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Experimental Investigation and Calculation of Methane Hydrate Formation Conditions in the Presence of Ethylene Glycol and Sodium Chloride

C. Eichholz,[‡] A. Majumdar,[†] M. A. Clarke,[†] L. R. Oellrich,[‡] and P. R. Bishnoi*,[†]

Department of Chemical and Petroleum Engineering, The University of Calgary, 2500 University Drive N.W.,
Calgary, Alberta, Canada T2N 1N4, and Institut für Technische Thermodynamik und Kältetechnik,
Universität Karlsruhe, Germany

Experimental three-phase hydrate equilibrium data (aqueous liquid solution, vapor, and incipient solid hydrate) for methane hydrates in aqueous solutions of ethylene glycol and sodium chloride are presented. The data are obtained in the temperature range of (262 to 282) K and pressure range of (2.1 to 9.5) MPa. The incipient hydrate formation pressures are also calculated using the recently developed equation-of-state method of Clarke and Bishnoi. The computed results are compared with the experimental data.

Introduction

Gas hydrates, or more exactly, clathrate hydrates are solid compounds of water and low molar mass nonpolar or slightly polar gases. Generally, they are stable at high pressures and low temperatures. Hydrates grow in a recurring crystal structure, and in the case of pure methane, the structure I is formed. Detailed descriptions of physical and structural properties of gas hydrates can be found in the literature.[1,2]

Hydrates generally are perceived as troublemakers for the gas and oil industry. They are known to cause plugging of pipelines or valves and erosion of equipment surfaces. Viscosity changes in crude oil, due to the formation of hydrates, can also be a handicap for the oil industry. At drilling sites, dissociation of solid hydrates present in natural formations may cause damage and leakage due to uncontrolled gas release, blowouts of the wellhead, etc. The decomposition of in situ gas hydrates on marine floors could influence the stability of submarine shelves; also, the released methane contributes to greenhouse effects.

Gas hydrates are no longer only seen as source of trouble. Nowadays, several hydrate fields (off shore as well as on shore) are being investigated to examine the viability of extracting gas from the deposits. Gas hydrates have a high energy density, and thus hydrate deposits in nature could present a new energy resource. In addition, the use of hydrates for gas storage and transportation is considered a viable option. Concentration of solutions or fruit juices and desalination of seawater with the help of gas hydrates may bring significant energy savings. Taking advantage of a driving force of a gas in mixtures to form hydrates may lead to design simple separation processes for gas mixtures.

To avoid the problems associated with the hydrate formation, to exploit the hydrates as an energy resource or to utilize hydrates to develop new technologies, there is a need to obtain phase equilibrium data and develop prediction methods for pure water as well as for aqueous systems containing inhibitors like electrolytes and alcohols. The thermodynamic inhibitors shift the three-phase equilibrium line in a way that the formation of hydrates becomes more difficult. The hydrate suppression ability of the inhibitors is a consequence of their ability to reduce the activity of water. Generally they are alcohols, glycols, and electrolytes. Ethylene glycol has been used as a common inhibitor in the industry for many years. Experimental hydrate equilibrium data for aqueous systems of ethylene glycol (EG) are available[3−10] for methane, ethane, propane, carbon dioxide, hydrogen sulfide, mixtures of methane and propane, and mixtures of methane and carbon dioxide. The experimental data on hydrate equilibrium for mixtures of methane and carbon dioxide in aqueous solutions of EG in the presence of calcium chloride and mixtures of calcium chloride and sodium chloride are reported by Dholabhai et al.[6] and Bishnoi et al.[7,8] Majumdar et al.[11] report data for the hydrate equilibrium of hydrogen sulfide, carbon dioxide, and ethane in the aqueous solutions of EG and sodium chloride. However, experimental hydrate equilibrium data for methane in the aqueous solutions of EG and sodium chloride have not been reported. Such data are useful in industrial design applications as well as for testing predictive models. Hence, in the present work, experimental three-phase (aqueous liquid solution, vapor, and incipient solid hydrate) equilibrium data for methane hydrates in aqueous solutions of EG and sodium chloride are presented. The data are obtained in the temperature range of 262−282 K and pressure range of 2.1−9.5 MPa. The incipient hydrate formation pressures are also calculated using the recently developed equation-of-state method of Clarke and Bishnoi.[12,13] The computed results are compared with the experimental data.

