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Equilibrium Studies on the System Water + Hydrogen Peroxide + Urea + Carbon Dioxide

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To develop a new method for separating the residual liquid of peroxide urea production by the formation of gas hydrate, the equilibrium of the system water + hydrogen peroxide + urea + carbon dioxide was studied under the conditions of $P = (1.2 \text{ to } 1.9)$ MPa and $T = (272.15 \text{ to } 275.15)$ K. The equilibrium pressure and temperature of gas hydrate formation were investigated at the different concentrations of hydrogen peroxide and urea with the anionic surfactant sodium dodecyl sulfate (SDS) and the sodium dodecyl benzene sulfonate (SDBS) in the system and without either. It was found that the equilibrium pressure of gas hydrate formation increased with the increase of temperature and the mass fraction of hydrogen peroxide and urea. The addition of anionic surfactant SDBS and SDS lowered the equilibrium pressure of the gas hydrate formed. The equilibrium pressure of the gas hydrate formed was calculated by Chen−Guo thermodynamic model, and the calculated values were in accord with the experimental results.

Introduction

Urea peroxide, $CO(NH_2)_2 \cdot H_2O_2$, has typical features of a strong ability of sterilization, high efficiency, and low residue, leading to extensive use in the fields of bleaching, textile, water processing, daily chemicals, pharmaceuticals, and agriculture, and so forth. At present, the production of urea peroxide commonly used the reaction of hydrogen peroxide and urea of hydro-processes; theoretically, the solid peroxide urea can be generated when the mole ratio of urea and hydrogen peroxide is about 1:1. However, because of the dissolution of these two substances and decomposition of hydrogen peroxide in water, after all urea peroxide is separated from the system, the residual liquid still contained a low mass fraction of hydrogen peroxide and urea, and this resulted in the decrease of urea peroxide yield. There is a difficult problem to be solved: how to recycle the residual liquid and at the same time prevent the loss of hydrogen peroxide from decomposition effectively.[1] Therefore, to improve the production process of urea peroxide, it is essential to look for a new, safe, and efficient separation method at low temperatures to condense the residual liquid of the production process of urea peroxide.

Compared with supercritical fluid extraction, cryogenic separation, and crystallization separation, the new separation technology based on the application of gas hydrate has a lot of benefits such as the mild conditions, low energy consumption, high efficiency, and being environmentally friendly. Its application has been investigated in the fields of seawater desalination,[2] concentrations of solution,[3] gas separation,[4] biological engineering, and biotechnology.[5] The liquid−solid phase equilibrium data containing the compositions of liquid and gas hydrate after gas hydrate formation were the theoretical base of separation processes by gas hydrate,[6] but few were reported; moreover, there was no quantitative research reported on the liquid entrained in gas hydrate. In this paper, the phase equilibrium containing gas hydrate formation from the system water + hydrogen peroxide + urea + carbon dioxide was investigated. The equilibrium conditions of temperature and pressure of gas hydrate and the catalyzing effects of the anionic surfactant sodium dodecyl sulfate (SDS) and the sodium dodecyl benzene sulfonate (SDBS) were studied. The equilibrium pressure of gas hydrate formation was calculated by Chen−Guo thermodynamic model.

Experimental Section

Materials. Hydrogen peroxide (H_2O_2, $w = 0.30$, analytical reagent), urea ($CO(NH_2)_2$, analytical reagent), formaldehyde (HCHO, analytical reagent), and permanganate ($KMnO_4$, analytical reagent) were supplied by Tianjin Second Reagents Corporation. The SDS (analytical reagent) and the SDBS (analytical reagent) were supplied by Tianjin Kewei Reagents Corporation. CO_2 ($w = 0.995$) was supplied by Tianjin Anlida Gas Industry Corporation. The distilled water was obtained from Tianjin Pure Chemicals Company.

