The Influence of Electrolytes Composition on the Dissociation Rate of Natural Gas Hydrates Obtained in Model Stratum Waters

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Abstract. The study of the hydrates formation and decomposition kinetics in solutions of electrolytes is of interest due to the possibility of natural gas storing and transporting in a hydrate state, since the presence of impurities in water is inevitable under appropriate industrial processes. The kinetic parameters of decomposition reactions of natural gas hydrates obtained in model solutions simulating the composition and concentration of stratum waters of East Siberian fields are studied. These deposits are located within the Leno-Tunguskaya and Lena-Vilyuiskaya oil and gas provinces (OGP). The deposits of the Leno-Tunguskaya OGP are characterized by abnormally low reservoir temperatures and pressures (10° C and 16 MPa). The stratum waters belong to the chloride-calcium type, and by the type of the predominant cation either to the calcium or to the sodium subgroup of waters. The mineralization of stratum water can reach 400 g / l and higher. The abnormal high reservoir pressure is 36.3 MPa, the temperatures reach +66 ºС for deposits of the Lena-Viluiskaya OGP. Mineralization of stratum water is from 40 to 180 g / l, there may be waters of chloride-calcium (subgroups of calcium and sodium) and sodium bicarbonate (subgroup of sodium) types. Therefore, hydrates of natural gas were obtained in model solutions of calcium and sodium chlorides, and also in solutions of sodium bicarbonate. The rate constants of hydrate decomposition reactions are determined by the Erofeev equation. The shape of the kinetic curves of hydrate decomposition depends on the type and degree of the model stratum water mineralization. The values of the constants n for the decomposition reactions of all hydrate samples are greater than one. This means that these reactions occur in the kinetic region, that is, the rate of hydrates decomposition is determined by the rate of physical desorption of the gas from the clathrate lattice. It has been established that the rate of hydrates decomposition increases with increasing mineralization, and it is higher in the presence of calcium chloride solutions than sodium chloride.

1. Introduction
Gas hydrates are solid crystalline compounds of water and low-molecular weight hydrocarbons [1-4]. They are of interest as a potential natural gas resource [5-7], as a medium for the storage and transportation of natural gas [8-10] and so on. The study of the hydrates formation and decomposition kinetics in solutions of electrolytes is of interest due to the possibility of natural gas storing and transporting in a hydrate state, since the presence of impurities in water is inevitable under appropriate industrial processes. An analysis of contemporary literature has shown that most of the publications...
devoted to this problem are related with the construction of thermodynamic dependences of the effect of electrolyte solutions on the equilibrium curves of the hydrate formation [11-17], while publications devoted to experimental study of this process are obscure [18-21].

2. Experimental

The decomposition processes of natural gas hydrates obtained in 100 ml of distilled water, as well as in solutions of sodium chloride and sodium bicarbonate of various concentrations at a gas pressure equal to 8 MPa, were investigated. Concentrations of salt solutions corresponded to the general mineralization of stratum waters of hydrocarbons deposits of Eastern Siberia.

To study the kinetic features of hydrates decomposition, it was necessary to determine the rate of release of the gas trapped in the hydrates. For this purpose, the experimental setup was assembled (Figure 1). The following experiment was performed on it: the sample of the hydrate was placed in a sealed chamber (1) immersed in a thermostat (2) set at a temperature of 278 K. A gas counter of a drum type was connected to the chamber GSB-400 (3). If it is necessary to further study the released gas, it could be taken to the gas burette (4). The volume of evolved gas was measured every minute.

Figure 1. The installation scheme for the natural gas hydrates decomposition.

Based on the obtained values of the released gases volumes, the relative degree of solutions conversion into hydrates ($\alpha_{\text{H}_2\text{O}}$) was calculated by the formula:

$$\alpha_{\text{H}_2\text{O}} = \frac{V_i}{\max V_{\text{H}_2\text{O}}}$$  (1)

where $V_i$ – the volume of gas released from the hydrate obtained in the mineralized solution at the current time; $\max V_{\text{H}_2\text{O}}$ – the maximum volume of gas released from the hydrate formed in distilled water.

Based on the calculated values, curves of $\alpha_{\text{H}_2\text{O}}$ dependence on the conversion time and concentration of the studied solutions were plotted.