Experimental Apparatus and Procedure

The hydrate equilibrium data in this work are obtained using the experimental apparatus and procedures similar to those described by Dholabhai et al.[6] and Mahadev and Bishnoi.[14] The heart of the apparatus is a high-pressure

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* To whom correspondence may be addressed. E-mail: bishnoi@ucalgary.ca.
[†] The University of Calgary.
[‡] Universitaet Karlsruhe.

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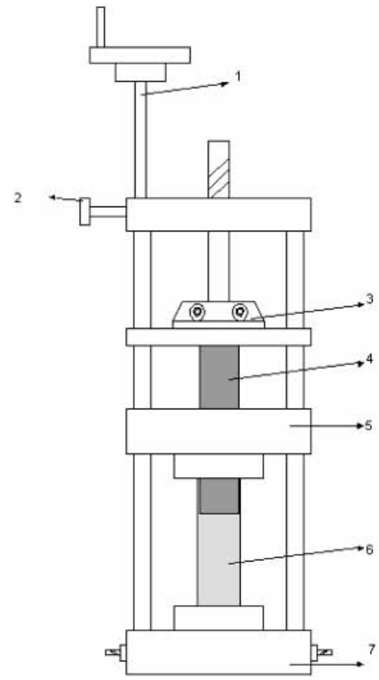

Figure 1. Schematic drawing of the equilibrium cell. 1, Gear drive mechanism for piston movement; 2, gear lock; 3, piston head with ports; 4, piston; 5, stanless steal flange; 6, sapphire tube; 7, stainless steel flange with ports.

Table 1. Experimental Methane Hydrate Equilibrium Conditions in Aqueous Solutions of Ethylene Glycol and Sodium Chloride

EG mass %	NaCl mass %[a]	T/K	P_{exp}/MPa	T^b/K	P^b/MPa
19.16	0	266.5	2.136	266.1	2.108
		272.6	3.815	272.6	3.769
		279.5	8.620	279.8	8.574
5.77	3.77	271.1	2.811	271	2.777
		274.5	3.968	274.6	3.932
		277.9	5.491	277.9	5.471
		281.2	8.109	281.1	8.076
15.36	3.77	267.1	2.392	267.1	2.353
		270.8	3.735	270.8	3.706
		274.3	5.314	274.4	5.264
		279.4	9.558	279.5	9.531
23.88	3.77	262.8	2.264	262.8	2.231
		266.6	3.308	266.7	3.291
		270.3	5.055	270.3	5.032
		276.1	9.489	276	9.450
3.77	15.67	264.9	2.772	264.9	2.732
		268.4	4.191	268.5	4.142
		272.2	6.384	272.2	6.345
12.07	15.01	263.6	3.497	263.5	3.448
		267.0	5.156	267.0	5.120
		270.6	7.690	270.5	7.637

[a] On wet basis. [b] Data denote the no hydrate point.

variable-volume equilibrium cell.[15,16] A schematic of the cell is shown in Figure 1.

The high-pressure cell consists of a sapphire tube (19.05 mm i.d. × 38.1 mm o.d. × 114.3 mm long), which is held by top and bottom stainless steel flanges. Three studs are keeping the tube and the two flanges together. The volume, ranging from (64 to 74) mL, can be changed by means of a movable piston that can be moved up and down with a manual gear assembly. Both the bottom flange and the piston have several junctions for charging the liquid and vapor phases, for the pressure measurement, for the vapor-phase sampling, and for the introduction of the thermocouple. The thermocouples are calibrated using a precision thermometer in the range of 263 K to 292 K with a standard deviation of the least-squares fit of 0.09 K. A magnetic stir bar is utilized to mix the liquid cell content driven by a rotating magnet, which is placed below the cell. The cell is immersed into a constant-temperature bath. An EG−water solution is used as a coolant. The cell pressure is measured with a Rosemount differential pressure transmitter (DP). The span of the DP is 11 MPa with a combined uncertainty of 0.25% of the span. It is calibrated against a dead-weight tester. The cell pressure and the temperatures measured with the DP and the thermocouples, respectively, are sampled at predetermined intervals. They are displayed and stored on a PC using a data logger.

