J. Chem. Eng. Data 1993, 38, 650–654

Equilibrium Conditions for Carbon Dioxide Hydrate Formation in Aqueous Electrolyte Solutions

Pankaj D. Dholabhai, Nicolas Kalogerakis, and P. Raj Bishnoi*

Department of Chemical and Petroleum Engineering, The University of Calgary, 2500 University Drive Northwest, Calgary, Alberta, Canada T2N 1N4

Three-phase equilibrium conditions (aqueous solution + vapor + hydrate) of carbon dioxide in electrolyte solutions containing NaCl, KCl, $CaCl_2$, and their binary mixtures and in a synthetic sea water were experimentally obtained in the temperature range of 259–281 K and in the pressure range of 0.9–4.1 MPa using a "pressure search" method. The ionic strengths of the solutions ranged from 0.41 to 6.74 *m*.

Introduction

Natural gas components are known to form gas hydrates, which are icelike crystalline compounds. The hydrates are formed by a combination of water and gas molecules under suitable conditions of temperature and pressure. The gas molecules occupy the cavities contained in the two lattice structures (structure I and Structure II) formed by water. Carbon dioxide forms structure I hydrates. The three-phase equilibrium curve (aqueous solution + vapor + incipient hydrates) on the P–T plane divides the hydrate-forming zone from the non-hydrate-forming zone. Inhibitors like methanol and electrolytes suppress the hydrate formation; i.e., for a given temperature, the equilibrium pressure in a solution containing inhibitors is higher than that in pure water.

Information on the hydrate-forming conditions for natural gas components and their mixtures is vital to the oil and gas industry. Formation of hydrates in gas pipelines and processing equipment could lead to catastrophic consequences. This information is also essential to the industry for the exploitation of the huge naturally occurring gas reserves in the form of hydrates and for drilling through the hydrate zones. Some of these reserves exhibit very high CO_2 content. CO_2 is also used in enhanced oil recovery. In addition, its massive emissions from power plants and other combustion processes have been identified as a major cause of the greenhouse effect. Recently at the First International Conference On Carbon Dioxide Removal held in Amsterdam in 1992, it was suggested that CO_2 be extracted from these sources and stored in the oceans in the form of hydrates (*1–3*). Literature on hydrate equilibrium conditions for hydrocarbons and CO_2 in pure water is extensive. Holder et al. (*4*) and Sloan (*5*) have compiled the sources of published hydrate equilibrium data.

Hydrate equilibrium data on CO_2 and its mixtures with hydrocarbon gases in pure water have been reported by several researchers (*6–12*). However, there are very few studies reported on CO_2 equilibrium conditions in aqueous electrolytes (*6, 7*), and none in mixed electrolytes. It is important to study the hydrate equilibria in electrolytes since they are present in the naturally occurring waters. Englezos and Bishnoi (*13*) coupled the statistical thermodynamic model of van der Waals and Platteeuw (*14*) with the available activity coefficient models (*15, 16*) for electrolyte solutions to compute the hydrate equilibrium conditions in single and mixed electrolytes. Since there were no experimental data in mixed electrolytes to compare the predictions with, a systematic program of obtaining data in mixed electrolytes was started at the University of Calgary. The data on the hydrates of methane, ethane, and propane have already been obtained (*17–19*). In the present work, experimental data on the equilibrium conditions of carbon dioxide gas hydrates in pure water and single and mixed electrolytes are reported.

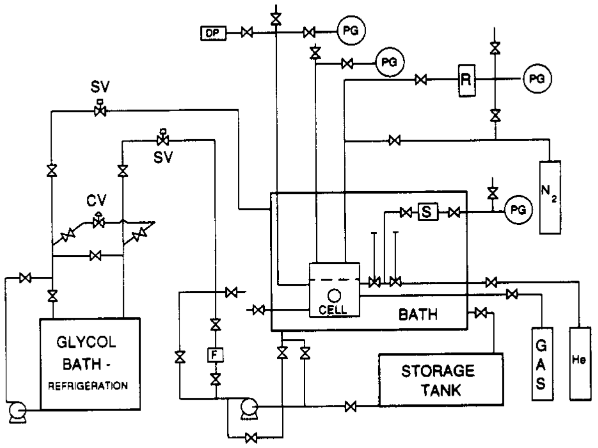

Figure 1. Schematic of the experimental apparatus: DP, pressure transmitter; R, nitrogen reservoir; S, sampling bomb; F, filter; PG, pressure gauge; SV, solenoid valve; CV, control valve.

