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Experimental and Theoretical Study on Gas Hydrate Phase Equilibria in Seawater

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Experimental data of methane hydrate in artificial seawater have been determined in a pressure range from (3.42 to 22.5) MPa. An evaluation of available literature data on gas hydrate equilibria in natural and synthetic sea waters has been performed aiming on a practical simplification for prediction gas hydrate equilibria in seawater systems.

Introduction

Gas hydrates are solid inclusion compounds of water encaging small non- to slightly polar guest molecules into regular cavities and thereby stabilizing the crystal structure. Typical hydrate-forming agents include the major natural gas constituents up to isobutane. Gas hydrates can form at temperatures above the freezing point of pure water and usually at elevated pressures. The location and shape of the equilibrium line is strongly dependent on the guest molecule species as well as on water activity in the surrounding aqueous phase. The latter is influenced by any water-soluble additive, isobarically shifting equilibrium temperatures toward lower values and thereby acting as a so-called thermodynamic inhibitor. This phenomenon can be regarded to be analogous to the effect of the isobaric freezing point depression in liquid systems. The practical relevance of thermodynamic hydrate inhibition is mainly restricted to three fields:

1. To prevent unwanted hydrate formation in natural gas production and processing lines, usually alcohols are added to the gas-condensate streams.

2. Large off-shore natural gas hydrate deposits have been discovered in the past century partially being in contact with saline seawater. In this case, huge amounts of fossil carbon are trapped within marine sediments that could provide a significant extension to the era of fossil fuels.[1−3]

3. The third field deals with separation processes directly utilizing controlled formation and dissociation of gas hydrates as a separation step such as the desalination of seawater.[4−6]

For the two latter cases knowledge about the location of hydrate phase equilibria in the presence of seawater plays an important role for predicting production rates and for overall process design. In previous works we have systematically investigated the effect of different electrolytes and electrolyte mixtures on the location of the hydrate equilibrium line.[7−10] We would like to conclude these works by looking at a complex electrolyte mixture that represents seawater. In the past several authors have dealt with measuring and predicting gas hydrate phase equilibrium conditions in seawater systems. Rouher and Barduhn[11] were the first to publish gas hydrate equilibrium data in seawater, with the prospect of developing a desalination process using isobutane hydrates. Englezos and Bishnoi[12] presented a model for predicting water activity and from this methane hydrate stability conditions in artificial seawater. Handa[13] dealt with the measurement of methane solubility and hydrate stability in seawater. Bishnoi and Dholabhai[14] and Doholabhai et al.[15,16] performed experiments on methane, propane, and carbon dioxide hydrate equilibrium conditions in synthetic sea waters. Ohgaki et al.[17] performed phase equilibrium measurements in the carbon dioxide hydrate system with pure water and synthetic seawater. Phase equilibrium data for methane hydrate were also determined by Dickens and Quinby-Hunt[18] and Maekawa and Ima[19] for natural sea waters. Finally Tishchenko et al.[20] published a correlation for predicting methane hydrate equilibrium lines in sea waters possessing different salinities.

Experimental Section

Three phase (hydrate−liquid−gas, HLG) equilibrium points of methane hydrate in artificial seawater were determined using an isochoric method. A 1 L autoclave was half filled with the water salt mixture and the content continuously stirred with a high performance stirrer driven by magnetic coupling. Heating rates between (0.01 and 0.1) $K \cdot h^{-1}$ when approaching the equilibrium point were adjusted. Detailed descriptions of the experimental apparatus and procedure are reported elsewhere.[7,8,21] Obtained equilibrium data possess an absolute uncertainty below ± 0.03 K and ± 25 kPa for temperature and pressure, respectively. The uncertainty in the synthetic seawater composi-

Table 1. Overview Seawater Compositions

	reported compositions[a]		this work	
compound	100 *w*	100 *x*	100 *w*	100 *x*
NaCl	2.200–2.644	0.694–0.835	2.422	0.767
KCl	0.065–0.076	0.016–0.019	0.070	0.017
$CaCl_2$	0.071–0.116	0.012–0.019	0.101	0.017
$MgCl_2$	0.256–0.970	0.050–0.099	0.564	0.109
Na_2SO_4	0.331–0.407	0.043–0.052	0.378	0.049
$SrCl_2$	0–0.002	0–0.002		
KBr	0–0.011	0–0.001		
NaF	0–0.009	0–0.001		
H_2O	96.49–96.85	97.90–98.15[b]	96.47	97.93[b]
salinity, $g \cdot L^{-1}$	32.5−36.4		36.6	

[a] Refs 14−18, 20, 32, and 33. [b] Assuming complete dissociation of salts.