Apparatus. The measurement device of the phase equilibrium was designed and produced by Hai'an Oil Scientific Instruments Company in Jiangsu Province. The stainless steel cell with watching window can bear 20 MPa, and the largest volume is 70 cm^3. The small magnetic stirrer inside the cell is rotated by the magnetic at the bottom of the cell, and there are temperature gauges and pressure gauges on the top of the cell. The liquid and gas can be taken from the sampling tubes with cutoff valves on the right of the cell. Carbon dioxide is forced into the cell from the tube on the left of the cell. In this experiment, the cell is dipped into the thermostat which keeps temperature stable through the refrigerants (solution of ethanol) in precooling tank; the temperature is measured by use of a K-type themistor probe calibrated by a Pt resistance thermometer (25 Ω) defined by ITS-90, and the digital is displayed by a XMTA-7511 temperature measuring instrument with 0.1 K uncertainty. The pressure is recorded by a WP-C701-00-12-P precision pressure gauge with 0.01 MPa uncertainty and DBY-300 pressure transducers. The schematic diagram is shown in Figure 1.

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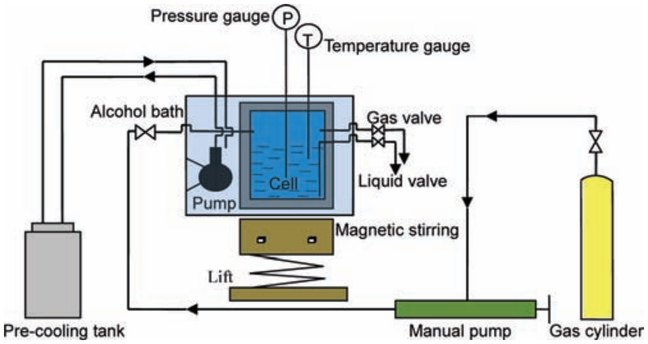

Figure 1. Schematic diagram of the experimental apparatus.

The comparison of the experimental pressure determined by the article apparatus with the literature data[7] of the gas hydrate formation for the binary system water−carbon dioxide is shown in Table 1; it shows that the accuracy of data measured by the experimental device is feasible.

Experimental Procedure. First, a solution of a certain mass fraction of hydrogen peroxide and urea was prepared; when the temperature reached experimental conditions, the solution was precisely added to the cell. Then CO_2 was pumped into the cell to replace the air; the valve outlet pipe was closed, pressure sealed, and the magnetic stirring moved. When a large amount of gas hydrate crystal formed, the valve inlet pipe of manual pump was closed, and the system was kept stable for (4 to 6) h. If there was no change of gas hydrate crystal amount in the cell after being stable for (4 to 6) h, the pressure was also not changed; at this moment, the pressure was the equilibrium pressure at this temperature. In this experiment, the determination of minimum pressure adjusting range was 0.05 MPa. By changing the temperature and repeating the steps above, we would get the gas hydrate equilibrium pressure at different temperatures. Then the fixed temperature changed the mass fraction of hydrogen peroxide and urea, respectively, and by repeating the steps above, we also got the gas hydrate equilibrium pressure data at different mass fractions of hydrogen peroxide and urea.

When the system in cell reached equilibrium, the sample liquid valve was opened, and the liquid was taken out; meanwhile the pressure was maintained stable through the manual pump until no liquid flew from the cell. Then the liquid was recorded, and chemical analysis was taken. Last, the pressure was reduced, and the residual wet solid phase in cell was decomposed into liquid; then all of the rest liquid was taken out, and chemical analysis was taken.

Hydrogen peroxide was analyzed by the titration of $KMnO_4$ standard solution. Urea was analyzed by formaldehyde.[8] The content of water was determined by subtraction.