The samples are prepared by mass, using a top-loading Mettler balance with a readability of 0.001 g. Sodium chloride (Merck) with a certified purity of 99.9% and 99.5% EG (Anachemia) are added to demineralized and twice-distilled water to prepare the experimental solutions. The experimental gas, methane, with a purity of 99.97% is supplied by PRAXAIR.

Prior to each series with a new sample, the cell is rinsed several times with distilled water and once with the experimental solution. The whole system is repeatedly flushed with methane. For the experiment, about 15 cm^3 of the sample are introduced into the cell. Four equilibrium points are detected for each solution. The “pressure-search” method[17] is used to find the incipient equilibrium point. The hydrates are detected visually.

Once the temperature is constant, the corresponding pressure is detected by reducing the pressure range, which includes the equilibrium pressure. The span is defined by two limits where hydrates form and decompose. Setting the new pressure between the limits reduces the range. At the pressures where the hydrates stay stable or deplete, a new upper or lower limit is found. This procedure is repeated until the pressure span is small and only minimal quantity of hydrates are present in the solution. If these conditions remain constant for 3−4 h, they are taken as the equilibrium point. If the remaining hydrates decompose by reducing the pressure by a maximum of 50 kPa, the equilibrium point is considered the incipient hydrate point.

Experimental Results and Discussion

The experimental three-phase equilibrium data for the EG solutions, studied in this work, are presented in Table 1. The table reports the equilibrium pressures (P_{exp}) at the corresponding temperatures along with the pressures and temperatures where hydrates are not stable.

Figure 2 shows the experimental data, obtained in this work, for the 19.16 mass % EG solution and the experimental data of Rock[18] for the 19.09 mass % EG solution. The two sets of experimental data are in close agreement. The figure also shows the predictions using the Trebble−Bishnoi equation of state (TBEOS)[19,20] for the vapor and liquid phases and the statistical thermodynamic model of van der Waals and Platteeuw[21] for the solid hydrate phase. It is seen from the figure that the experimental data are consistent with and in good agreement with the predictions. It is noted that the errors in the pressure predictions generally increase as the temperature increases. The maximum absolute relative error in the pressure is found to be 2.25%. The predictions for pure water are included to indicate the shift of the equilibrium line due to the inhibitor addition.

