

Kinetics and Thermodynamics of Gas Hydrate Formation in CaCl_2 , MgCl_2 and NaCl Aqueous Solutions

Vladimir Istomin^{1*}, Anna Troinikova¹, Sergey Dolgaev¹, Valery Kvon¹, Pavel Nefedov¹,
Mikhail Genkin², Sergey Igumnov², Tatyana Rozarenova²

¹*Scientific-Research Institute of Natural Gases and Gas Technologies-
GAZPROM VNIIGAZ, Russia*

²*URALCHEM JSC, Russia*

*Corresponding author: vlistomin@yandex.ru

Abstract

Experimental studies of electrolyte solutions effect on the methane hydrate formation kinetics were carried out. Aqueous solutions of sodium, calcium and magnesium chlorides were studied as hydrate inhibitors. The induction time and the hydrate formation rates as a function of inhibitor concentration were experimentally investigated. The driving force (a ratio of methane fugacity under experimental and equilibrium conditions) of the hydrate formation in aqueous solutions is equal to 2.0. It was shown that at the same driving force the hydrate formation rate is strongly decreasing as concentration of salt in the solution is increasing.

Introduction

The methanol and MEG are the main hydrate inhibitors in gas industry. The hydrate inhibitors – electrolytes are also used in the practice of gas conditioning. The electrolyte solutions for hydrate plugging preventing in pipelines were used in gas industry in 60s – 70s. In particular, the concentrated solutions of calcium chlorides with anti-corrosion additions are experimentally used; the solutions of natural brine (like bischofite) are used also. It was an experience of practical application of calcium chloride solutions in field pipelines in Russian southern gas fields. The methanol was predominantly used as a hydrate inhibitor for prevention of hydrate plugging in 70s – 80s. Now there are many gas fields at the late stages of development. Thereby it seems rational to come back for application of electrolyte solutions at infield pipelines for preventing hydrate as well as ice formation.

There are a lot of papers on thermodynamics phase equilibrium of gas hydrates in electrolyte aqueous solutions [1-5]. For instance, Bishnoi and Dholbhai investigated the gas hydrate formation in the mixture electrolyte and methanol [1]. The tested system was consisted on the same cumulative amount of inhibitor, such as 5 wt % NaCl + 15 wt % methanol or 5 wt % methanol + 15 wt % NaCl . It was observed the equilibrium temperature under the same pressures wasn't differed much in these solutions (within 3-5 K). It was detected that the sodium chloride have the higher inhibition effect than methanol under the same concentration.

The kinetics of hydrate formation in NaCl and KCl aqueous solutions in temperature range of 270-274 K with mineralization up to 8 wt % was studied in semi-batched 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 is diffused to the hydrate surface through the water film. The kinetics of CO_2 and CO_2 gas mixtures hydrate formation was studied in aqueous solutions of NaCl in stirred reactor [7, 8]. The kinetic characteristics of methane gas hydrate formation in distilled water and aqueous saline solutions (saline concentration up to 5 wt %) were studied in [9]. The hydrate growth mechanism includes number of 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.

Hydrate formation kinetics was studied in synergetic inhibitor (salt solutions with addition of polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap)) [10]. The performance of PVP and PVCap in the presence of salt was evaluated by monitoring hydrate formation using a set of two identical stirred tank vessels and with calorimetry to determine phase transitions. In NaCl solutions that mimicked ocean salinity, KHIs significantly prolonged the induction time, similar to the effect in a pure water.

The purpose of the work is to study the hydrate formation kinetics in electrolyte aqueous solutions. At the paper we studied the sodium, calcium and magnesium chloride to understand their influence primary on the of hydrate formation kinetics. The sodium chloride was studied at different concentrations. Calcium and magnesium chlorides were investigated as an integrated inhibitor supplied by URALCHEM JSC Russia (ratio of $\text{CaCl}_2 / \text{MgCl}_2$ was taken as 5.2/1.0). Methane was used as the hydrate-forming gas in the experiments.

Experiments

The experimental studies on the effect of electrolytes on hydrate formation were conducted on the multifunction laboratory setup (Figure 1). The laboratory setup allows to investigate both thermodynamic and kinetic parameters of hydrate-forming processes by using water solutions (salts, methanol, MEG, LDHI etc.).