Results and Discussion

Phase Equilibrium of the System without SDS and SDBS. Data in Table 2 are the experimental results of the system water + hydrogen peroxide + urea + carbon dioxide without surfactants; the liquid entrained in the wet solid phase is on the basis of the theory that hydrogen peroxide is not formed into hydrate and all of the hydrogen peroxide in the wet solid phase comes from the liquid entrained in the wet solid phase. The formula is as follows:

$$m_1 = m_2 \cdot c_1 / c_2$$

where m_1 is the mass of liquid entrained in gas hydrate; m_2 is the mass of equilibrium in the wet solid phase; c_1 is the mass fraction of hydrogen peroxide in the wet solid phase; c_2 is the mass fraction of hydrogen peroxide in equilibrium liquid after the gas hydrate is separated from the system.

Of course, we could also calculate the mass of liquid entrained with the urea in wet solid phase, but considering that the precision of chemical analysis of hydrogen peroxide is higher, in this paper the mass of liquid entrained is calculated with the hydrogen peroxide mass fraction in the wet solid phase. Data in Table 2 show that the mass fraction of hydrogen peroxide and urea or the temperature is higher, the equilibrium pressure of gas hydrate formation is higher, and the time of gas hydrate formation is longer. Figures 2 and 3 respectively show the relation of equilibrium pressure with the mass fraction of urea or H_2O_2. When the mass fraction reaches a certain value, gas pressure is increased again, and the gas hydrate is not formed on the experimental condition. So, in Table 2, there are only the liquid−solid phase equilibrium data when the mass fraction of the feeding hydrogen peroxide and urea are in a certain range. From the ratio between the gas hydrate and the liquid entrained in the equilibrium wet solid phase, it is known that the amount of liquid entrained in gas hydrate is higher than the pure hydrate amount; the gas hydrate wet solid phase is far different from the one of ordinary mineral crystallization.

Phase Equilibrium of the System with SDS and SDBS. Data in Table 3 instruct the relationship of equilibrium pressure, temperature, and composition in the system water + hydrogen peroxide + urea + carbon dioxide with surfactants SDBS and SDS (the mass fraction is 0.00003). The influence of the mass fraction of hydrogen peroxide and urea and temperature on the pressure of gas hydrate formation is consistent with that of Table 2. Comparing the data in Table 2 with Table 3, surfactants can reduce the equilibrium pressure of the formation of hydrate,[9] shorten the time of gas hydrate formation, and reduce the mass of liquid entrained. It shows that the surfactant can accelerate the rate of gas hydrate formation, change the thermodynamic condition, and make the hydrate more dense. Comparing SDBS with SDS, the effect of SDS on the gas hydrate formation of this system water + hydrogen peroxide + urea + carbon dioxide is more significant. Figures 4 and 5 respectively show the relation of equilibrium pressure with the mass fraction of urea or H_2O_2 under the conditions of SDS and SDBS at 273.15 K.

Calculation of Equilibrium Pressure of the System. The thermodynamic models for predicting gas hydrate formation were mainly the models of van der Waals−Platteeuw[10] and its modification model[11] based on classical statistical thermodynamics. Chen and Guo developed a new gas hydrate model based on the gas hydrate formation mechanism;[12] the new model had a higher calculation accuracy compared with other thermodynamic models based on the isothermal adsorption principle, so this paper made use of it to calculate the equilibrium pressure.

Two hypotheses in model calculation were made as follows: (a) CO_2 dissolved was ignored in water; (b) the gas phase was pure CO_2 because the steam pressures of H_2O and H_2O_2 were very low in experimental conditions.

The water activity was calculated by the universal functional activity coefficient (UNIFAC) equation; the fugacity of CO_2 was calculated by the Soave−Redlich−Kwong (SRK) equation.

According to the data in Table 2, such as the components of the equilibrium liquid phase, equilibrium temperature, and equilibrium pressure, we can fit the Chen−Guo model by applying the method of mathematics and using Matlab and firstOpt mathematical optimization software.

Table 1. Equilibrium Pressure−Temperature of CO_2 Hydrate[a]

T/K	272.15	273.15	274.15	275.15	276.15	277.15	278.15
P_{lit}/MPa[7]	1.08	1.20	1.35	1.50	1.70	1.95	2.17
P_{exp}/MPa	1.09	1.19	1.36	1.51	1.72	1.96	2.19

[a] P_{lit} is the data in literature; P_{exp} is the data of this experiment.

