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Phase Equilibria of R22 ($CHClF_2$) Hydrate Systems in the Presence of NaCl, KCl, and $MgCl_2$

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The three-phase (hydrate−aqueous liquid−vapor) equilibria of the R22 ($CHClF_2$ = chlorodifluoromethane) hydrate forming systems in aqueous solutions containing NaCl, KCl, and $MgCl_2$ were measured at pressures ranging from 0.140 to 0.790 MPa, temperatures between 273.9 and 287.8 K, and several compositions of each electrolyte. The upper quadruple points (hydrate−liquid R22−aqueous liquid−vapor) were also measured at each electrolyte concentration. The addition of electrolytes to the aqueous solutions caused inhibition of the hydrate formation. A thermodynamic model that predicts the three-phase hydrate equilibria was developed. The inhibiting effect of electrolytes was accounted for using a Pitzer model. A van der Waals and Platteeuw model and Redlich−Kwong−Soave equation of state with a modified Huron−Vidal mixing rule were used. The calculated results were found to be in good agreement with the experimental data.

Introduction

A clathrate hydrate (or gas hydrate) is an inclusion compound which is formed by repulsive interactions between water and relatively small guest molecules entrapped in the cavities of a three-dimensional lattice-like structure consisting of hydrogen-bonded water molecules. Those nonstoichiometric crystalline compounds can occur in the form of three distinct structures, I, II, and H, which contain differently sized and shaped cavities. Structure I and II hydrates consist of two types of cavities and structure H hydrate consists of three types of cavities. Especially, the structure H hydrate needs both large and small guest molecules to stabilize the structure. The R22 ($CHClF_2$ = chlorodifluoromethane) hydrate is known to form the structure I hydrate. The R22 molecules are found to be relatively too large to fit into the small cavities and, therefore, they occupy only large cavities of the structure I to the extent that the hydrate particles are stabilized. The dissolved solutes of alcohols and electrolytes in water greatly change the energy of intermolecular interaction in the liquid phase and then cause the inhibition of the hydrate formation. The inhibition of hydrate formation has been applied to prevent plugging problems during production and processing in the oil and gas industries. On the other hand, hydrates could be used for the development of seawater desalination, gas storage, and separation processes.[1−3]

Although hydrate-forming conditions of various hydrocarbons, carbon dioxide, etc., in pure liquid water have been measured comprehensively, only a few investigators have reported the hydrate phase equilibrium behavior for the binary R22 + water system.[4,5] Furthermore, the effect of inhibitors on the formation conditions of the R22 hydrate-forming system has not been reported yet. Recently, Chun and Lee have studied the phase equilibria of the R22 hydrate formation system containing sucrose, glucose, and lactic acid and developed the appropriate thermodynamic model considering the inhibition behavior.[6] The equilibrium hydrate formation conditions of various hydrate-forming gases in water and in aqueous solutions containing several inhibitors have also been predicted by several methods.[7−9] The objective of this work is then to obtain the three-phase (hydrate−aqueous solution−vapor, $H-L_w-V$) equilibria of R22 hydrate-forming systems in the presence of three electrolytes of NaCl, KCl, and $MgCl_2$ together with the upper quadruple points, at which four phases (hydrate−liquid R22−aqueous liquid−vapor, $H-L_{R22}-L_w-V$) coexist.

Experimental Section

Materials. The R22 gas used for the present study was supplied by Ulsan Chemical Co. and had a stated purity of 99.5 mol %. The HPLC-grade water was supplied from Sigma−Aldrich Chemical Co. with a purity of 99.1 mol %. NaCl and KCl with a minimum purity of 99.0 mol % of certified ACS grade were supplied by Aldrich Chemical Co., and $MgCl_2$ having 98.0 mol % purity of certified ACS grade was supplied by Sigma Chemical Co. All chemicals were used without further purification.