Figure 2 shows that the value of $\alpha_{\text{H}_2\text{O}}$ for all solutions of sodium sodium bicarbonate is greater than one, whereas for sodium chloride solutions this parameter is less than one. These facts indicate that the present anions have different effects on hydrate formation in electrolyte solutions. If the presence of bicarbonate anions contributes to the formation of hydrates, the presence of chloride anions reduces the completeness of the solution conversion into hydrates with increasing salt concentration in the solution (Figure 3a).
Figure 2. Dependence of the relative degree of conversion ($\alpha_{\text{H}_2\text{O}}$) on time, nature and concentration of hydrate-forming solution.

Figure 3. Dependence of the relative degree of natural gas hydrates conversion ($\alpha_{\text{H}_2\text{O}}$) on the concentration of chloride (a) and sodium bicarbonate (b) solutions.

For solutions of sodium sodium bicarbonate, the non-linear dependence of $\alpha_{\text{H}_2\text{O}}$ on the concentration is observed, where the maximum on the presented curve corresponds to the concentration of sodium bicarbonate equal to 0.5 mass% (Figure 3 b).

To determine the effect of sodium bicarbonate and chloride anions on the kinetic features of the decomposition of natural gas hydrates formed in mineralized solutions, the rate constants of expansion were calculated by the Erofeev equation (2), which is most often used for the analysis of isothermal solid-phase reactions [22]:

$$\alpha = 1 - \exp(-kt^n)$$  \hspace{1cm} (2)

where $k$ is the generalized rate constant; $t$ is the decomposition time, $n$ is the kinetic parameter.

The applicability of the Erofeev equation (2) for modeling the kinetics of hydrate formation from mixtures of hydrocarbon gases is shown in [23].

The kinetic parameters $n$ and $k$ can be found by using of the double logarithm of the equation (2) and representing it in the form:

$$\lg\left[-\lg(1-\alpha)\right] = n\lg t + \lg k + \lg (\lg e)$$  \hspace{1cm} (3)

In this form (3), the Erofeev equation is a straight line, which makes it easy to calculate the values of the parameters $n$ and $k$ (see Figure 4-5), constructing logarithmic anamorphoses. In this case, the
parameter \( n \) characterizes the main driving force of the reactions under consideration, for example, if \( n > 1 \) the process proceeds predominantly in the kinetic region, and \( n < 1 \) - in the diffusion one.

\[
K = n k^{1/n}
\]  

(4)

The found kinetic parameters and the rates of hydrate decomposition processes calculated on their basis at a temperature of 278 K are given in Table 1.
Table 1. Kinetic characteristics of decomposition reactions of hydrates synthesized in different liquid phases

| Solution | H₂O   | NaCl 5% | NaCl 10% | NaCl 15% | NaHCO₃ 0.25% | NaHCO₃ 0.5% | NaHCO₃ 1% | NaHCO₃ 2% |
|----------|-------|---------|----------|----------|---------------|-------------|----------|----------|
| n Reaction Area | 1.4995 | 2.2636  | 1.7913   | 1.3304   | 1.2132        | 1.0264      | 1.0146   | 1.1585   |
| K, min⁻¹   | 0.0289 | 0.0037  | 0.0468   | 0.1269   | 0.0739        | 0.0656      | 0.0762   | 0.0633   |

It can be seen from the table that for the decomposition processes of hydrates formed both from solutions of sodium bicarbonate and from solutions of sodium chloride, of all considered concentrations, the kinetic parameter $n > 1$, that is, the rate of decomposition of hydrates is determined by the rate of physical desorption. It should also be noted that the rate of decomposition of hydrates formed in solutions of sodium chloride is higher than the rates of decomposition of hydrates formed in water and sodium bicarbonate solutions. At the same time, the rate of decomposition of hydrates formed in solutions of sodium bicarbonate with a concentration of 0.5% is half that of hydrates formed in distilled water.

Thus, it has been established that the presence of anion in water solutions promotes more complete hydrate formation than distilled water, and also significantly slows down the rate of decomposition of these hydrates. The most complete conversion of natural gas into hydrate occurs in solutions of sodium bicarbonate with a concentration of 0.5%, which contributes to the slowest decomposition of such hydrate. The presence of chloride anions in solution, as their concentration increases, reduces the ability of natural gas to form hydrates, and also increases the rate of their decomposition.

The results presented in this paper can be used in the industrial production of hydrates for the purpose of natural gas storing and transporting. In particular, it has been shown that for the production of natural gas hydrates it is advisable to use solutions of sodium bicarbonate with a concentration of 0.5%, since they are 20-40% more effective in forming hydrates than in distilled water and more thermodynamically stable.

3. References

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