Table 2. Phase Equilibrium Data of the System Water (1) + Hydrogen Peroxide (2) + Urea (3) + Carbon Dioxide (4) without Surfactants[a]

	feed			equilibrium liquid			wet solid phase			P_{exp}	t	calculated values	
T/ K	m_0/g	x_2	x_3	m_e/g	x_2	x_3	m_{real}/g	m_{entr}	R	MPa	min	P_{cal}/MPa	100 ARD
272.15	27.171	5.08	5.08	11.813	5.79	5.78	3.230	11.902	0.271	1.30	197	1.242	4.50
	27.735	4.98	10.05	14.262	5.45	10.98	2.116	11.039	0.192	1.35	206	1.288	4.61
	26.260	5.01	15.10	15.358	5.50	16.61	1.938	8.479	0.229	1.42	219	1.426	0.41
	27.765	5.02	17.11	16.560	5.45	18.53	1.909	8. 947	0.213	1.45	227	1.502	3.59
	26.906	7.06	5.05	11.982	7.76	5.54	2.046	12.420	0.165	1.36	225	1.272	6.44
	25.975	9.88	5.02	13.134	10.85	5.51	1.827	10.494	0.174	1.44	355	1.308	9.18
	26.349	9.49	8.42	14.017	10.32	9.18	1.911	10.147	0.188	1.48	267	1.442	2.57
	27.471	9.56	12.73	18.431	10.20	13.49	1.248	7.278	0.171	1.53	278	1.671	9.22
	27.459	11.03	5.06	14.661	11.87	5.44	1.700	10.829	0.157	1.49	285	1.370	8.04
	25.793	14.89	10.91	22.866	15.30	11.20	0.219	2.230	0.098	1.65	325	1.756	6.39
273.15	28.792	3.14	5.09	12.551	3.79	6.12	4.416	11.201	0.394	1.40	203	1.289	7.91
	26.587	3.23	16.17	14.122	3.63	17.82	2.957	9.501	0.311	1.51	224	1.640	8.61
	22.984	5.06	5.06	12.207	5.66	5.61	2.148	8.262	0.260	1.45	232	1.377	5.05
	25.866	5.03	7.02	13.161	5.57	7.76	2.113	10.123	0.209	1.47	236	1.351	8.12
	26.769	5.06	11.58	15.569	5.49	12.55	1.982	9.066	0.219	1.51	248	1.549	2.57
	25.407	5.06	15.07	15.466	5.46	16.06	1.360	8.016	0.170	1.55	258	1.626	4.93
	25.661	7.06	5.06	10.068	7.76	5.58	2.081	13.208	0.158	1.52	265	1.406	7.50
	24.862	7.18	10.23	15.064	7.70	10.95	1.657	8.028	0.206	1.58	277	1.658	4.92
	25.656	9.18	6.22	15.577	9.98	6.76	1.713	7.954	0.215	1.59	316	1.625	2.20
	24.905	10.11	5.02	17.890	10.98	5.46	1.639	4.977	0.329	1.61	325	1.634	1.47
275.15	26.184	2.96	5.07	9.525	3.74	6.386	5.53	11.086	0.498	1.66	234	1.515	8.76
	29.613	2.93	10.58	12.302	3.39	11.983	3.32	13.272	0.250	1.72	247	1.735	0.84
	26.491	2.97	15.03	12.430	3.36	16.466	2.84	10.901	0.260	1.77	255	1.878	6.13
	27.569	5.08	3.07	14.666	5.89	3.557	3.48	8.958	0.389	1.75	260	1.648	5.84
	31.608	5.09	5.04	17.204	5.73	5.688	3.07	10.744	0.285	1.77	269	1.630	7.90
	30.074	5.09	10.49	18.007	5.55	11.366	1.95	9.553	0.204	1.83	278	1.911	4.44
	29.511	5.07	14.92	19.430	5.48	16.096	1.93	7.812	0.247	1.87	289	1.985	6.15
	28.741	7.01	2.99	17.235	7.66	3.279	2.08	8.997	0.232	1.84	291	1.661	9.71
	29.382	7.01	5.09	20.294	7.47	5.421	1.49	7.234	0.205	1.87	304	1.755	6.13
	28.879	8.07	5.02	20.906	8.66	5.381	1.63	5.941	0.274	1.90	326	1.857	2.25