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Table 2. Experimental Dissociation Pressures for Methane Hydrate Synthetic Seawater ($w(\text{NaCl}) = 0.03$)

T / K	p / MPa
291.07	22.50
289.27	17.70
287.83	14.67
285.35	10.81
280.07	6.01
274.52	3.42

Table 3. Constants for Calculating Langmuir Coefficients

		small cage		large cage	
guest	hydrate	C^0_{1j}	ε_{1j}	C^0_{2j}	ε_{2j}
species	structure	10^{-4} MPa^{-1}	kJ·mol^{-1}	10^{-4} MPa^{-1}	kJ·mol^{-1}
i-C_4H_{10}	II			0.0271	48.58
C_3H_8	II			0.816	40.20
CO_2	I	5.97	16.26	0.636	31.40
CH_4	I	0.603	24.10	1.27	26.89

Table 4. Deviations from Predicted (HYCAL08) to Experimental Dissociation Pressures of Gas Hydrates in the Sea Waters[a]

source	hydrate former	number of data points	average relative deviation
Rouher and Barduhn[11]	i-C_4H_{10}	25	6.2 %
Bishnoi and Dholabhai[14]	C_3H_8	4	0.30 %
Doholabhai et al.[16]	CO_2	5	0.73 %
Ohgaki et al.[17]	CO_2	14	3.3 %
Handa[13]	CH_4	2	1.9 %
Doholabhai et al.[16]	CH_4	4	0.6 %
Dickens and Quinby-Hunt[18]	CH_4	11	1.4 %
Maekawa and Ima[19]	CH_4	14	1.5 %
this work	CH_4	6	1.9 %
overall[b]		54	1.5 %

[a] Prediction performed using SSW. [b] Except data from Rouher and Barduhn[11] due to strong systematic deviations.

tion was defined by averaging seawater compositions of different sources. A summary of reported concentration ranges as well as the composition used for this work is given in Table 1.

Computational Model. To evaluate available gas hydrate equilibrium data from a water activity point of view our in-house model for predicting gas hydrate equilibria (HYCAL08) was used. Only a brief introduction to the model will be given. Further details on HYCAL08 can be found in previous publications.[7,10,21]

The basis for calculating hydrate phase equilibria is the condition of equal chemical potentials for all components within all phases. Thus, at any of the three phase HLG equilibrium points, chemical potentials μ_W of water within the gas, liquid, and hydrate phase need to be equal. Introducing the hypothetical empty hydrate lattice as reference state, the necessary equilibrium condition can be expressed as follows,

$$\Delta\mu_W^{\beta-H} \overset{!}{=} \Delta\mu_W^{\beta-L} = \Delta\mu_{oW}^{\beta-L} - RT\cdot\ln(a_W) \tag{1}$$

with β, H, and L refer to the reference, hydrate, and liquid phases respectively, subscript o to pure water, R the molar gas constant, T absolute temperature, and a_W the water activity. Within this expression the difference in chemical potential between pure liquid water and the empty hydrate lattice $\Delta\mu_{oW}^{\beta-L}(T, p)$ was calculated using a classical thermodynamic correlation function as suggested by Holder et al.[22] Necessary thermodynamic reference data was taken from literature.[23-25,10] The difference in chemical potential between water in the hydrate phase and the reference state can be calculated by means of statistical thermodynamics using the solid solution theory as developed by van der Waals and Platteuw.[26] One obtains the expression given below:

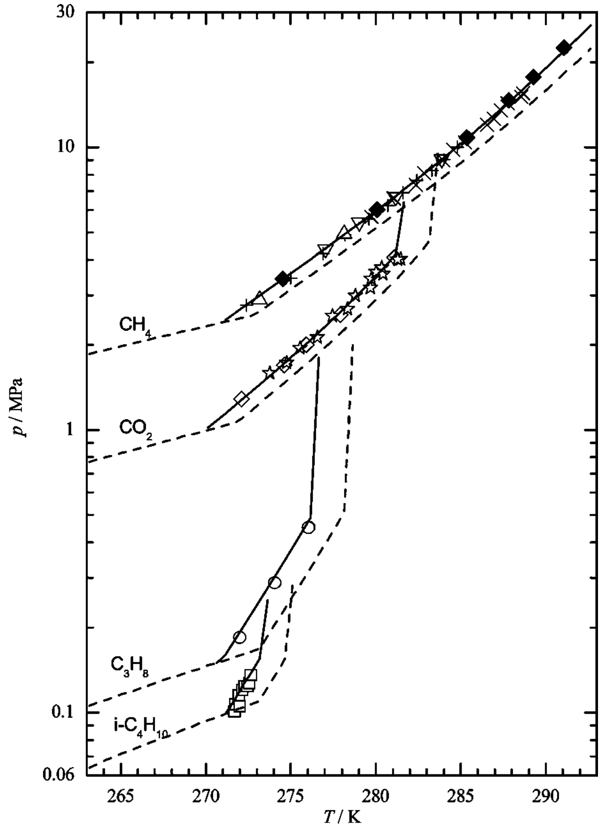

Figure 1. Experimental and predicted equilibrium data for gas hydrates in sea waters. □, Rouher and Barduhn;[11] ○, Bishnoi and Dholabhai;[14] ◇, Doholabhai et al.;[16] ☆, Ohgaki et al.;[17] △, Handa;[13] ▽, Doholabhai et al.;[15] +, Dickens and Quinby-Hunt;[18] ×, Maekawa and Ima;[19] ◆, this work. HYCAL08 predictions: solid line, SSW ($w = 0.03$ NaCl); dashed line, pure water.

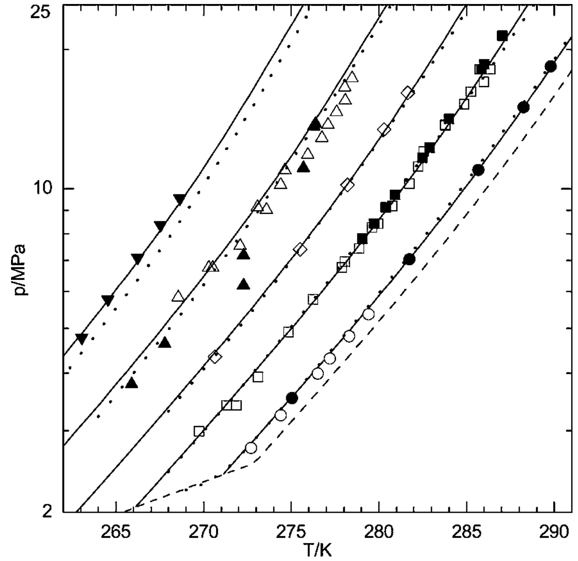

Figure 2. Experimental and predicted equilibrium data for methane gas hydrates in (water + NaCl). Experimental $w_{\text{NaCl}} = 0.03$: ○, Dholabhai et al.;[15] ●, Rock.[8,21] $w_{\text{NaCl}} = 0.10$: ■, Windmeier;[10] □, Maekawa et al.[19] $w_{\text{NaCl}} = 0.15$: ◇, Rock.[8,21] $w_{\text{NaCl}} = 0.20$: ▲, Kobayashi et al.;[35] △, Maekawa et al.[19] $w_{\text{NaCl}} = 0.241$: ▼, de Roo et al.[36] Predictions of NaCl systems: dashed line, HYCAL08;[10] dotted line, CSMGEM.[34] Prediction of pure water: dashed line, HYCAL08.[10]

Table 5. Overview of Gas Hydrate Data Range for Literature Seawater and Water: Single Salt Systems Containing NaCl

gas	inhibitor	temperature range in K	pressure range in MPa	no. of data points	phases	ref
i-C_4H_{10}	seawater	271.7 to 272.7	0.10 to 0.14	27	$H-L_W-G$	11
C_3H_8	seawater	272.0 to 276.1	0.18 to 0.45	4	$H-L_W-G$	14
	NaCl	267.6 to 277.7	0.15 to 0.50	29		
CO_2	seawater	272.1 to 281.1	1.29 to 4.07	5	$H-L_W-G$	16
CH_4	seawater	277.0 to 283.9	4.36 to 9.06	4	$H-L_W-G$	15
	NaCl	272.7 to 279.4	2.74 to 4.81	6		
CO_2	seawater	273.8 to 281.5	1.59 to 4.02	25	$H-L_W-G$	17
		280.6 + 282.0	4.89 + 5.44	2	$H-L_W-L_{CO_2}$	
		279.6	4.15	1	$H-L_{CO_2}-G$	
CH_4	seawater	272.4 to 284.8	2.76 to 1.00	11	$H-L_W-G$	18
CH_4	seawater	279.8 to 288.7	5.68 to 15.5	14	$H-L_W-G$	19
CH_4	NaCl	275.9 to 288.6	4.71 to 21.44	20	$H-L_W-G$	10
CH_4	NaCl	270.7 to 289.8	3.54 to 18.42	10	$H-L_W-G$	8, 21
CH_4	NaCl	265.9 to 284.3	2.59 to 13.66	15	$H-L_W-G$	35
CH_4	NaCl	261.8 to 278.0	0.24 to 1.10	23	$H-L_W-G$	36

$$\Delta\mu_{W}^{\beta-H} = -RT \cdot \sum_{i} \nu_i \cdot (1 - \sum_{j} \theta_{ij}) \qquad (2)$$

