KINETICS OF METHANE HYDRATE FORMATION IN HIGHLY MINERALIZED WATER SOLUTIONS

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ABSTRACT

The East Siberian gas-condensate fields in Russia have some specific conditions for gas production. The low gas-bearing horizon temperatures, high mineralization of formation water, the salt deposits in porous space in gas-bearing horizon and low water dew point of natural gas complicate the technology of natural gas recovery. All these factors cause the technological problems as the secondary hydrate formation in bottom-hole area and hydrate and salt plugging in wellbore and gathering pipelines. The investigation of hydrate formation kinetics is necessary in wide range of pressure and temperature to optimize thermodynamic conditions in wellbore and gas gathering pipelines. The study of methane hydrate formation in highly mineralized solutions proves the methods of hydrate plugging prevention.

The kinetics of methane hydrate formation in highly mineralized solutions was studied. The experimental hydrate cell was constructed based on gas-liquid reactor with "pressure-temperature" automatic control system. The control system was able to measure the methane quantity to maintain the gas pressure in the process of gas hydrate formation. The procedures to study the kinetics of hydrate formation in mineralized water were developed in pressure range 2.5 – 15.0 MPa. The hydrate formation in aqueous solutions of Na chlorides was studied. The kinetic model for hydrate formation in mineralized water was presented. The dependency of kinetic constants on the process driving force was discussed.

It was experimentally shown the formation rate of the methane hydrate in mineralized water was lower at the same driving force in comparison with pure water. This was explained by the diffusion mechanism of hydrate formation.

Keywords: gas hydrate kinetics, salt solution

NOMENCLATURE

α, β empirical coefficients a_{H2O} water activity in solution C salt concentration in aqueous phase [g/l] f gas fugacity at experimental pressure P_{ex} [MPa] f_{eq} gas fugacity at equilibrium pressure P_{eq} [MPa] F calculated criterion of Fisher F_{table} table criterion of Fisher ΔG energy of Gibbs [J/mol] ΔG_{eq} energy of Gibbs at equilibrium pressure P_{eq} [J/mol] ΔG_{ex} energy of Gibbs at experimental pressure P_{ex} [J/mol] *K* kinetic constant *m* molality of aqueous NaCl solution [g NaCl/ kg H₂O] P_{eq} equilibrium pressure [MPa] *P* experimental pressure[MPa] *R* gas constant, 8.314 [J/(molK)] *T* temperature [K] *x* mole fraction

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INTRODUCTION

The experimental research on gas hydrate formation from electrolyte solutions is up-to-date due to the progress in gas-condensate field's development. High mineralization formation water is important characteristic in East-Siberian gascondensate fields. The literature review analysis shows that most of investigations on gas hydrate formation are devoted to the research of thermodynamic equilibrium in aqueous electrolyte solutions [1-5]. The kinetics of gas hydrate formation in electrolytes was studied only in few papers . The kinetics of hydrate formation in NaCl and KCl aqueous solutions in temperature range of 270-274 K with mineralization up to 8% was studied in semi-bathed reactor (stirrer rotation frequency – 400 rpm) [6]. The diffusion mechanism of hydrate formation and hydrate particle growth were discussed. It was supposed the liquid water film was located on the hydrate particle surface. The gas diffused to the hydrate surface through the water film. The kinetics of CO2 and CO2 gas mixtures hydrate formation was studied in aqueous solutions of NaCl in stirred reactor [7]. The kinetic characteristics of methane gas hydrate formation in distilled water and aqueous saline solutions (saline concentration up to 5%) were studied in [9]. The hydrate growth mechanism had a few stages: gas dissolution, metastable hydrate cluster formation and hydrate particles growth. The reversibility of process stages was considered and formal kinetics equation was proposed. The pressure in reactor chamber wasn't maintained constant in the experiment. The methane absorption was calculated based on the pressure drop in the reactor.

At present paper the experiments were carried out in a wide range of NaCl concentrations and growth mechanism were proposed based on the modified kinetic model. Based on experimental data the model simulations were performed for the deposit water of Chayanda gas-condensate field (East Siberia of Russia).

EXPERIMENTAL

The special experimental set-up was designed for gas hydrate kinetic investigation (Fig. 1) and special method of kinetic experiments in electrolyte aqueous solutions was developed. The scheme of experimental set-up is presented in Fig. 2.