[a] x_i ($i = 2, 3$) is the concentration of the i^{th} component expressed in mass fraction, ω (%). m_0 is the total mass of the feed. m_e is the mass of the equilibrium liquid. m_{real} is the mass of water in gas hydrate, not containing the mass of CO_2. m_{entr} is the mass of liquid entrained in the solid phase. R is the ratio of m_{real} to m_{entr}. P_{exp} is the equilibrium pressure of experiment, MPa. t is the formation time of gas hydrate. P_{cal} is the equilibrium pressure calculated by the Chen−Guo model, MPa. 100 ARD is the average relative deviation (ARD), $(|P_{exp} - P_{cal}|)/(P_{exp})$.

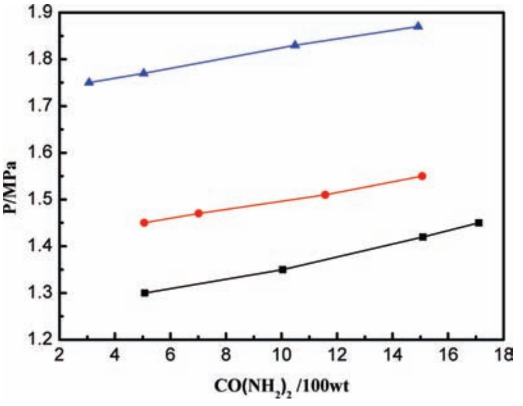

Figure 2. Relation of equilibrium pressure with the mass fraction of $CO(NH_2)_2$ at different temperatures on the condition of the mass fraction of H_2O_2 of about 5. ■, T = 272.15 K; ●, T = 273.15 K; ▲, T = 275.15 K.

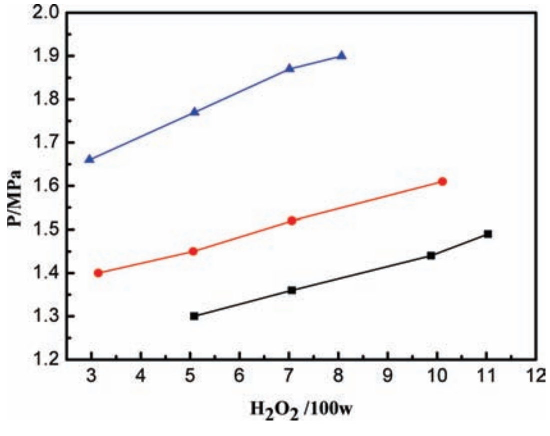

Figure 3. Relation of equilibrium pressure with mass fraction of H_2O_2 at different temperatures on the condition of the mass fraction of $CO(NH_2)_2$ of about 5. ■, T = 272.15 K; ●, T = 273.15 K; ▲, T = 275.15 K.

The calculated results of the parameters were as follows: $a = 2.099 \cdot 10^6$, $b = -3.397$, and $c = 268.683$.

When the results of a, b, and c are obtained, the gas hydrate equilibrium pressure in the system water + hydrogen peroxide + urea + carbon dioxide can been calculated and seen in Table 2. It shows that there is a certain bias between the calculated value of equilibrium pressure and the measured value; this bias may come from the fact that the model neglects CO_2 dissolved in solution. The dissolved CO_2 can not only react with water to form HCO_3^- which had influence on the water activity value but also reduce the fraction of water phase and then make the water activity lower. However, on the whole, the experimental data are in accord with those calculated, and calculation errors remained within 10 %.