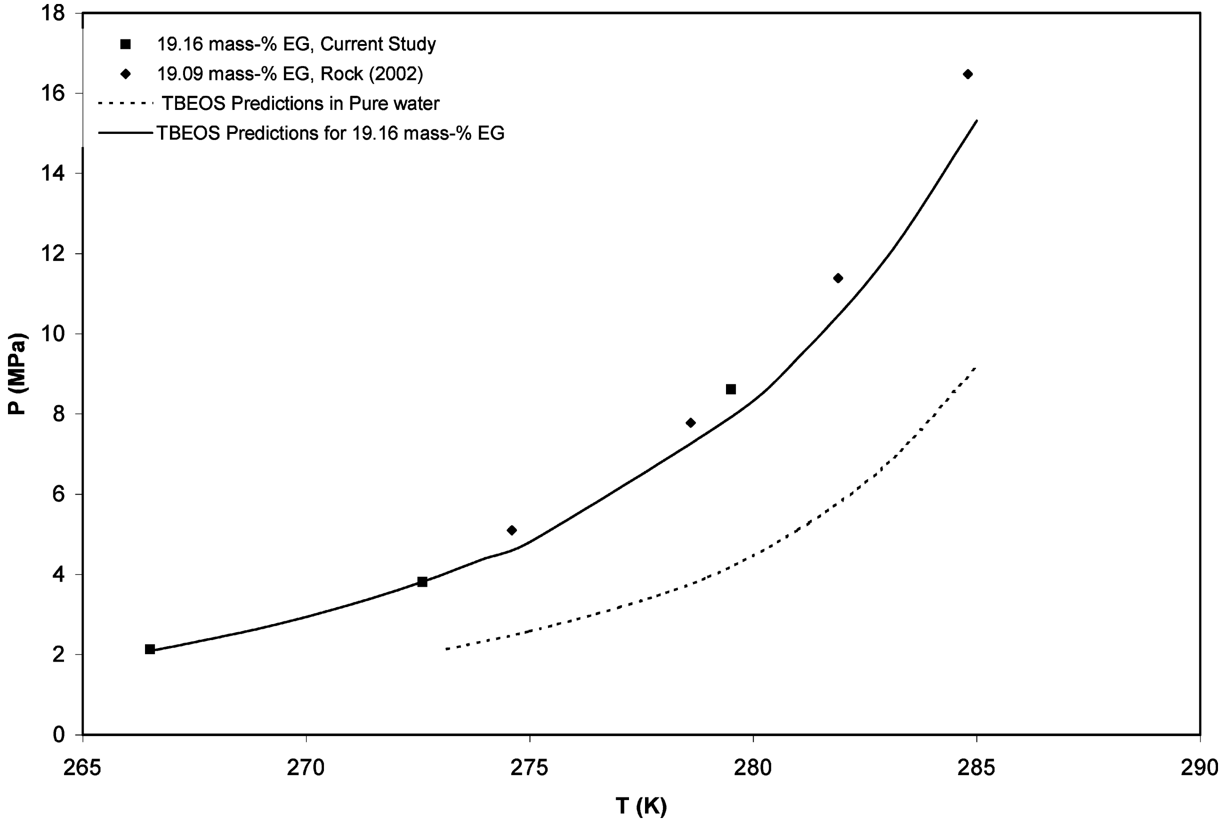

Figure 2. Incipient methane hydrate formation conditions in aqueous solutions of EG.

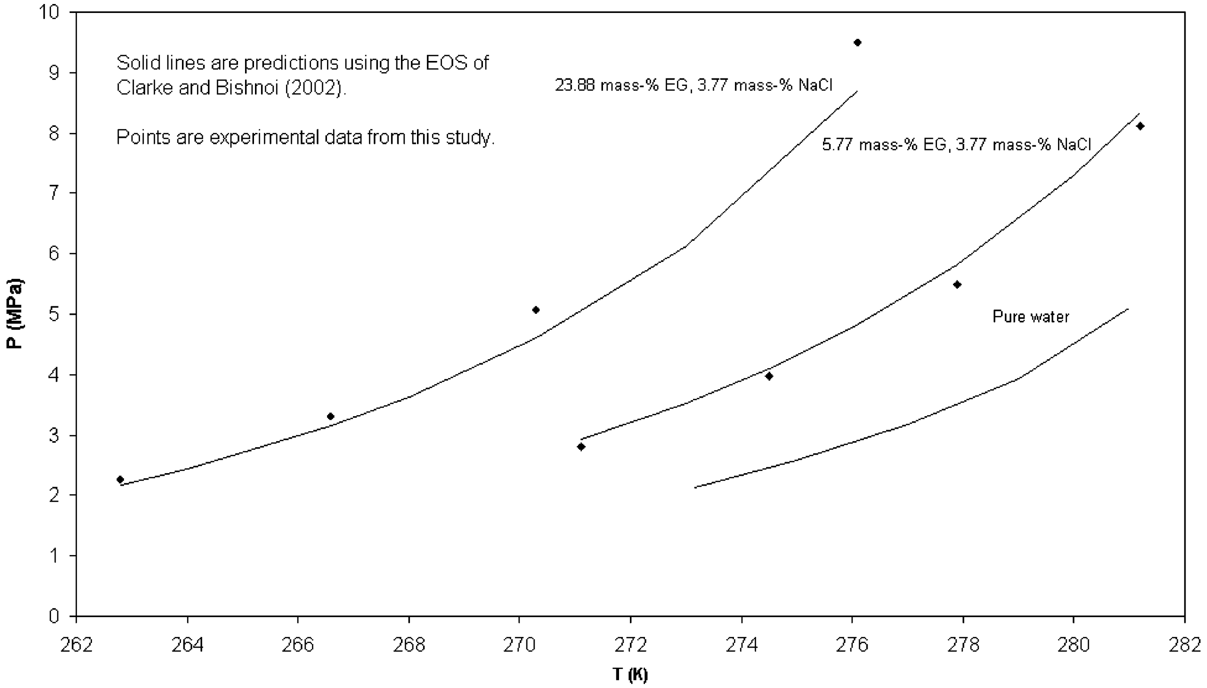

Figure 3. Incipient methane hydrate formation conditions in aqueous solutions of EG and NaCl.