The hydrate reactor was designed for the study of natural gas hydrate formation and decomposition

under pressure up to 15 MPa in the wide temperature range. The chamber was a high pressure gas/liquid reactor. Construction material was stainless steel AISI 316. The reactor height was 600 mm, inner chamber diameter was 60 mm. The 10 mm-thick viewing window laid from top to downward the reactor chamber. The reactor volume could be highlighted through the sapphire window. The pressure and temperature transducers and safety emergency depressurization valve were mounted on the chamber cover.



Figure 1 Hydrate cell



Figure 2 Principle scheme of the experimental setup to study kinetic process of gas hydrate formation

1 – hydrate high pressure jacketed reactor «Sonar» by «Premex»; 2 – gas hydrate forming bottle; 3 – system to control temperature (t-stat); 4-9 – cutoff valve; 10,11 – вентиль регулирующий (controlpressure valve); 12, 13 – atmospheric valve; 14 – drive of stirrer; PI – analog gauge; PE – digital gauge; TE – electronic thermometer (resistive thermometer); C – controller; FI – flow meter.

The automatically controlled electromagnetic valves were used to maintain the baric conditions

in the reactor. The high constancy of methane pressure was achieved due to the high accuracy of pressure regulation by controlled gas flow. Massflow control valve was consisted of measuring element (capillary with thermo-resist transducer) and controlling element (electromagnetic valve). The accuracy of gas flow measurement was 0.8% of span. The thermostat system had special closed circuit cooling liquid expansion tank. The cooling of thermostat was common cycle cvcle «evaporator-condenser». The hydrate reactor was controlled by special computer system which was able:

- to program temperature;
- to switch on/off the thermostat;
- to control pressure in reactor;
- to control stirrer frequency;
- to control gas flow by electromagnetic valve;
- to record and store data;
- to make laboratory report.

Before the thermostatting, the reactor chamber was filled with 100 ml of distilled or mineralized water. In order to saturate water by methane the pressure in reactor was lower by 0.05 MPa than the pressure under experimental equilibrium temperature. The saturation of aqueous solution was carried out under liquid phase stirring. The experimental pressure was set under heat equilibrium condition. The hydrate formation was stopped after absorption of 6×10^{-3} normal m³ in liquid phase. The aqueous solution NaCl with concentration 0 - 150 g/l was used as a model of formation water. More high saline concentrations were required experimental pressures more than 150 MPa. On the other hand high mineralization could raise spontaneous crystallization in the reactor volume.

The hydrate formation rate can be limited by:

- kinetics of chemical reaction;
- mass transport (diffusion of methane molecules to the surface of growing particles);
- heat transfer (heat transfer from the surface of growing particles).

We suppose the heat transfer as a limiting factor wasn't significant due to the high turbulence flow in the stirring reactor. In order to determine the hydrodynamic experimental regime the rate of hydrate formation against the stirrer frequency was studied (Fig. 3).

Figure 3 The dependence of reaction rate from stirrer frequency

The experiments showed the rate of methane absorption during hydrate formation increased with the increase of stirrer frequency. Under stirrer frequency 650-700 rpm the hydrate formation rate become maximal and wasn't further increase with the stirrer frequency. This proved the kinetic limitations under stirrer frequency more than 700 rpm. So rotation frequency 700 rpm was chosen for further experiments.

EXPERIMENTAL RESULTS

The experimental temperature was in the range of 274.15-285.15 K and pressure was in the range of 7.0-15.2 MPa. The thermodynamic conditions of experiments (temperature, pressure, fugacity) is presented in Tables 1 and 2. The methane fugacity was calculated based on the state equation [11]. The verification of the equation showed the deviations in fugacities weren't much then 0.2% compared with the standard reference equation state of methane [12]. The thermobaric conditions for the experiments with mineralized solutions were chosen on the assumption of the constancy of the driving force of the process which was the difference of Gibbs energies under experimental and equilibrium conditions.

	T, K					
	274.15	277.15	281.15	283.15	285.15	
р	10.00	10.00	11.00	13.00	14.00	
P, MPa	8.50	8.50	10.50	12.00	13.00	
	7.00	8.00	10.00	11.00	12.00	
T 1 1	4 551				0	

Table 1 The thermodynamic conditions of experiments in distilled water.