Apparatus. A schematic diagram of the experimental apparatus used in this work is given in a previous paper.[5] The apparatus was constructed to measure the clathrate hydrate dissociation pressures through the visual observation of phase transitions. The equilibrium cell was made of 316 stainless steel and had an internal volume of about

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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 contents were vigorously stirred by a magnetic spin bar with an external magnet immersed in a water bath. 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 thermometer (Cole-Parmer, 8535-26) with a resolution of ±0.1 K. This thermometer was calibrated using a ASTM 63C mercury thermometer ranging from −8 to +32 °C with a resolution of ±0.1 °C. A pressure gauge (Ujin Co., W1081) having a pressure range of 0−1.0 MPa was used below 0.9 MPa with a precision of ±0.01 MPa. A high-pressure metering pump (Milton Roy, 2396-31) was used to pressurize the system up to the pressure region that could not be pressurized by the gas cylinder itself.

Procedure. The experiment was begun by charging the equilibrium cell with about 20 cm^3 of the aqueous solutions containing NaCl, KCl, and $MgCl_2$. The air that may enter into the system during the charging process was eliminated from the cell by flushing with R22 gas several times. After the cell was pressurized to a desired pressure with R22 gas, 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 a very small amount of crystals existed, by visual observation, 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 as the equilibrium pressure of the $H-L_w-V$ phase region at the corresponding temperature.

The upper quadruple point ($H-L_{R22}-L_w-V$) measurement was initiated by charging R22 to the state at which three phases of aqueous solution, liquid R22, and vapor coexisted. Because liquid R22 was immiscible with water and the density of liquid R22 was lower than that of water, the liquid R22 layer was located just above the aqueous solution phase. The system temperature was lowered to form the immiscible solutions completely into hydrates and kept constant until the system pressure became stable. Then, the temperature slowly increased to dissociate hydrates into aqueous solution and liquid R22 phases. Until the amount of hydrate particles remained very small, the temperature increased more slowly. When four phases were clearly observed, the temperature and pressure at that point were determined as the upper quadruple point.

Results and Discussion

The phase equilibrium data of three ternary water + R22 + NaCl, water + R22 + KCl, and water + R22 + $MgCl_2$ systems in the hydrate-forming regions are obtained experimentally and tabulated in Table 1 with the upper quadruple points measured at three different concentrations of 5, 10, and 15 mass % in aqueous solutions. Three-phase equilibrium lines ($H-L_w-V$) and upper quadruple points ($H-L_{R22}-L_w-V$) are plotted in Figures 1−3 along with the corresponding compositions. The hydrate equilibria of the binary R22 and water system[5] are also given for comparison. The inhibition effect on the $H-L_w-V$ equilibrium conditions of the R22 hydrate-forming system appeared at all electrolyte concentrations. In 5 mass % concentration of each electrolyte, three systems show very similar equilibrium behavior, but as the composition of electrolytes increases, the system containing $MgCl_2$ has more inhibition effect than the other two systems. The inhibition caused by NaCl appeared to be greater than that by KCl when the R22 hydrate was formed.

Table 1. Equilibrium Hydrate Formation Conditions for Three Water + R22 + NaCl, KCl, and $MgCl_2$ Systems

system	concentration	*T*/K	*p*/MPa
water + R22 + NaCl	5 mass % NaCl	287.3[a]	0.775[a]
		284.8	0.544
		282.9	0.430
		280.5	0.320
		278.3	0.226
		276.2	0.167
	10 mass % NaCl	284.0[a]	0.705[a]
		282.2	0.533
		281.1	0.450
		279.5	0.363
		277.6	0.285
		275.4	0.209
	15 mass % NaCl	280.1[a]	0.618[a]
		278.3	0.484
		276.5	0.379
		275.0	0.311
		274.0	0.273
water + R22 + KCl	5 mass % KCl	287.8[a]	0.790[a]
		285.3	0.549
		283.1	0.412
		280.9	0.305
		277.9	0.203
		275.3	0.140
	10 mass % KCl	285.6[a]	0.734[a]
		284.6	0.628
		283.2	0.514
		281.1	0.387
		278.2	0.257
		275.8	0.183
	15 mass % KCl	283.2[a]	0.686[a]
		282.2	0.566
		280.3	0.439
		277.6	0.297
		275.1	0.199
water + R22 + NaCl	5 mass % NaCl	287.4[a]	0.783[a]
		286.5	0.676
		284.6	0.527
		282.2	0.392
		280.9	0.321
		277.9	0.215
		275.8	0.161
	10 mass % $MgCl_2$	283.3[a]	0.688[a]
		281.1	0.511
		279.2	0.402
		277.5	0.311
		274.7	0.207
	15 mass % $MgCl_2$	278.4[a]	0.591[a]
		277.1	0.516
		275.9	0.426
		273.9	0.319