Experimental Setup

A detailed description of the apparatus and the procedure is given by Englezos and Bishnoi (*17*). However, the salient features are described here.

Experimental Apparatus. A schematic diagram of the apparatus is given in Figure 1. The main component of the apparatus consists of a stainless steel variable-volume equilibrium cell. The volume of the cell can be changed by moving a floating piston vertically. The maximum and the minimum volumes of the cell are 293.6 and 221.2 cm^3. The cell is equipped with two marine-type Plexiglass windows for visual observation, a magnetic stirrer, and suitable connections for charging/discharging of materials. The temperature of the cell contents is measured with two platinum resistance thermometers (RTDs). The pressure in the cell is measured with (i) a 0–15-MPa a Heise gauge and (ii) a differential pressure transmitter (DP). The signals from the RTDs and the DP are taken up by a miniSAFE data acquisition system. A Zenith 286 computer receives the pressure and temperature values from the miniSAFE and saves them at preset sampling intervals. The cell is immersed in a cooling bath in which a

---

* To whom correspondence should be addressed.

0021-9568/93/1738-0650$04.00/0

Table I. Compositions of the Aqueous Solutions

solution	composition, mass % on wet basis NaCl	KCl	$CaCl_2$	solution	composition, mass % on wet basis NaCl	KCl	$CaCl_2$
Na3-1	3.00			Na5-1	5.00		
Na3-2	3.02			Na5-2	5.00		
Na3-3	3.02						
Na10-1	10.02			Na15	15.00		
Na10-2	10.00						
Na20	20.03			K3		3.00	
K5		5.01		K10		10.02	
K15		14.97		Ca3			3.03
Ca5			5.02	Ca10			9.99
Ca15			14.97	Ca20			19.96
Na3K3	3.01	3.02		Na5K5	5.00	5.01	
Na7K10	6.99	10.00		Na15K5	15.01	5.03	
Na15K5	15.01	5.03		Na3Ca3	3.03		3.03
Na2Ca8	2.02		8.00	Na8Ca2	8.01		2.03
Na5Ca15	5.02		14.70	Na15Ca5	15.01		5.03

Table II. Composition of Synthetic Sea Water

component	mass % on wet basis	component	mass % on wet basis
NaCl	2.391	$MgCl_2$	0.507
KCl	0.069	$CaCl_2$	0.115
KBr	0.011	NaF	0.005
Na_2SO_4	0.401	$SrCl_2$	0.002

glycol + water mixture is circulated from a refrigerated/heated bath. The set of point of the temperature controller on this bath can be changed by multiples of 0.1 K. The temperature in the cell generally oscillates within 0.1 K during a 24-h period.

For the experiments with carbon dioxide, the span of the DP was adjusted to 0–12 MPa. The low-pressure side of the DP was left open to the atmosphere. The stated accuracy of the Heise gauge was ±15 kPa (±0.1% of its span) and that of the DP ±30 kPa (±0.25% of its span). The resolution of the Heise gauge was 20 kPa. The Heise gauge was calibrated against a dead weight tester. The standard deviation of the linear least-squares fit was 15.3 kPa. For each data point, the pressure read off the Heise gauge was "corrected" using the least-squares equation. The prevailing atmospheric pressure was then added to the corrected pressure. The pressure computed from the DP readings was used as a check against the constancy of the system pressure. The accuracy of the RTDs was ±0.06 K. The resolution of the miniSAFE was 2.93 kPa and 0.005 K. All the experiments were performed at a constant cell volume.

Materials and Preparation of Electrolyte Solution. The electrolytes used were of Certified ACS grade supplied by Fisher Scientific Co. Deionized water was distilled in the laboratory before use. Coleman Instrument Grade carbon dioxide (Union Carbide) with a certified purity of 99.99% was used.

Appropriate quantities of the electrolyte were weighed on a top-loading Mettler balance with a readability of 0.01 g and added to a known mass of the water. The mixture was stirred at room temperature to dissolve the electrolyte.

Experimental Procedure. Before charging a solution, the cell was rinsed thoroughly 2–3 times with water. About 115 cm^3 of the solution was charged into the cell, and the vapor phase of the cell was then purged with CO_2 to drive away the air that may have entered during the charging process. The solution was then allowed to cool to the required temperature.