Table 3. Phase Equilibrium Data of the Quaternary System Water (1) + Hydrogen Peroxide (2) + Urea (3) + Carbon Dioxide (4) with Surfactants at 273.15 K[a]

	feed			equilibrium liquid			wet solid phase			P_{exp}	t
surfactant	m_0	x_2	x_3	m_e	x_2	x_3	m_{real}	m_{entr}	ratio	MPa	min
SDBS	27.472	3.04	5.04	10.251	4.42	6.82	8.475	8.630	0.982	1.28	175
	26.687	5.04	5.05	10.807	6.40	6.15	5.235	10.175	0.514	1.37	197
	27.456	5.05	7.02	12.035	6.14	7.96	4.622	10.525	0.439	1.41	206
	25.677	5.07	11.48	11.569	6.09	12.98	3.954	9.694	0.408	1.46	199
	26.358	5.02	15.05	13.466	5.89	16.06	3.547	8.929	0.397	1.48	208
	27.469	7.06	5.07	13.068	7.97	5.59	3.062	11.227	0.273	1.49	215
	25.406	10.05	5.03	14.078	10.98	5.78	2.056	9.160	0.224	1.57	227
SDS	26.692	3.02	5.08	9.445	4.63	6.92	8.924	7.975	1.119	1.27	152
	27.984	5.06	5.04	10.605	6.56	6.11	6.180	10.936	0.565	1.36	165
	25.786	5.03	7.04	10.128	6.31	8.11	4.859	10.377	0.468	1.39	175
	26.646	5.05	11.33	11.483	6.33	12.68	5.004	9.744	0.514	1.44	182
	25.467	5.07	15.08	12.167	6.17	16.06	4.532	8.606	0.527	1.46	194
	26.626	7.05	5.06	12.068	8.42	5.85	4.082	10.208	0.400	1.47	203
	25.498	10.05	5.03	15.128	11.28	5.52	2.578	7.557	0.341	1.55	213

[a] x_i ($i = 2, 3$) is the concentration of the i^{th} component expressed in mass fraction, ω (%). m_0 is the total mass of the feed, g. m_e is the mass of equilibrium liquid, g. m_{real} is the mass of water in gas hydrate, not contain the mass of CO_2, g. m_{entr} is the mass of liquid entrained in the solid phase, g. R is the ratio of m_{real} to m_{entr}. P_{exp} is the equilibrium pressure of experiment. t is the formation time of gas hydrate.

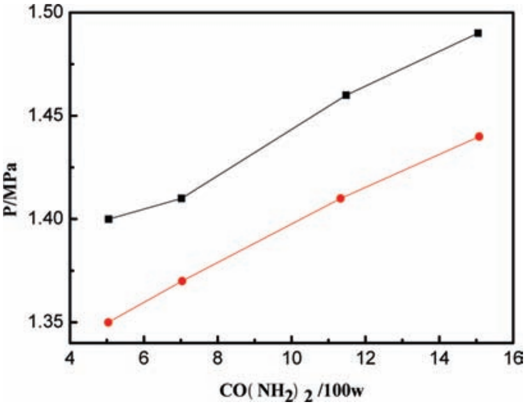

Figure 4. Relation of equilibrium pressure with mass fraction of $CO(NH_2)_2$ at 273.15 K with SDS and SDBS and the mass fraction of H_2O_2 of about 5. ■, SDBS; ●, SDS.