[a] Upper quadruple point (hydrate−liquid R22−aqueous liquid−vapor).

The phase equilibrium calculation is conducted to examine the equilibrium criteria of the hydrate-forming system by adopting the fugacity equality of a component in all coexisting three and four phases. For the equilibria of the hydrate-forming systems, the equilibrium criteria become

$$\hat{f}_i^{H} = \hat{f}_i^{L_{R22}} = \hat{f}_i^{L_w} = \hat{f}_i^{V} \qquad (1)$$

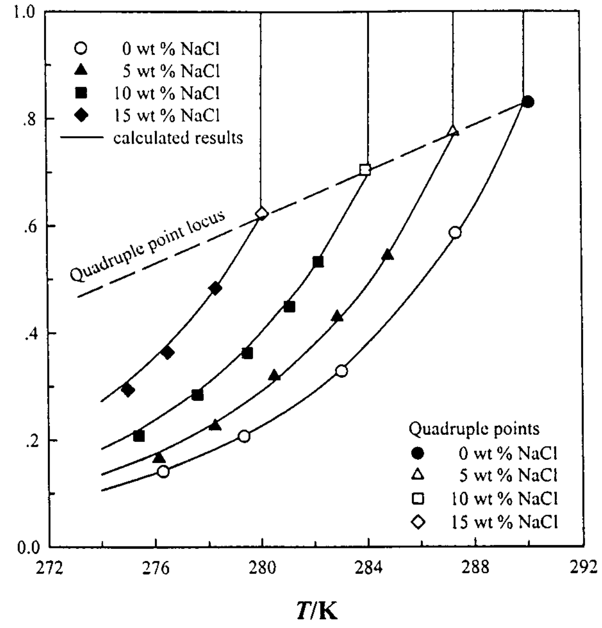

Figure 1. Experimental and predicted hydrate formation pressures of the ternary water + R22 + NaCl system.

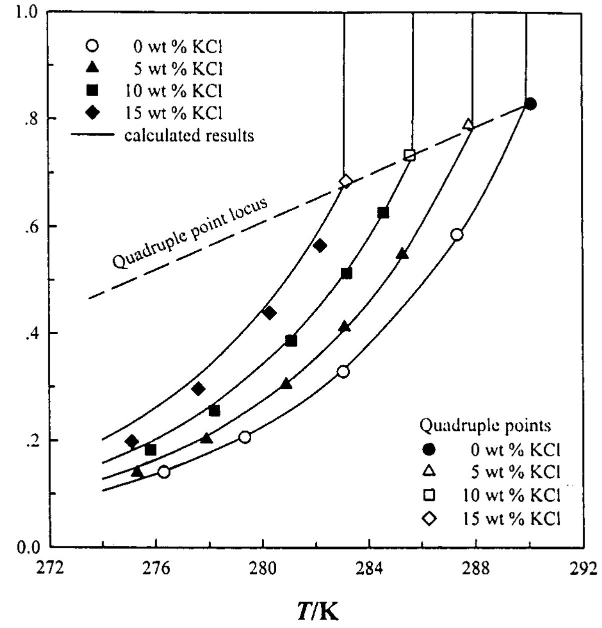

Figure 2. Experimental and predicted hydrate formation pressures of the ternary water + R22 + KCl system.