Once the desired temperature was reached, the pressure in the cell was increased beyond the expected equilibrium value by introducing the gas from the cylinder. As soon as the hydrates formed, the pressure was reduced to a value slightly less than the expected equilibrium pressure. The pressure reduction was brought about by the controlled venting of the gas, taking care that the temperature did not decrease by more than 0.1 K. The system was then left to equilibrate. If the temperature and pressure of the system remained constant for 3–4 h with a very small quantity of the hydrates present in the solution, the constant pressure and temperature were

Table III. Experimental Carbon Dioxide Hydrate Equilibrium Conditions

solution	T/K	P/MPa	solution	T/K	P/MPa	solution	T/K	P/MPa
pure water	273.75	1.340	Na3-1	278.95	2.955	Na3-2	273.21	1.434
	275.51	1.640		277.03	2.309	Na3-3	280.92	3.907
	277.10	1.985		275.17	1.837			
	279.04	2.520		272.20	1.304			
Na5-1	277.97	3.004	Na10-1	277.19	3.781	Na15	273.01	3.239
	275.03	2.016		277.01	3.671		271.05	2.469
	273.05	1.597	Na10-2	276.12	3.155		268.20	1.703
	271.18	1.306		276.07	3.149		265.38	1.212
Na5-2	279.96	3.766		274.08	2.409			
				271.01	1.656			
				268.03	1.162			
Na20	266.85	2.630	K3	281.09	3.834	K5	280.47	3.905
	265.29	2.208		279.99	3.233		280.43	3.861
	263.29	1.606		278.68	2.760		279.43	3.324
				276.75	2.154		278.61	2.960
				274.57	1.654		276.03	2.129
				272.67	1.326		274.13	1.700
							272.06	1.325
K10	277.86	3.485	K15	269.03	1.415	Ca3	275.52	1.827
	276.34	2.807		272.22	2.095		272.58	1.302
	273.08	1.848		274.58	2.901		278.15	2.529
	269.02	1.130		276.01	3.575		280.87	3.702

Table IV. Experimental Carbon Dioxide Hydrate Equilibrium Conditions

solution	T/K	P/MPa	solution	T/K	P/MPa	solution	T/K	P/MPa
Ca5	278.21	2.805	Ca10	270.85	1.511	Ca15	273.17	3.221
	280.07	3.657		268.05	1.102		270.12	2.138
	275.06	1.872		273.96	2.198		267.37	1.497
	271.08	1.184		277.26	3.460		263.42	0.960
				277.86	3.824			
Ca20	266.65	2.690	Na3K3	279.87	3.976	Na5K5	269.97	1.347
	264.58	2.052		279.29	3.573		271.72	1.660
	262.00	1.504		276.07	2.317		274.11	2.258
	259.19	1.051		274.02	1.814		277.32	3.432
				271.50	1.326			
Na7K10	267.57	1.482	Na15K5	262.93	1.218	Na3Ca3	279.17	3.595
	270.48	2.180		266.30	1.872		277.32	2.738
	273.07	3.044		268.18	2.388		275.73	2.227
	274.08	3.455		269.82	3.050		271.78	1.375
							270.99	1.258
Na8Ca2	267.77	1.086	Na2Ca8	277.48	3.697	Na5Ca15	267.34	2.935
	271.07	1.623		276.32	3.101		266.29	2.490
	273.16	2.112		272.72	1.909		264.11	1.878
	276.00	3.089		267.79	1.053		261.09	1.288
							259.15	1.042
Na15Ca5	267.39	2.665	sea[a]	274.57	1.699			
	265.67	2.112		275.94	2.001			
	263.54	1.609		277.91	2.556			
	259.02	0.909		281.09	4.072			
				272.14	1.288			

[a] Synthetic sea water.

taken as the equilibrium conditions and the experiment was terminated. If the system pressure was higher than the equilibrium pressure, then the pressure would decrease continuously. In such a case the pressure was readjusted to a lower value. On the other hand, if all the hydrates had decomposed, then the hydrates were formed once more as described above, the pressure was adjusted to a value slightly higher than that at which all the hydrates had decomposed, and the observations were continued. Once the equilibrium conditions were established, the temperature of the system was changed and the procedure repeated to obtain another equilibrium condition.

For the first experiment with a fresh electrolyte solution, the "expected" equilibrium pressure was not available and, therefore, the search for the equilibrium pressure involved a large pressure interval. For the subsequent experiments with the solution, the expected equilibrium pressure was estimated using the pressure for the first data and the slope of the linear curve obtained by plotting the pure water data in the form of the log of pressure against inverse temperature (eq 1 below).