	Mineralization, g/l					
	0	20	50	100	150	
P _{eq} , MPa	2.965	3.066	3.434	4.333	5.718	
f _{eq} , MPa	2.767	2.858	3.170	3.918	5.008	
f=f _{eq} *2.19	6.065	6.265	6.947	8.587	10.977	
P, MPa	7.15	7.41	8.43	12.40	15.22	

Table 2 The thermodynamic conditions of experiments in solution with various NaCl concentrations at T = 274.15 K.

In the experiments the amounts of methane absorbed in the process of hydrate formation under various thermobaric conditions were studied. The kinetic curves with various NaCl concentrations in solution are presented in figure 4. We can see the rate of hydrate formation in highly mineralized water solution (NaCl, 150 g/l) was lower at least six times in comparison with distilled water.

Figure 4 . The kinetic curves with various NaCl concentrations in solution at the same value of the parameter $f/f_{eq}=2,19$.

We can mark two evident stages of the hydrate formation process in the kinetic curves (Fig. 4): i) nucleation stage (initial part of the curves);

ii) growth stage (medium part of the curves).

The induction period in the experiments didn't exceed 30 minutes. It can be explained by the strong dependency of the induction time from methane saturation of water. As it can be seen from kinetic curves the rate of methane hydrate growth in the nucleation stage is much higher than following growth rate of the hydrate crystals. It can be explained by the high concentration of the dissolved gas in the initial period (in the beginning of the process we saturated water solution by methane under the pressure slightly less then equilibrium hydrate pressure). The following change of the curve slope (hydrate formation rate)

was determined by mass crystallization process [1].

We simulated the only of hydrate growth stage by the reason of randomness of the nucleation stage. The main experimental result was the strong decrease of hydrate formation rate in the high mineralized water solutions under the same driving force (ΔG) (same ratio of the experimental methane fugacity to the equilibrium one).

DISCUSSION

The first stage of hydrate formation process was nucleation of the hydrate particles. Nucleation was the predominantly heterogeneous process: the hydrate clusters are forming in the interface gas/liquid from molecules of water and gas. Critical dimensions of the hydrate clusters were in the range 10 - 100 nm. These hydrate clusters were able for further growing [1].

The next stage of hydrate growth could take place both in the volume of liquid and in the gas/liquid interface. One can suppose the main place could be the heterogeneous gas/liquid interface. The methane bubbles were uniformly distributed in the water volume due to the intensively liquid stirring. The surface of the hydrate particles was watered due to the permanent contact with water. The growth of the hydrate particle was accomplished by gas diffusion to the particle surface through thin liquid film. So the particle growth rate was governed by the gas concentration in the volume near hydrate particle (Fig. 5).

The scheme is explained the decrease of hydrate particles growth rate with the increase of salt concentration in solution. It is know the diffusion coefficient of gas in saline water is lower than in pure water. The saline water thin film is like coreshell that prevents effective methane diffusion to the particle surface. This diffusion drop leads to the decrease of hydrate particle growth in saline solution in comparison with growth in pure water.

By definition the driving force is the difference of experimental and equilibrium values. The driving force of the hydrate formation process is defined by various ways in literature: difference between experimental and equilibrium fugacities [13,14], difference between experimental and equilibrium temperatures of hydrate formation and so on. We suppose that in our case the driving force can be expressed as a difference of Gibbs energies in experimental and equilibrium conditions:

$$\Delta G = \Delta G_{ex} - \Delta G_{eq} = RTln(f) - RTln(f_{eq}) = RTln\frac{f}{f_{eq}} \quad (1)$$

Figure 5 Diagram changes of the concentrations gas during hydrate formation at two mechanisms the processes at the interface an aqueous solution of the gas - hydrate

(1) Reaction limited by kinetics of the process;

(2) Reaction limited by gas diffusion to the particle surface through thin liquid film (for the high salt concentration).