The fugacities of a specific component in the vapor and liquid phases are calculated using the Redlich−Kwong−Soave equation of state[10] incorporated with a modified version of the Huron−Vidal mixing rule.[11] The UNIFAC group-contribution model is used as the excess Gibbs energy model of the Huron−Vidal mixing rule.[12] The interaction parameters between CClF and H_2O groups were given by Chun and Lee.[6] The fugacity of water in the hydrate phase, $\hat{f}_w^H$, based on the van der Waals and Platteeuw model[13] is given by the following equation:

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

where ν_m is the number of cavities of type m per water molecule in the hydrate phase, C_{mj} the Langmuir constant of component j on cavity type m, and $\hat{f}_j^V$ the fugacity of component j in the vapor phase with which the hydrate phase is in equilibrium. The Langmuir constant considers the interaction between guest and water molecules in the hydrate cavities. The Kihara potential function has been adopted in eq 2 because this potential was reported to give better results than those of the Lennard-Jones potential for calculating the hydrate dissociation pressures.[14] The fugacity of water in the empty hydrate lattice, f_w^{MT}, above the melting point is given by

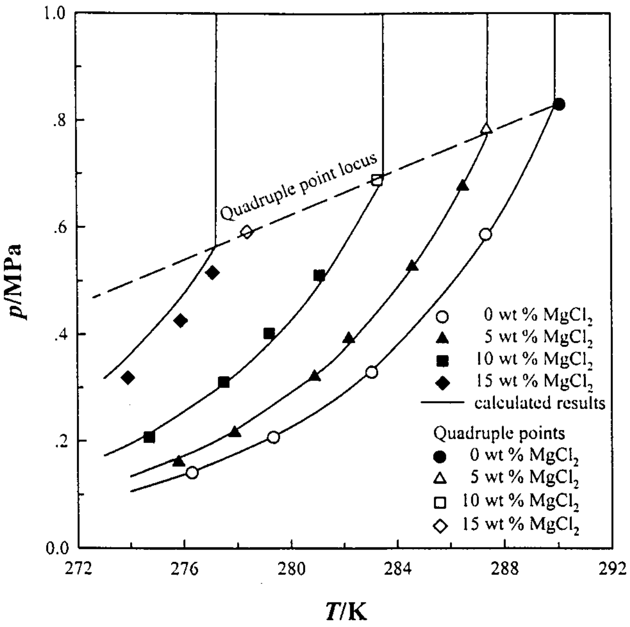

Figure 3. Experimental and predicted hydrate formation pressures of the ternary water + R22 + $MgCl_2$ system.

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

where the chemical potential difference of water between the empty hydrate and liquid phases, $\Delta\mu_w^{MT-L}$, is calculated using the method proposed by Holder et al.[15]

$$\frac{\Delta\mu_w^{MT-L}}{RT} = \frac{\Delta\mu_w^0}{RT} - \int_{T_0}^{T} \frac{\Delta h_w^{MT-1} + \Delta h_w^{fus}}{RT^2}\, dT + \int_0^P \frac{\Delta v_w^{MT-1} + \Delta v_w^{fus}}{RT}\, dP \qquad (4)$$

The predictive model of electrolyte-bearing systems is based on the assumption that no ions are present in the vapor phase and salts are entirely excluded from the hydrate phase. Englezos and Bishnoi[16] and Bakker et al.[17] introduced the model of Pitzer[18] to calculate the activity of water in aqueous solutions from the osmotic coefficient at various temperature and pressure conditions. This method has been chosen for the calculation of gas solubilities in the aqueous electrolyte solution in this work. In the presence of electrolytes, the solubility decreases because the interactions between the water molecules and the ions are stronger than the interactions between the water and the dissolved gas (salting out). Because the gas solubility in the aqueous electrolyte solution is low enough to neglect the gas−electrolyte interactions, the gas−water and electrolyte−water interactions are considered only in this work.