Experimental Results and Discussion

Experimental three-phase equilibrium data of aqueous electrolyte solutions, CO_2 hydrate, and vapor are tabulated in Tables III and IV. The compositions of the electrolyte solutions are given in Tables I and II.

Pure Water. In Figure 2 the experimental data in pure water from this work along with those reported in the literature (*6–11*) are plotted. The dashed curve in this figure was computed by the repeated application at a given temperature of the multiphase flash method of Bishnoi et al. (*20*) until the hydrate phase was incipient. As seen from this figure, the predictions match the data very well. The solid curve was obtained from a "best fit" regression of all the data plotted in the linearized form of

$$\ln(P/\mathrm{MPa}) = A/(T/\mathrm{K}) + B \qquad (1)$$

where P is pressure and T is the temperature. The standard error of estimate of the pressure was 73.91 kPa for all the data and 74.54 kPa for all the data excluding those from this work. The standard error of estimate was 13.72 kPa for data from this work only. The results of fitting eq 1 to all the data obtained in this work are given in Table V.

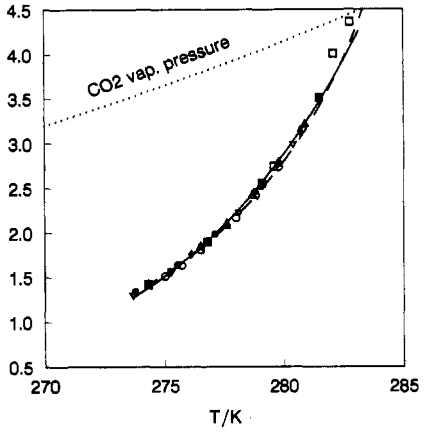

Figure 2. Experimental equilibrium data for CO_2 hydrates in pure water: (○) ref 7; (◇) ref 8; (□) ref 9; (△) ref 10; (▽) ref 6; (■) ref 11; (●) this work, pure water. The solid curve was obtained using regressed constants for eq 1 from Table V. The dashed curve was obtained from predictions.

Electrolyte Solutions. The experimental data with the electrolyte solutions are plotted in Figures 3–7. The solid curves in these figures, as in Figure 2, are obtained from the regression using eq 1. The data of Chen (*6*) for 10.17–10.59 mass % NaCl and those of Larson (*7*) for 5.6 mass % NaCl are also plotted in Figure 3. It is to be noted that whereas the data of Chen (*6*) for 10 mass % NaCl match our data closely, those of Larson (*7*) for 5.6 mass % NaCl lie between our 3 and 5 mass % data. The inhibiting effect of the electrolytes can be seen clearly in these figures: at a given pressure, the equilibrium temperature is lower for higher ionic strength. Equation 1 was fitted to the data in electrolyte solutions. The values of parameters A and B for each electrolyte solution studied together with the standard error of estimate of pressure are given in Table V. The solid curves in Figures 3–7 were drawn using the parameters A and B.

Table V. Constants *A* and *B* (Equation 1) and Standard Error of Estimate (pressure)

solution	*A*	*B*	std Error/kPa	solution	*A*	*B*	std error/kPa
pure water	−9127.46	33.63	13.72	Na3-1 Na3-2 Na3-3	−9637.49	35.64	60.33
Na5-1 Na5-2	−9474.99	35.18	50.49	Na10-1 Na10-2	−9505.50	35.59	79.79
Na15	−9323.15	35.31	43.27	Na20	−9796.83	37.69	47.10
K3	−9623.87	35.56	50.12	K5	−9788.35	36.24	62.13
K10	−9562.36	35.64	54.18	K15	−9831.13	36.88	56.25
Ca3	−9620.34	35.54	78.26	Ca5	−9474.89	35.10	80.77
Ca10	−9452.99	35.33	85.59	Ca15	−8929.01	33.83	71.83
Ca20	−8660.92	33.46	19.35	Na3K3	−9892.96	36.71	72.14
Na5K5	−9537.47	35.61	39.79	Na7K10	9539.63	36.05	4.35
Na15K5	−9370.37	35.83	48.30	sea	−9822.28	36.31	99.67
Na3Ca3	−9590.45	35.61	68.68	Na8Ca2	−9368.48	35.06	39.99
Na2Ca8	−9580.42	35.81	80.30	Na5Ca15	−8727.40	33.70	54.23
Na15Ca5	−8857.44	34.09	25.97				