Taking into account that under the same driving force the process rate decrease with the mineralization increase (process kinetics depend on the water activity a_{H2O}) we processed experimental data using the analytic expression:

$$\left(\frac{\mathrm{dn}}{\mathrm{d\tau}}\right)_{\mathrm{P,T}} = \mathbf{K} \cdot \mathbf{a}_{\mathrm{H_{2}O}} \cdot \exp(-\alpha \cdot \mathbf{m}) \cdot \left[\mathrm{RTln}\left(\frac{\mathbf{f}}{\mathbf{f}_{\mathrm{eq}}}\right) \right]^{\mathrm{p}} \quad (2)$$

The factor $exp(-\alpha \cdot m)$ in equation (2) is taking into account the decrease of methane solubility in mineralized solution in comparison with pure water in the experiments. The factor was chosen like a factor in Sechenov equation [15] which describes the decrease equilibrium gas solubility depending on the aqueous solution mineralization. The temperature dependency of kinetic constant K is well described by Arrhenius type equation. It is to be noted that activation energy in the equation is effective value because the kinetic model (2) doesn't take into account all kind of formation mechanisms. The experimental data processing gives the following formulae:

$$\left(\frac{\mathrm{dn}}{\mathrm{d\tau}}\right)_{\mathrm{P,T}} = 1..895 \mathrm{exp}\left(-\frac{3.908 \cdot 10^4}{\mathrm{RT}}\right) a_{\mathrm{H_2O}} \mathrm{exp}(-0.628 \cdot \mathrm{m}) \mathrm{RTln}\left(\frac{\mathrm{f}}{\mathrm{f_{eq}}}\right) (3)$$

where a_{H2O} – water activity in solution; m – molality of aqueous NaCl solution [g NaCl/ kg H₂O]; T – temperature of the process, K; R = 8.314 J/(mol K); f_{ex} – gas fugacity at experimental pressure, MPa; f_{eq} – gas fugacity at equilibrium pressure, MPa.

In comparision equation 2 and 3 one can see that parameter β is practically equal to 1 (under different approximation it was changed in the narrow range 1.0 - 1.2). It proves that driving force is adequate to the experimental conditions.

In order to prove the formula (3) we verified the experimental data (Figs. 6-8).

Figure 6 The comparison experimental and calculated points at T=281.15 K, P=10.5 MPa, C=0 g/l.

Figure 7 The comparison experimental and calculated points at T=274.15 K, P=7.41MPa, C=20 g/l.

Figure 8 The comparison experimental and calculated points at T=274,15K P=14,7MPa, C=150 g/l.

Fisher criterion was calculated and compared with the table values (for C=0 g/l F = 2,32; $F_{table} = 2,63$; C=20 g/l F = 2,45; $F_{table} = 2,65$; C=150 g/l F = 1,81; $F_{table} = 2,64$). According to the obtained values it was concluded that the proposed model is adequate at the temperature range of the experiments at 95% confidence interval.

Equation (3) can be used to evaluate a hydrate formation rate at different ionic composition of the aqueous solutions and various total mineralizations.

For example, the dependence of the rate of hydrate formation was used to modeling for the solution having a similar composition of reservoir water from Botuobinsky horizon Chayandinskoye deposit shown in Table 3.

	Concentration			
	mol/l	g/l	mas. %	
CaCl ₂	1.73	191.9	15.45	
MgCl ₂	0.35	32.9	2.65	
NaCl	1.99	116.4	9.37	
KCl	0.12	8.8	0.71	
Total	4.18	350.00	28.18	

Table 3 Composition of the simulated reservoir water on the example water from Botuobinsky horizon Chayandinskoye deposit.

The plot of the hydrate formation relative rate for the thermobaric conditions of the Chayandinskoye deposit which shows hydrate formation rate in the mineralized water (Tab. 3) in relation between the rate of hydrate formation in the distilled water (Fig. 9).

Figure 9 The dependence between the rate of hydrate formation in mineralized solution and the rate of hydrate formation in distilled water.

CONCLUTIONS

The rates of hydrate formation in the stirring reactor from NaCl aqueous solutions of various concentrations were studied. The driving force of the process was determined as the difference of Gibbs energies under experimental and equilibrium conditions. The mechanism of the hydrate formation process was proposed. The kinetic equation for the rate of hydrate formation was proposed. The equation parameters were studied. It was shown the hydrate formation rate decreased with the NaCl concentration increase under the constant value of the driving force. It was experimentally shown the aqueous solutions of electrolytes was not only thermodynamic hydrate inhibitors but kinetic inhibitors also.

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