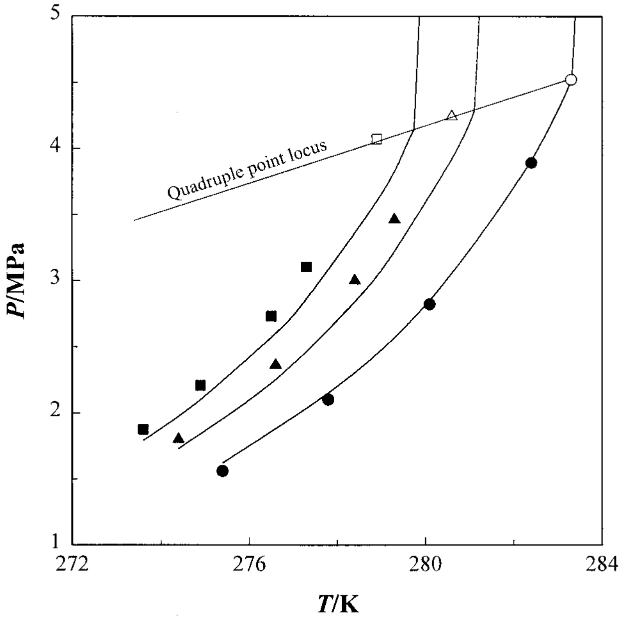

Figure 3. Hydrate phase equilibria of the ternary water + fructose + carbon dioxide system: (●) 0 mass % fructose; (▲) 20 mass % fructose; (■) 30 mass % fructose; (empty symbols) upper quadruple points; (—) calculated results.

molecule in the hydrate phase, C_{mj} is the Langmuir constant of component j on cavity type m, and $\hat{f}_j^V$ is the fugacity of component j in the vapor phase with which the hydrate phase is in equilibrium. The Langmuir constant basically considers the interaction between guest and water molecules in the hydrate cavities. The Kihara potential function has been adopted in eq 2, since this potential was reported to give better results than the Lennard-Jones potential for calculating the hydrate dissociation pressures (McKoy and Sinanoglu, 1963). The fugacity of water in the empty hydrate lattice, f_w^{MT}, above the melting point is given by

$$f_w^{MT} = f_w^L \exp\left(\frac{\Delta\mu_w^{MT-L}}{RT}\right) \quad (3)$$

where the chemical potential difference of water between the empty hydrate and liquid phases, $\Delta\mu_w^{MT-L}$ was calculated using the method proposed by Holder et al. (1980).

$$\frac{\Delta\mu_w^{MT-L}}{RT} = \frac{\Delta\mu_w^0}{RT} - \int_{T_0}^{T}\frac{\Delta h_w^{MT-I} + \Delta h_w^{fus}}{RT^2}\,dT + \int_0^P\frac{\Delta v_w^{MT-I} + \Delta v_w^{fus}}{RT}\,dP \quad (4)$$

The predictive model of carbohydrate-bearing systems is based on the assumption that carbohydrates are present only in the aqueous liquid phase but not in the vapor and hydrate phases. The calculation procedure of the predictive model is composed of two consecutive steps. According to the van der Waals and Platteeuw model (1959), the fugacities of guest components in the vapor phase are in equilibrium with that in the hydrate phase. Therefore, the equilibrium criteria of guest components between hydrate and vapor phases are automatically satisfied. The equality between the fugacity of water in the hydrate and that in the liquid phase was further checked to yield a final

Table 2. Calculated Upper Quadruple Points of Carbohydrate-Containing Solutions

system	concn	T/K	P/MPa
water + CO_2 + sucrose	20 mass % sucrose	282.04	4.38
	30 mass % sucrose	281.32	4.30
water + CO_2 + glucose	10 mass % glucose	282.08	4.39
	20 mass % glucose	281.05	4.27
	30 mass % glucose	279.69	4.15
water + CO_2 + fructose	20 mass % fructose	281.11	4.28
	30 mass % fructose	279.74	4.14

equilibrium condition for the hydrate-forming system given below.

$$\sum_m \nu_m \ln(1 + \sum_j C_{mj}\hat{f}_j^{\mathrm{V}}) = \frac{\Delta\mu_{\mathrm{w}}^{\mathrm{MT-L}}}{RT} - \ln a_{\mathrm{w}} \qquad (5)$$

To consider the inhibition effect of carbohydrates on the equilibrium hydrate-forming conditions, the activity of water in eq 5 was assumed to be the product of the water mole fraction in the binary CO_2 + water system and the activity of water in the binary carbohydrate + water system, adopting the simple and empirical method proposed by Englezos and Hall (1994).

Calculated results obtained from the predictive model are represented in Figures 1−3 along with experimental data. The quadruple points (Table 2) were determined from an intersection between the computed $H-L_w-V$ and $H-L_w-L_{CO_2}$ equilibrium lines. The inhibition effects of carbohydrates on the carbon dioxide hydrate formation conditions increased as the concentration of carbohydrates in aqueous solution increased. The deviation between experimental and computed results also increased as the carbohydrate concentration increased. In the water + carbon dioxide + sucrose system, the absolute average deviations (AADs) between experimental data and predictions were 3.0 and 6.9% in 20 and 30 mass % sucrose solutions, respectively. The hydrate formation conditions of the water + CO_2 + glucose system could be predicted with an AAD of 2.7, 3.8, and 9.6% in 10, 20, and 30 mass % glucose solutions, respectively. The AADs in 20 and 30 mass % fructose solutions were 5.2 and 5.3% for the water + CO_2 + fructose system, respectively.

Conclusions

Experimental three-phase $(H-L_w-V)$ equilibrium data of the carbon dioxide hydrate formation system containing carbohydrates were determined in order to clarify the inhibition effect on hydrate formation. At the same mass concentrations, the inhibition effects of glucose and fructose showed similar trends and the inhibition strength of sucrose appeared to be the least among those of the three carbohydrates. The upper quadruple points $(H-L_w-L_{CO_2}-V)$ were also determined experimentally and compared with the calculated results. Both were in good agreement particularly at the low carbohydrate concentration range, but with a little deviation at the higher concentration.

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