The experimental equilibrium data for the aqueous solutions of EG and sodium chloride are shown in Figures 3 and 4. The figures also show the predicted values of the hydrate equilibrium conditions. The predictions are made using the TBEOS for the vapor, the statistical thermodynamic model of van der Waals and Platteeuw for the solid hydrate phase, and the equation of state recently proposed by Clarke and Bishnoi,[12,13] which is given in eq 1, for the liquid aqueous solution containing EG and NaCl. The TBEOS[19,20] can be obtained from eq 1 by neglecting the electrolyte terms, which are the third through to the seventh terms on the right-hand side of the equation. It is noted from the figures that the experimental data are consistent with and in good agreement for engineering applications with the predictions. It is again noted that the errors in the pressure predictions generally increase as the

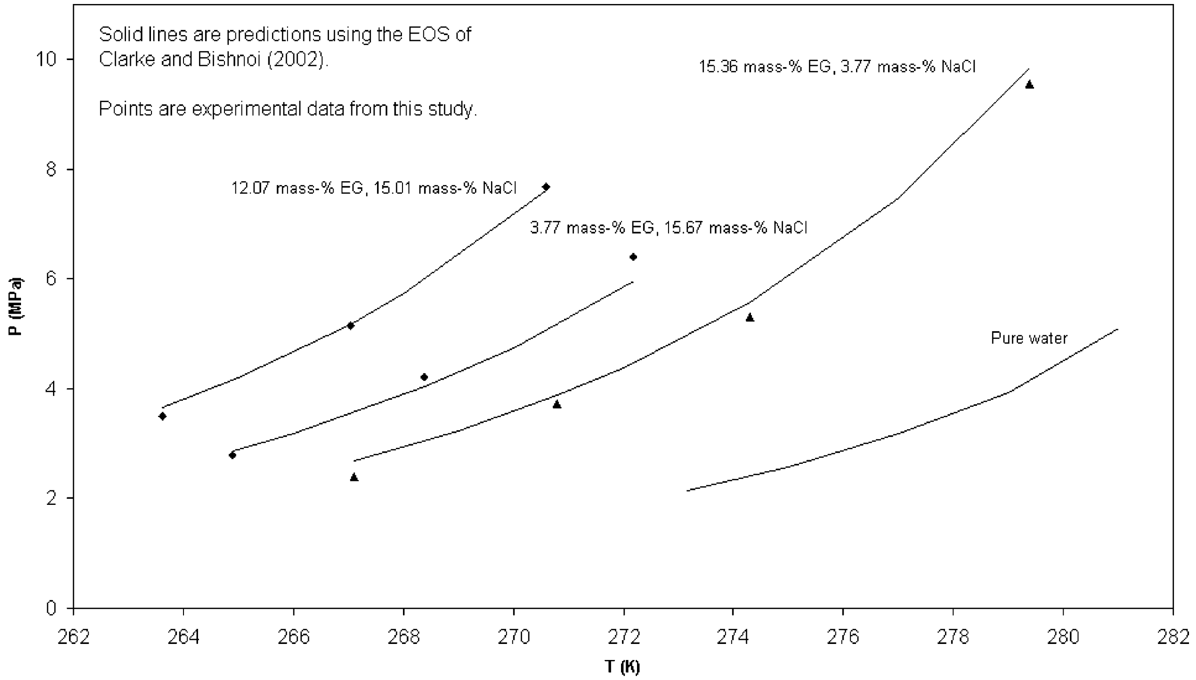

Figure 4. Incipient methane hydrate formation conditions in aqueous solutions of EG and NaCl.