Indices i and j refer to cavity type and guest molecule species, υ_i to the number of cages per water molecule, and θ the fractional filling of each cavity type, respectively. The problem of predicting the phase equilibrium is thus reduced to correctly correlating fractional cage fillings. For this purpose the application of a simple Langmuir adsorption isotherm has been found to be suitable.

$$\theta_{ij} = \frac{C_{ij} f_j^{G}}{1 + \sum_{j} C_{ij} f_j^{G}} \qquad (3)$$

Fugacities f_j^{G} of guest molecules in the vapor phase were calculated using the SRK-EOS[27] incorporating a modification of the energy parameter as proposed by Mathias and Copeman.[28] Langmuir coefficients C_{ij} (see Table 3) have been fitted simultaneously to experimental pure guest/water equilibrium data and hydration numbers. The temperature dependence of C_{ij} is modeled using a correlation according to Anderson et al.[29] with ε_{ij} representing the depth of the potential well of guest species j in cavity i.

$$C_{ij} = C_{ij}^{0} \cdot e^{-\varepsilon_{ij}/RT} \qquad (4)$$

For calculation of the water activity and thereby predicting inhibited hydrate phase equilibria the LIQUAC model as developed by Li et al.[30] has been implemented. The gas solubility in pure and inhibited systems are calculated using the method of PSRK[31] together with LIQUAC. Rearranging eq 1 one can also obtain values of the water activity from experimental equilibrium data.

Results and Discussion

Seawater compositions given in Table 1 show reported salinities ranging between $32.5 < S < 36.4\ g \cdot L^{-1}$ and resulting in water mole fractions between $0.979 < x_{W<} < 0.982$ (complete dissociation of salts). The composition used for this study corresponds to a salinity of $S = 36.6\ g \cdot L^{-1}$ and a water mole fraction of $x_W = 0.979$ and can thus be assumed to be a representative for a highly saline seawater and thereby as a conservative approach to the location of the hydrate phase equilibrium line. Additionally the composition of a model seawater containing only NaCl was defined by iterative rms-based optimization to the available experimental seawater equilibrium data (simultaneous minimization of pressure deviations). This model seawater contains $w = 0.03$ of NaCl and shall henceforth be referred to by "simplified seawater" (SSW). Examples for the excellent suitability of HYCAL08 for predicting hydrate phase equilibria in inhibited systems were recently given by Windmeier.[10]

The experimental results of this work are given in Table 2 and along with the available data taken from the literature in Figure 1. There is very good agreement between this work and the literature. Regarding the quite different compositions of sea waters used by other authors, this agreement was found quite surprising. The solid line of Figure 1 gives the HYCAL08 prediction of the three phase equilibrium curves according to the SSW. There is satisfactory agreement between experimental seawater data with the single NaCl composition fluid. Discrete deviations between the experimental data and the SSW prediction are shown in Table 4. Using the SSW, experimental seawater results could be reproduced with an overall uncertainty of 1.5 % (average relative deviation).

To demonstrate the consistent applicability of the HYCAL08 prediction over a wide range of electrolyte concentrations, Figure 2 shows a comparison of representative literature data for the system pure water and the single salt NaCl with results obtained from calculations applying HYCAL08 and the program package CSMGEM from Sloan and Koh.[34] At the highest NaCl concentrations $w = (0.2$ and $0.24)$ at a given pressure CSMGEM predicts slightly higher equilibrium temperatures with the results obtained with HYCAL08 nearly matching the experimental data from de Roo et al.[36]

The temperature and pressure ranges of the literature data for single gas/seawater systems and (water + NaCl) together with the number of experimental data points are summarized in Table 5.

Conclusions

Although gas hydrate equilibria for different guest molecules in natural and synthetic sea waters of various sources were compared, it was found that the prediction of three phase equilibrium lines can be simplified and generalized by using a model seawater containing $w = 0.03$ of NaCl. For predictive purposes in this case neither the utilization of a multielectrolyte model nor the respective determination and input of model parameters are necessary.

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