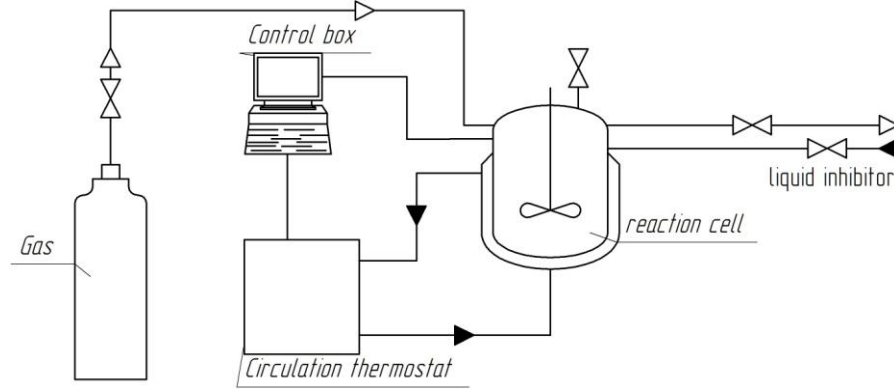


Figure 1: Experimental setup for investigation of the thermodynamic and kinetic parameters of hydrate formation

The gas valves operated by a controller were used to maintain the settled conditions of pressure apparatus. It provides highly accurate pressure regulation at the expense of variable gas supply. The regulator/flow meter consists of two main parts: the measuring element and the regulating member. Error of gas flow rate measurements is 0.8 wt %.

Before starting experiment, the reactor was filled with 100 ml of an inhibitor aqueous solution. The experiments were carried out in stirred inhibitor aqueous solutions and in stable thermobaric conditions. The settled pressure and temperature were maintained by PID-controller. In the first stage of experiments, the inhibitor aqueous solution was saturated by methane with mechanical stirring. We suppose that the saturation was necessary to reveal the “real induction time” without the period of gaseous saturation of solution. The saturation was carried out under the pressure ~ 0.05 MPa less than calculated equilibrium hydrate formation pressure.

The kinetic experiments were carried out under the same driving forces of hydrate formation reaction. The driving force was determined as a difference of Gibbs energies ΔG of thermobaric states in experimental and equilibrium conditions (equation 1).

$$\Delta G = RT \ln(f) - RT \ln(f_{eq}) = RT \ln\left(\frac{f}{f_{eq}}\right) \quad (1)$$

where:

ΔG - Gibbs free energy, J/mol;

R - gas constant, 8.314, J/(molK);

T - temperature, K;

f - gas fugacity at experimental pressure P_{ex} , MPa;

f_{eq} - gas fugacity at equilibrium pressure P_{eq} , MPa.

The ratio of experimental and equilibrium fugacities f/f_{eq} was equal 2. The experimental thermobaric conditions of hydrate formation kinetics in the CaCl_2 , MgCl_2 and NaCl solutions are presented in the table 1. The induction period and the rate of gas consuming in the process of hydrate formation were measured in the experiments.

Table 1 : The thermodynamic conditions of experiments in aqueous solutions under various electrolyte concentrations

Aqueous Solutions	Temperature, K	Concentration, wt %	Pressure, MPa
NaCl	274.15	1.97	7.41
		4.84	8.43
		9.37	12.4
$\text{CaCl}_2 + \text{MgCl}_2$	274.15	2	7.75
		4	8.43
		8	11.3
Distilled water	274.15	100	7.15

Results and Discussion

The kinetic curves of methane consumption necessary to form the hydrates were logged for each type of electrolyte (Figure 2-3).]