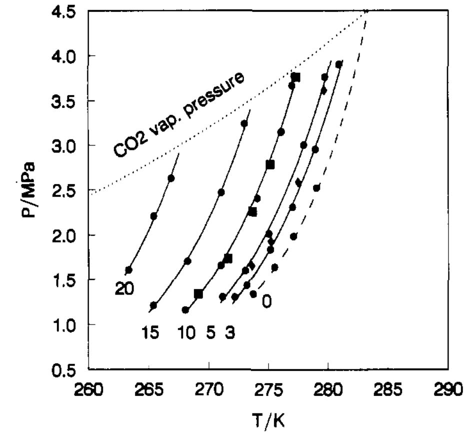

Figure 3. Experimental equilibrium data for CO_2 hydrates in pure water and NaCl solutions: (●) this work; (♦) ref 13, 5.6 mass % NaCl; (■) ref 12, 10.17–10.59 mass % NaCl. The numbers indicate mass percent NaCl in the solution. The solid curve was obtained using regressed constants for eq 1 from Table V. The dashed curve was obtained from predictions.

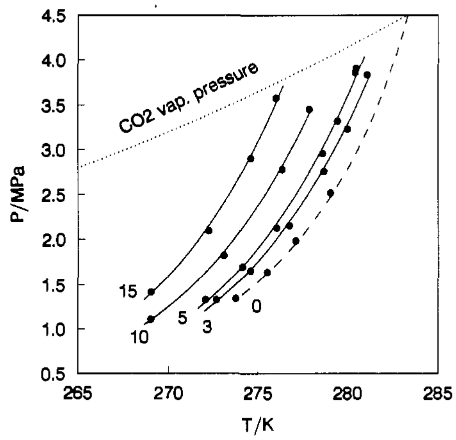

Figure 4. Experimental equilibrium data for CO_2 hydrates in pure water and KCl solutions. The numbers indicate mass percent KCl in the solution. The solid curve was obtained using regressed constants for eq 1 from Table V. The dashed curve was obtained from predictions.

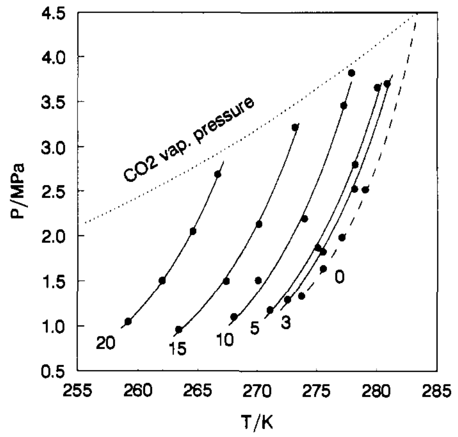

Figure 5. Experimental equilibrium data for CO_2 hydrates in pure water and $CaCl_2$ solutions. The numbers indicate mass percent $CaCl_2$ in the solution. The solid curve was obtained using regressed constants for eq 1 from Table V. The dashed curve was obtained from predictions.

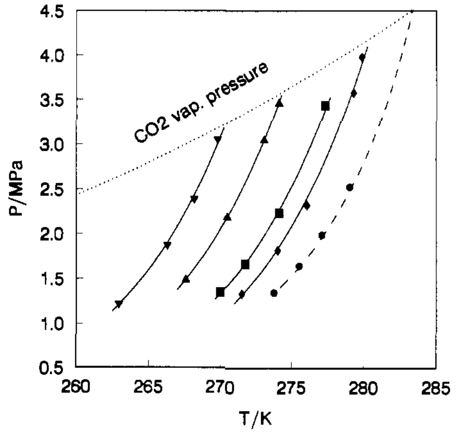

Figure 6. Experimental equilibrium data for CO_2 hydrates in pure water and solutions containing mixtures of NaCl and KCl: (●) pure water; (♦) Na3K3; (■) Na5K5; (▲) Na7K10; (▼) Na15K5. The solid curve was obtained using regressed constants for eq 1 from Table V. The dashed curve was obtained from predictions.

Conclusions

Experimental three-phase equilibrium conditions of aqueous solution, CO_2 hydrate, and vapor in pure water and electrolyte solutions containing NaCl, KCl, $CaCl_2$, and their binary mixtures and in a synthetic sea water solution were obtained in the temperature range of 259–281 K and the pressure range of 0.9–4.1 MPa. The data for pure water were in agreement with the literature values.

Acknowledgment

The authors acknowledge the assistance provided by Louise Perk in obtaining the data in the laboratory.