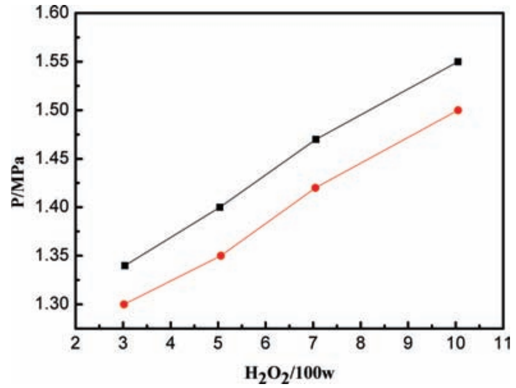

Figure 5. Relation of equilibrium pressure with mass fraction of H_2O_2 at 273.15 K with SDS and SDBS and the mass fraction of $CO(NH_2)_2$ of about 5. ■, SDBS; ●, SDS.

$$f_T^0 = a \exp\left(\frac{b}{T - c}\right)$$

Conclusions

The equilibrium pressure of gas hydrate formation increases in the system water + hydrogen peroxide + urea + carbon dioxide with the increase of hydrogen peroxide and urea mass fraction. After the separation from the liquid by natural settlement, the amount of liquid entrained in gas hydrate is very high, about 10 times of the pure gas hydrate amount. When the surfactant SDBS or SDS is added in the system water + hydrogen peroxide + urea + carbon dioxide, it can reduce the equilibrium pressure of the hydrate formation, shorten the time of gas hydrate formation, and reduce the mass of liquid entrained. Comparing surfactant SDBS with SDS, SDS is better than SDBS. The experimental data are in accord with the calculated data in the system water + hydrogen peroxide + urea + carbon dioxide by the Chen−Guo thermodynamic model.

Literature Cited

(1) Cao, J. L.; Li, M. Q.; Tan, Z. Y. Synthesis of Solid Disinfectant Urea Peroxide by Hydro-processes. *Chin. J. Process Eng.* **2005**, *5* (5), 517–520.

(2) Sun, C. Y.; Huang, Q.; Chen, G. J. Progress of thermodynamics and kinetics of gas hydrate formation. *J. Chem. Ind. Eng.* **2006**, *57* (5), 1031–1039.

(3) Khan, A. H. *Freezing in Desalination Processes and Mutistage Flash Distillation Practice*; Elsevier: Amsterdam, 1986; pp 55−68.

(4) Willson, R. C.; Bulot, E., Cooney, C. L. Use of Hydrates for Aqueous Solution Treatment. U.S. Patent 4678583, 1987; pp 7−17.

(5) Douglas, G.; Elliot, H. Process for Separating Selected Components from Multi-component Natural Gas Streams. U.S. Patent 5660603, 1997; pp 8−26.

(6) Sun, Z. G.; Fan, S. S.; Shi, L.; Guo, Y. K.; Guo, K. H. Equilibrium Conditions Hydrate Dissociation for a Ternary Mixture of Methane, Ethane, and Propane in Aqueous Solutions of Ethylene Glycol and Electrolytes. *J. Chem. Eng. Data* **2001**, *46* (4), 927–929.

(7) Dholabhai, P. D.; Bishnoi, P. R. Hydrate Equilibrium Conditions in Aqueous Electrolyte Solutions: Mixtures of Methane and Carbon Dioxide. *J. Chem. Eng. Data* **1994**, *39* (1), 191–194.

(8) Jin, G.; Jiang, W. Q.; Zhou, J. Y. *Quantitative Chemical Analysis Experiment*: China Science and Technology University Press: Hefei, 2005; pp 87−88.

(9) Wu, Q.; He, X. Q.; Zhang, B. Y. Thermodynamic Effect of Surfactant on Gas Hydrate Formation. *J. Chem. Ind. Eng.* **2006**, *57* (12), 2793–2797.

(10) Van der Waals, J. H.; Platteeuw, J. C. Clathrate Solutions. *Adv. Chem. Phys.* **1959**, *2* (1), 1–57.

(11) Parrish, W. R.; Prausnitz, J. M. Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures. *Ind. Eng. Chem. Res.* **1972**, *11* (1), 26–35.

(12) Chen, G. J.; Guo, T. M. Thermodynamic Modeling of Hydrate Formation Based on New Concepts. *Fluid Phase Equilib.* **1996**, *122* (1−2), 43–65.

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