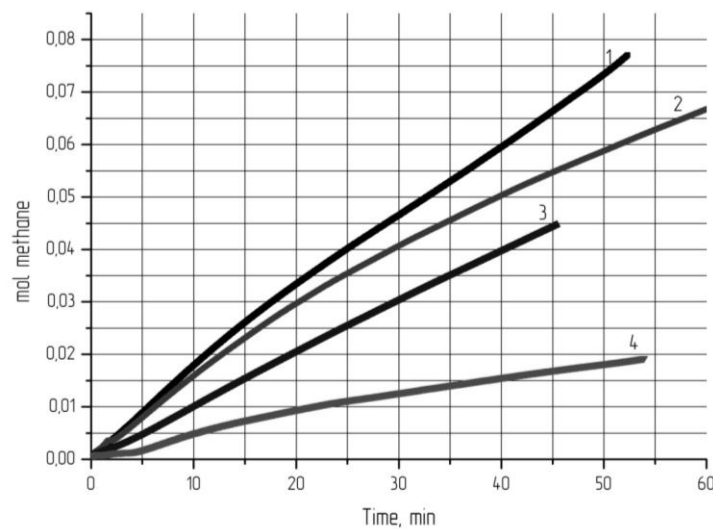


Figure 2 : Kinetics of methane hydrate formation in aqueous solutions of various NaCl concentrations
1 – 0 wt %, 2 – 1.97 wt %, 3 – 4.84 wt %, 4 – 9.37 wt %

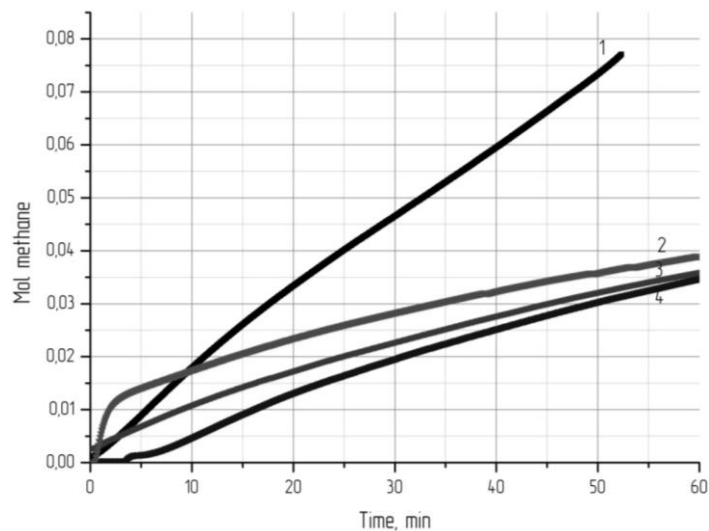


Figure 3 : Kinetics of methane hydrate formation in aqueous solutions of various $\text{CaCl}_2 + \text{MgCl}_2$ concentrations
1 – 0 wt %, 2 – 2 wt %, 3 – 4 wt %, 4 – 8 wt %

Two principal stages of the hydrate formation process can be identified in the kinetic curves (Fig. 2-3):

I) nucleation stage (initial part of the curves);

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

The induction period in aqueous NaCl solutions wasn't exceed of 30 minutes. However, in the experiments with mixture of $\text{CaCl}_2 + \text{MgCl}_2$ solutions the induction periods were exceeded several hours in spite of previous gas saturation. This was due to the anticorrosive agent as a part of combined inhibitor of hydrates and corrosion based on CaCl_2 and MgCl_2 .

The rate of methane hydrate formation of nucleation stage is much higher than growth stage (Fig. 2 - 3). 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 than equilibrium hydrate pressure). The following changes of the curve slope (hydrate formation rate is linear area) was determined by regression analysis. The main result of experiments was the strong decrease of hydrate formation rates in the high concentration solutions under the same driving force (same ratio of the experimental methane fugacity to the equilibrium one). It was characterized by linear plots in the hydrate curves. The rates of hydrate formation were calculated from the experimental data. The rate curves of hydrate formation was approximated by straight-line segments as (eq. 2):

$$v = \kappa * t + b \quad (2)$$

where:

v – quantity of absorbed methane, mol;

t – time, min;

k and b – empirical coefficients.

The dependency of hydrate formation rates vs electrolyte concentration in aqueous solutions are presented in Figure 4.