Table 2. Calculated Upper Quadruple Points (Hydrate−Liquid R22−Aqueous Liquid−Vapor) of Each System in Various Electrolyte Solutions

system	concentration	T/K	p/MPa
water + R22 + NaCl	5 mass % NaCl	287.30	0.767
	10 mass % NaCl	284.10	0.697
	15 mass % NaCl	280.05	0.618
water + R22 + KCl	5 mass % KCl	287.94	0.781
	10 mass % KCl	285.71	0.732
	15 mass % KCl	283.10	0.677
water + R22 + $MgCl_2$	5 mass % $MgCl_2$	287.42	0.770
	10 mass % $MgCl_2$	283.53	0.690
	15 mass % $MgCl_2$	277.22	0.564

The fugacity coefficient of water, φ_w, in the aqueous electrolyte liquid phase can be simply expressed as follows:

$$\ln \varphi_w = \ln \varphi_w^{EOS} + \ln \gamma_w^{EL} \tag{5}$$

This expression was also adopted by Aasberg-Petersen et al.[19] The first term for normal contribution can be calculated from any cubic equation of state and the second term for electrolyte contribution from the Pitzer model:

$$\gamma_w^{EL} = a_w/x_w \tag{6}$$

$$\ln a_w = -\frac{M_w \nu m}{1000}\phi \tag{7}$$

where M_w stands for the molecular weight of water, m for the molality of the electrolyte, ν for the number of ions the electrolyte dissociates into, and ϕ for the osmotic coefficient. The osmotic coefficient for single electrolyte solutions is as follows:

$$\phi - 1 = |z_+z_-|f^\phi + m\left(\frac{2\nu_+\nu_-}{\nu}\right)B_\pm^\phi + m^2\left[\frac{2(\nu_+\nu_-)^{3/2}}{\nu}\right]C_\pm^\phi \tag{8}$$

$$f^\phi = -A_\phi \frac{\sqrt{I}}{1 + 1.2\sqrt{I}} \tag{9}$$

$$B_\pm^\phi = \beta_0 + \beta_1 \exp(-\alpha I^{1/2}), \quad \alpha = 2.0 \tag{10}$$

where A_ϕ stands for the osmotic coefficient Debye−Hückel constant, I for the ionic strength, ν_i for the number of ions i in the electrolyte, z_i for the charge on ion i, $C_\pm^\phi$ for the Pitzer parameter, and β for the Pitzer parameter.

Calculated results obtained from the predictive model are presented in Figures 1−3 along with experimental data. The calculated upper quadruple points are determined from an intersection between the computed $H-L_w-V$ and $H-L_{R22}-L_w$ equilibrium lines and tabulated in Table 2. Estimated results from the predictive model show good agreement with the experimental data but deviate slightly from the experimental results at the high concentration of electrolytes. The average absolute deviations between experimental and computed data are 0.730, 0.914, and 1.050% for 5, 10, and 15 mass % NaCl solutions, 0.570, 0.778, and 2.793% for 5, 10, and 15 mass % KCl solutions, and 0.478, 1.193, and 4.013% for 5, 10, and 15 mass % $MgCl_2$ solutions, respectively. The activity of the water phase is not well represented by the Pitzer correlation at high salt concentration, thus resulting in an incorrect water fugacity.

Conclusions

Experimental three-phase ($H-L_w-V$) equilibrium conditions were determined for three ternary water + R22 + NaCl, water + R22 + KCl, and water + R22 + $MgCl_2$ systems. The upper quadruple points, at which the four phases ($H-L_{R22}-L_w-V$) coexisted, were also measured to indicate the maximum temperature and pressure location of three $H-L_w-V$ phases. All electrolytes of NaCl, KCl, and $MgCl_2$ exhibited an inhibition effect on the hydrate formation. Calculated results obtained from the thermodynamic model were in good agreement with the experimental data particularly at the low electrolyte concentration range but were in a little deviation at the higher concentrations. While the inhibition effect of electrolytes on the hydrate formation is a similar trend at 5 mass % concentration, $MgCl_2$ shows a larger inhibition effect than the two other electrolytes, and the inhibition strength of KCl appeared to be the least among three electrolytes as the concentration increases.

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