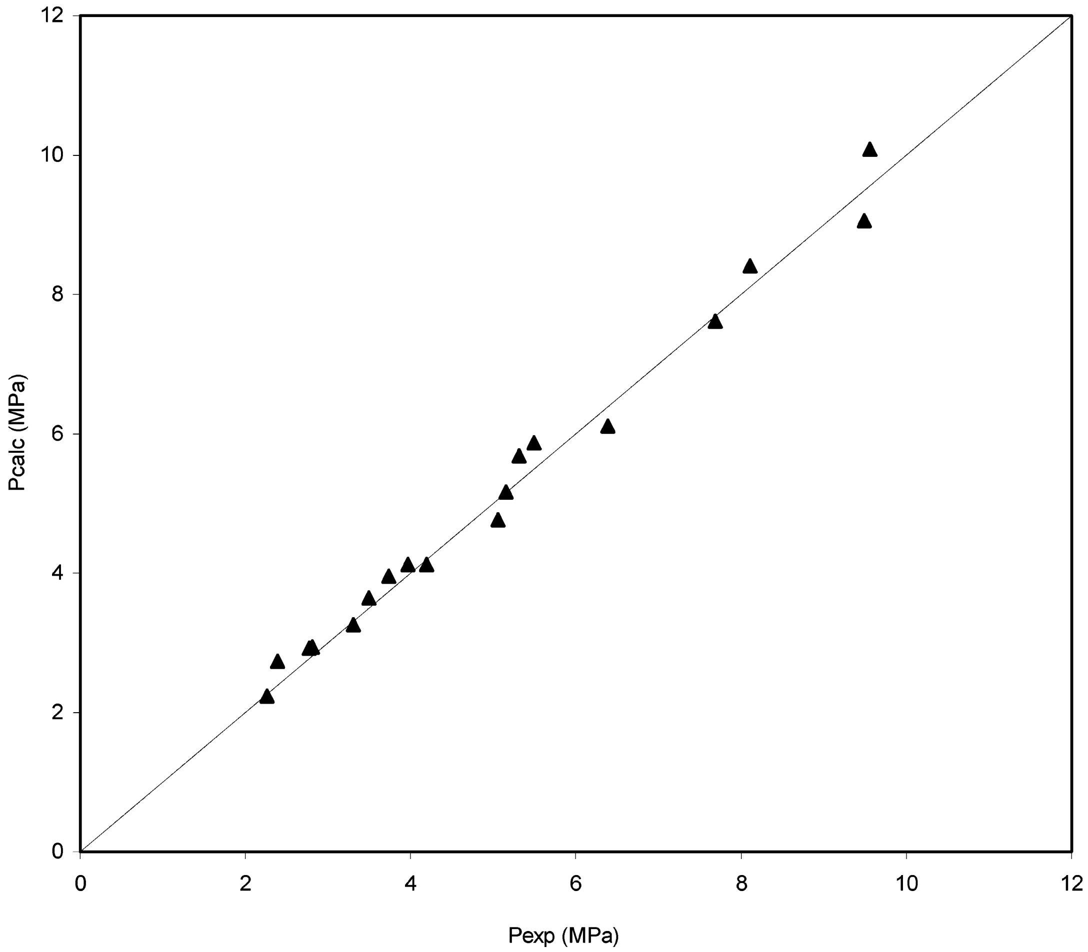

Figure 5. Comparison of the experimental and the calculated methane hydrate equilibrium pressures.

temperature increases. The deviations in the predicted pressures from the experimental pressures are shown in Figure 5. It is seen that the predictions are well distributed about the 45° line, indicating the validity of the model. The relative absolute errors in the predictions were all between 2 and 8%, except for the point for the solution containing 15.36 mass % EG and 3.77 mass % NaCl at 267.1 K, which had an error of 12%. It is further noted from the data and the predictions that sodium chloride is a stronger inhibitor than EG.

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2 + (b + c)nV - (bc + d^2)n^2} - RT\sum_{i=1}^{NI}\frac{(z_ie)^2Nn_i}{4\pi\epsilon_oD^2\sigma_i}\left(\frac{\partial D}{\partial V}\right)_{T,ni} - \frac{\alpha^2NRT}{4\pi D}\left(\frac{\partial D}{\partial V}\right)_{T,ni}\sum_{i=1}^{NI}\frac{\Gamma n_iz_i^{\,2}}{1 + \Gamma\sigma_i} + \frac{\alpha^2NRT}{4\pi}\left(\frac{\partial\Gamma}{\partial V}\right)_{T,ni}\sum_{i=1}^{NI}\frac{n_iz_i^{\,2}}{1 + \Gamma\sigma_i} - \frac{\Gamma^3RT}{3\pi N} - \frac{\Gamma^2VRT}{\pi N}\left(\frac{\partial\Gamma}{\partial V}\right)_{T,ni} \quad (1)$$

Conclusions

Experimental hydrate equilibrim data for methane in aqueous solutions of EG and sodium chloride are obtained in the temperature range (262 to 282) K and the pressure range (2.1 to 9.5) MPa using a variable-volume sapphire cell. Furthermore, incipient hydrate formation pressures are calculated using the new equation of state of Clarke and Bishnoi.[12,13] The calculated data agree well with the experimental results for engineering applications.

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