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Equilibrium conditions of the methane and natural gas hydrates formation in sodium bicarbonate solutions

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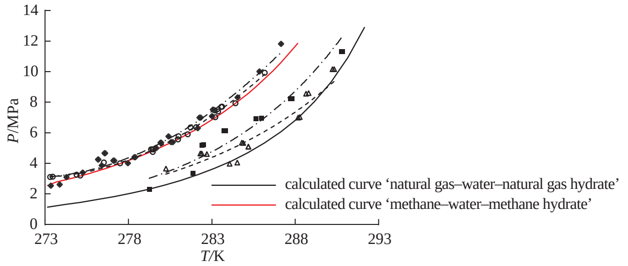
Empirical correlations were obtained to calculate the equilibrium pressure of the methane and natural gas (the Srednevilyui gas and condensate field) hydrates formation in sodium bicarbonate solutions, the hydration numbers and dissociation heats of these hydrates were determined. The values of the hydration numbers assume that methane forms hydrates with the CS-I structure and natural gas – CS-II. The dissociation heat of the natural gas hydrates is higher than that of the methane hydrates.



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The study of the hydrate formation features is of great importance for understanding the mechanisms of the hydrate formation, ensuring the safety of oil and gas production, implementation of hydrate technologies for the storage and transportation of raw hydrocarbons, separation of gas mixtures, utilization of greenhouse and toxic gases, water desalination, *etc*.[1–6] Therefore, there is a need to investigate the hydrate formation and dissociation processes in relation to the various factors: gases and hydrate-forming media composition, presence of the hydrate formation promoters or inhibitors, *etc*.[7–9]

A great deal of experimental works has been concerned with the study of equilibrium conditions of the gas hydrates formation in the presence of electrolyte solutions, especially sodium chloride solutions, that is associated with the discovery of huge gas hydrates deposits on the continental shelf. Gas hydrates in nature are also found in the areas of permafrost occurence where they are formed provided a gas presence, a water-saturated permeable reservoir and low mineralization of stratum waters at a certain combination of temperature and pressure. Stratum waters under the foot of permafrost rocks belong to the calcium chloride and sodium bicarbonate types and their mineralization varies in a wide range.[10] The only experimental work has been devoted to the study of equilibrium conditions of the hydrate formation in sodium bicarbonate solutions.[11] Therefore, there are no adequate analytical dependences to predict the equilibrium conditions of hydrate formation.

Here we present the results of exploration of the equilibrium conditions of methane and natural gas hydrate formation in 0.25 and 2 wt% sodium bicarbonate solutions given that the concentrations correspond to the mineralization range of sodium bicarbonate type stratum waters.[10] The experiments were carried out by the thermal analysis method. The technique was described in details in recent works.[12,13] To obtain hydrates, methane (99.99%) and natural gas of the Srednevilyui gas and condensate field of the following composition (mol%) were used: 93.88 methane, 4.44 ethane, 1.10 propane, 0.087 isobutane, 0.107 *n*-butane, 0.056 carbon dioxide and 0.33 nitrogen. The results obtained for the systems methane/natural gas–sodium bicarbonate solutions–methane/natural gas hydrate in comparison with the calculated equilibrium curves methane/natural gas–water according to the Sloan[1] method are shown in Figure 1. Each point, *i.e.*, equilibrium temperature and pressure, is an average of 5 experiments.

The equilibrium conditions in the systems methane–sodium bicarbonate solutions–methane hydrate and natural gas–sodium bicarbonate solutions–natural gas hydrate are shifted to lower temperatures and high pressures region in comparison with the hydrate formation in water. The higher the concentration of the solution, the greater the shift of the equilibrium curve. The equilibrium curve of methane hydrate formation in 0.25 wt% sodium bicarbonate solution in the temperature range of 273–286 K with high approximation accuracy ($R^2 = 0.9924$) is described by the equation:

$$\ln P = 31.474 - \frac{8358.3}{T} \quad (1)$$

and in 2 wt% solution ($R^2 = 0.9922$ in the temperature range of 273–287 K) – by the equation:

$$\ln P = 35.15 - \frac{9391.9}{T}, \quad (2)$$

where T/K and P/MPa.
For the system natural gas–sodium bicarbonate solution–natural gas hydrate in 0.25 and 2 wt% solutions the corresponding equations were obtained:

$$\ln P = 35.084 - \frac{9531.5}{T}, \quad (3)$$

$$\ln P = 42.091 - \frac{11537}{T}. \quad (4)$$

Table 1 Heat of dissociation of hydrates ΔH and hydration numbers n.