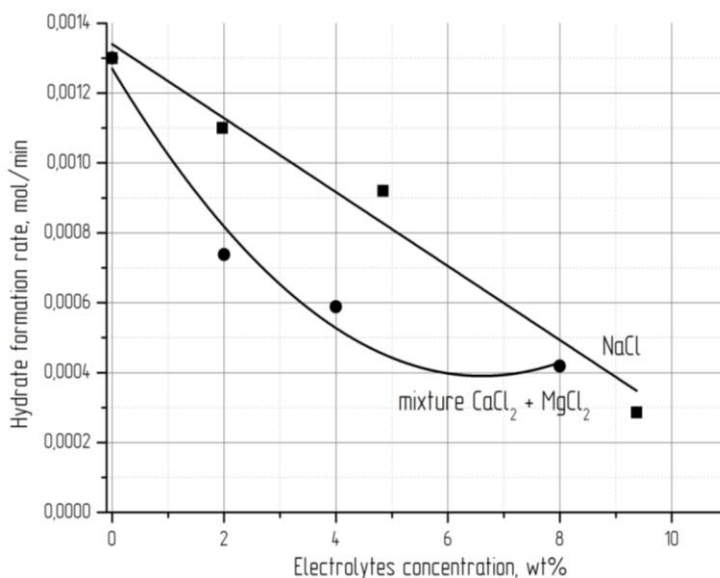


Figure 4 : The dependency of hydrate formation rates on electrolyte concentrations

Dependency of hydrate formation rates on electrolyte concentration showed the rate of hydrate formation in monovalent electrolyte NaCl decreased linearly. The mixture of divalent electrolytes ($\text{CaCl}_2 + \text{MgCl}_2$) was characterized by nonlinear changing of hydrate formation rate with concentration increase.

Conclusion

The kinetics of hydrate formation under pressures of 7 – 13 MPa and temperature 274.15 K in aqueous solutions of monovalent and divalent chlorine electrolytes was studied. It was shown the sharp hydrate formation rate decrease in electrolyte solutions in comparison with distilled water. The divalent chlorine electrolytes were characterized lower hydrate formation rates in comparison with monovalent ones. It was detected that the chlorine electrolyte solutions are both thermodynamic and kinetic inhibitors.

References

- [1] P.R. Bishnoi, P.D. Dholabhai, "Equilibrium conditions for hydrate formation for a ternary mixture of methane, propane and carbon dioxide, and a natural gas mixture in the presence of electrolytes and methanol", *Fluid Phase Equilibria*, 1999
- [2] V.A.Istomin, V.S. Yakushev, "Gas hydrates in natural conditions", (in Russian) 1992
- [3] V.A. Istomin, D.M. Fedulov, "Near wellbore formation thermodynamics at residual water salinity in the reservoir and the possibility of hydrate formation", *Vesti gazovoy nauki: Problems of operation of gas, gas condensate and oil and gas fields*, (in Russian) 2013
- [4] V.A. Istomin, D.M. Fedulov, I.I. Minakov, V.G. Kvon, S.V. Burakova, "Hydrates prevention in the bottom hole formation zone at high reservoir water salinity", *Vesti gazovoy nauki: Problems of operation of gas, gas condensate and oil and gas fields*, (in Russian) 2013
- [5] M. A. Clarke, P.R. Bishnoi, "Development of a new equation of state for mixed salt and mixed solvent systems, and application to vapour–liquid and solid (hydrate)–vapor–liquid equilibrium calculations", *Fluid Phase Equilibria*, 2004
- [6] P. D. Dholabhai, N. Kalogerakis, P. R. Bishnoi, "Kinetics of Methane Hydrate Formation in Aqueous Electrolyte Solutions", *The Canadian Journal of Chemical Engineering*, 1993

- [7] S.S. Fan, T.-M. Guo, "Hydrate Formation of CO₂-Rich Binary and Quaternary Gas Mixtures in Aqueous Sodium Chloride Solutions", *Journal Chemical Engineering Data*, 1999
- [8] T.-M. Guo, J.-H. Qiu, "Kinetic of Methane Hydrate formation in pure water and inhibitor containing systems", *Chinese Journal of Chemical Engineering*, 2002
- [9] K. M. Sabila, A. R.C. Duarte, J. Zevenbergen, M. M. Ahmad, S. Yusup, A. A. Omar, C. A. Peters, "Kinetic of formation for single carbon dioxide and mixed carbon dioxide and tetrahydrofuran hydrates in water and sodium chloride aqueous solution", *International Journal of Greenhouse Gas Control*, 2010
- [10] H. Sharifi, J. Ripmeester, V. K. Walker, P. Englezos, "Kinetic inhibition of natural gas hydrates in saline solutions and heptanes", *Fuel*, 2014
- [11] V.A. Istomin, S.I. Dolgaev, A.A. Dzhezherova, V.G. Kvon, P.A. Nefedov, "Kinetics of methane hydrate formation in highly mineralized water solutions", *Proceedings of the 8th International Conference on Gas Hydrates (ICGH8-2014)*, 2014