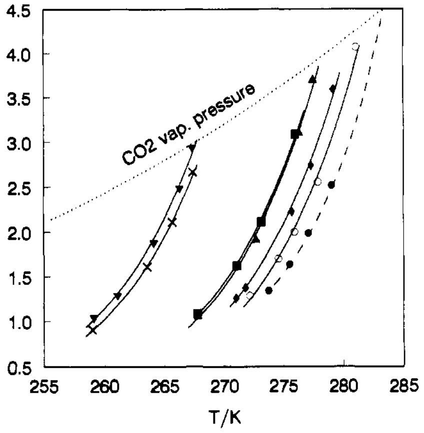

Figure 7. Experimental equilibrium data for CO_2 hydrates in pure water and solutions containing mixtures of NaCl and $CaCl_2$ and synthetic sea water: (●) pure water; (♦) Na3Ca3; (■) Na8Ca2; (▲) Na2Ca8; (▼) Na5Ca15; (×) Na15Ca5; (○) synthetic sea water. The solid curve was obtained using regressed constants for eq 1 from Table V. The dashed curve was obtained from predictions.

Literature Cited

(1) Saji, A.; Yoshida, H.; Sakai, M.; Tanii, T.; Kitamura, H.; Kamata, T. Paper presented at the First International Conference On Carbon Dioxide Removal, Amsterdam, March 1992.

(2) Nishikawa, N.; Morishita, M.; Uchiyama, M.; Yamaguchi, F.; Otsubo, K.; Kimuro, H.; Hiraoka, R. Paper presented at the First International Conference On Carbon Dioxide Removal, Amsterdam, March 1992.

(3) Austvik, T.; Loken, K.-P. Paper presented at the First International Conference On Carbon Dioxide Removal, Amsterdam, March 1992.

(4) Holder, G. D.; Zetts, S. P.; Pradhan, N. *Rev. Chem. Eng.* **1988**, *5* (1–4), 1.

(5) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Mercel Dekker, Inc.: New York, 1990.

(6) Chen, H.-S. The Properties of Carbon Dioxide hydrate. *The Growth Rate of Ice Crystals*: *The Properties of Carbon Dioxide Hydrate. A Review of Properties of 51 Gas Hydrates*; Research and Development Progress Report No. 830; Office of Saline Water, U.S. Department of the Interior: Washington, DC, 1972; p 1.

(7) Larson, S. D. Phase Studies of the Two-Component Carbon Dioxide-Water Systems Involving the Carbon Dioxide Hydrate. Ph.D. Thesis, University of Illinois at Urbana-Champaign, IL, 1955. Data taken from tables reproduced in ref 5.

(8) Robinson, D. B.; Mehta, B. R. *J. Can. Pet. Technol.* **1976**, *10*, 33.

(9) Ng, H.-J.; Robinson, D. B. *Fluid Phase Equilib.* **1985**, *21*, 145.

(10) Deaton, W. M.; Frost, E. M., Jr. *U.S. Bur. Mines Monogr.* **1946**, 8.

(11) Adisasmito, S.; Frank, R. J., III; Sloan, E. D., Jr. *J. Chem. Eng. Data* **1991**, *36*, 68.

(12) Adisasmito, S.; Sloan, E. D., Jr. *J. Chem. Eng. Data* **1992**, *37*, 343.

(13) Englezos, P.; Bishnoi, P. R. *AIChE J.* **1988**, *34*, 1718.

(14) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.

(15) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300.

(16) Patwardhan, V. S.; Kumar, A. *AIChE J.* **1986**, *32*, 1419.

(17) Englezos, P.; Bishnoi, P. R. *Ind. Eng. Chem. Res.* **1991**, *30*, 1655.

(18) Dholabhai, P. D.; Englezos, P.; Kalogerakis, N.; Bishnoi, P. R. *Can. J. Chem. Eng.* **1991**, *69*, 800.

(19) Bishnoi, P. R.; Dholabhai, P. D. *Fluid Phase Equilib.* **1993**, *83*, 455.

(20) Bishnoi, P. R.; Gupta, A. K.; Englezos, P.; Kalogerakis, N. *Fluid Phase Equilib.* **1989**, *53*, 97.

Received for review April 1, 1993. Revised August 2, 1993. Accepted August 10, 1993.[●] Financial assistance for this work was received from the Natural Sciences and Engineering Research Council of Canada (NSERC Strategic Grant), Ottawa, Canada.

[●] Abstract published in *Advance ACS Abstracts,* September 15, 1993.