Concentration of $NaHCO_3$ solution (wt%)	I/mol kg^{-1}	ΔH/kJ mol^{-1}	The value of the approximation reliability R^2	n	Temperature range/K
Methane–sodium bicarbonate solution–methane hydrate system					
0.25	0.030	69.491	0.9924	6.346	273–286
2.0	0.243	78.084	0.9922	7.628	273–287
Natural gas–sodium bicarbonate solution–natural gas hydrate system					
0.25	0.030	79.245	0.9847	7.139	280–290
2.0	0.243	95.919	0.9873	9.182	279–291

The value of the approximation reliability R^2 of equation (3) in the temperature range of 280–290 K is 0.9847 and of equation (4) in the temperature range of 279–291 K is 0.9873.

The dissociation heats of methane hydrates were calculated from the Clausius–Clapeyron equation. The possibility of using this equation to describe three-phase equilibria with hydrate formation has been substantiated by many scientists. Comparison of the dissociation enthalpies of mixed gas hydrates calculated by the Clausius–Clapeyron equation with direct measurements *via* the differential scanning calorimetry showed that this equation gives acceptable results.[14–16] The results are presented in Table 1. According to the earlier work,[17] the hydrate formation enthalpy for electrolyte solutions is a function of pressure P and ionic strength of the electrolyte solution I:

$$\frac{-\Delta H}{nR} = \frac{e_1 I^{e_2}}{1 + e_3 P + e_4(\ln P)}, \tag{5}$$

where coefficients are adjustable parameters determined from the experimental data of the hydrates formation in electrolyte solution equal to: $e_1 = 597.33$, $e_2 = -0.0409$, $e_3 = 0.0000227$ and $e_4 = -0.0751$.

Furthermore, the ionic strength of the solution depends on the ion concentration in the solution C_i:

$$I = \frac{1}{2}\sum_{i=1}^{n} Z_i^2 C_i\,, \tag{6}$$

where Z_i is the ion charge.

The authors[17] believe that e_n parameters can be applied to any gas and single salt or mixed electrolyte solution. Using the obtained dissociation heats of hydrates, the hydration numbers were calculated from the equations (5) and (6) (see Table 1).

The obtained data show that the dissociation enthalpies of methane and natural gas hydrates rise with an increase of the concentration of the sodium bicarbonate solution. It is known[1] that the dissociation enthalpy of a hydrate depends on the degree of the cavities filling out, and the enthalpy increases when only large cavities are filled. The higher heats of natural gas hydrates dissociation compared with the methane hydrates are probably due to their different structures.

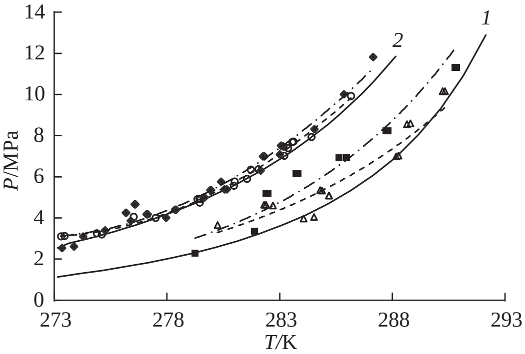

Figure 1 Equilibrium curves of the gas hydrate formation in the systems: (*1*) – calculated curve (natural gas–water–natural gas hydrate); △ – experimental points (natural gas–0.25 wt% $NaHCO_3$ solution–natural gas hydrate); ■ – experimental points (natural gas–2 wt% $NaHCO_3$ solution–natural gas hydrate); (*2*) – calculated curve (methane–water–methane hydrate); ○ – experimental points (methane–0.25 wt% $NaHCO_3$ solution–methane hydrate); ◆ – experimental points (methane–2 wt% $NaHCO_3$ solution–methane hydrate).

The calculated n values are typical for hydrates of the CS-I structure in the case of methane and CS-II – for natural gas. In methane hydrate obtained in 0.25 wt% sodium bicarbonate solution, both large and small cavities of the crystal structure are filled with gas molecules, whereas only large cavities are filled when the hydrate is formed from 2 wt% solution. The dissociation heat of the hydrate in 0.25 wt% solution is lower than for 2 wt% solution, inasmuch as the dissociation heat of the hydrate with filled small and large cavities is less than for a hydrate with only large cavities filled out.[1] Natural gas in sodium bicarbonate solutions forms hydrates with filling of both cavities, and in 2 wt% solution the proportion of large cavities filled with guest molecules is higher. To confirm the relationship between the structure of hydrates formed in sodium bicarbonate solutions and their dissociation enthalpy, additional structural studies of hydrates are required.

Thus, new data on the equilibrium conditions of the methane and natural gas hydrates formation in sodium bicarbonate solutions have been obtained. The calculated values of hydration numbers revealed the CS-I structure for the methane hydrates and CS-II for the natural gas hydrates. It has been shown that the dissociation heats rise with an increase of the sodium bicarbonate solutions concentration, while the dissociation heat of the CS-II hydrates is higher compared with the CS-I hydrates.

The obtained results complement the available information on the hydrate formation processes in electrolyte solutions. New data on the equilibrium conditions of the methane and natural gas hydrate formation may be useful for understanding the gas hydrate deposits formation in subpermafrost aquifers with sodium bicarbonate type of water.

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