

# Mechanism of Kinetic Hydrate Inhibitors

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A series of molecular dynamics and Monte Carlo simulations were performed to investigate the mechanism of kinetic inhibition of methane hydrate by short polymers. Effects of polymers on the hydrophobic hydration of non-polar solutes were investigated. Molecular simulations were compared to the experimental effects of chemical additives on hydrate formation. The inhibition mechanism was shown to consist of two main components. Inhibitor polymer side groups adsorb to the hydrate crystal surface by hydrogen bonding. By adsorbing on the hydrate crystal, the polymer forces the crystal to grow around and between the polymer strands, with a small radius of crystal curvature. Inhibitors also sterically block non-polar solutes such as methane from entering and completing a hydrate cavity. We observed weak interaction between non-polar solute and hydrophobic part of the inhibitor side groups in the model.

## Introduction

The oil and gas industry is expanding into deepwater and northern regions for exploration and production of oil and gas. As ambient temperatures decrease, the industry is facing increasing costs in inhibiting gas hydrate formation due to the development of oil and gas deposits.

Gas hydrates are likely to form in cold flowlines unless water is removed from the fluid, the pipe is effectively insulated, or inhibitors are used. Since complete dehydration of condensates and/or natural gas is not feasible in subsea tieback flowlines between a remote subsea well and the offshore platform, and effective insulation is beyond current economic limits, the most effective solution includes the use of hydrate inhibitors.

Reasons for using low dosage hydrate inhibitors (LDHI) are not limited to the cost of methanol. One of BP's values is to cause no damage to environment. This can be done by limit discharges of water with methanol. MMS and EPA regulations require that the discharged water must pass the toxicity test.

More methanol is required as water production rates increase over time. Economics limit the designed throughput of methanol injection facilities so that high water cuts may be underinhibited. Cost saving associated with the removal of additional subsea valves and umbilical lines required to inject methanol may reach 50 million dollars per field if LDHI are used instead.

Additional cost penalty exists for producing oil that was in contact with methanol. A crude with elevated methanol content can poison refinery catalysts, and is normally traded at a lower cost.

The goal of this paper was to relate the accumulated insight into the mechanism of kinetic hydrate inhibitors to the measurable quantities and to

facilitate the development of competitive commercial LDHI chemistries by the inhibitor manufacturers. The new inhibitors should ideally be developed without the use of costly specialized equipment.

## Modeling Methods

In our initial simulation work the Cerius<sup>2</sup> software was used for modeling the inhibitor adsorption on {100} and {111} planes of sI and sII hydrates with the DREIDING forcefield (Mayo, et al., 1990).

Some force fields (CHARMm, DREIDING) use a hydrogen bond potential to describe interactions between atoms involved in hydrogen bonds. The used module of the Cerius<sup>2</sup> program didn't have explicit hydrogen-bonding between the hydrate surface and an inhibitor monomer although it used the DREIDING forcefield. In Cerius<sup>2</sup> hydrogen bonding was modeled by the charge-charge interaction. This is a common approach for simulation of water-based systems (Jorgensen, 1983), (Rodger, 1994). However, this approach does not give a complete set of water-water interactions and results in lower ice melting temperature (e.g. 200 K for SPC water). The major reasons for writing our own code were to improve the potential model by adding the hydrogen bonding interaction and to be able to sample any variable at any time during the simulation neither of which could be explicitly done using Cerius<sup>2</sup>.

The main Monte-Carlo routine was written by Professor James Haile of Clemson University while on sabbatical at Colorado School of Mines. Hydrogen bonding interaction of up to 5 kcal/mole was then included in the hand-written code for the simulation of chemicals' interactions with a SPC-water-based (Berendsen, et al., 1981) hydrate surface along with the dispersion (Lennard-Jones) and electrostatic (Coulombic) interactions:

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$$\text{Electrostatic: } E = \frac{1}{4\pi\epsilon} \cdot \frac{Q_i Q_j}{R_{ij}^2}$$

$$\text{Dispersion: } E = LJ_{12-6} = D_{ij} \left[ \left( \frac{R_{ij0}}{R} \right)^{12} - 2 \left( \frac{R_{ij0}}{R} \right)^6 \right]$$

$$\text{H-bond: } E = LJ_{12-10} = D_{ij} \left[ 5 \left( \frac{R_{ij0}}{R} \right)^{12} - 6 \left( \frac{R_{ij0}}{R} \right)^{10} \right]$$

Prior to using the code, its components were tested:

- 1) The interaction potentials were calculated by hand for a test pair of molecules and were found to be same as calculated by the program.
- 2) The rotation and translation algorithms were tested for proper reorientation and positioning of monomers using a set of discrete angles (0,45, 90°) and steps in each dimension.
- 3) The sampling bin size of the radial correlation function was optimized. The area of produced correlation function was integrated to yield a normalized value of 100 as required.
- 4) Proper functioning of cubic and rhombic periodic boundary conditions was verified.
- 5) It was shown that the starting position of a moving molecule near the fixed molecule does not affect the resulting strength or place of adsorption by performing 8 simulations of one water molecule moving around a fixed PVP monomer.

The following variables were also tested: position of hydrate slice; thickness of slice; length of equilibration; attractive effect of non-bonded interactions; number of runs required for each slice; size of the hydrate surface (1x1 or 2x2 unit cells area).

In order to determine that the run time was sufficiently long to sample all energy states, the radial distribution functions between water oxygen and the atoms of the pyrrolidone ring were compared for an average of eight 100,000 steps runs with an average of eight 500,000 steps runs. The distribution functions precisely overlap, having no variation in shape.

For simulations of monomer adsorption on hydrate surface each simulation was conducted 10 times in order to sample the potential space sufficiently. Results after 4-5 runs usually reproduced themselves. Initially, strong forces (Coulombic and hydrogen-bonding) were turned off and the monomer was moving about the periodic hydrate surface in order to assume a random position and orientation above the surface. Then these forces were turned on, and the monomer was allowed to equilibrate for 50000 MC attempts. After that, the simulation variables were sampled for 100000 steps.

In simulations of polymer adsorption to hydrates the pivot Monte Carlo method was used for obtaining a new conformation of a polymer by making a bold change in backbone structure. Many of the pivot attempts got

rejected because of the higher energy final state, but the accepted move produces an “essentially new” configuration (Madras and Sokal, 1988). This algorithm allowed us to use the existing Monte Carlo code and run simulations with atomically correct polymer chains and hydrate surfaces.

The simulation of methane adsorption on hydrate showed condensation at 100K and 5 atm, which suggests that the adsorption model is adequate.

At one atmosphere the volume occupied by 1 mole of methane is about 22.4 liters. This translates to 37,191 Å<sup>3</sup> per methane molecule at 1 atm. The volume of the simulation box above the hydrate surface was 7597 Å<sup>3</sup> which is 5 times smaller than the volume per molecule of methane at one atmosphere. This suggests that the simulation pressure can be estimated as 5 atm.

Simulations for methane adsorption on hydrate surface indicate that methane condenses at a temperature of 100 K. Vapor pressure calculation was performed for methane using the empirical equation obtained from the reference (Reid, et al, 1987). Vapor pressure of 5 atm is exerted at 90.1 K, which is close to the value of 100 K obtained in the simulation. However, the freezing temperature of methane is 90.7 K which means that instead of condensing, methane freezes at this temperature.

## Results and Discussion

The results presented in this work are mainly from Makogon (1997b). Lederhos et al. (1996) described PVP, PVCap and VC-713 as kinetic inhibitors. The running-average energies averaged over 8 runs are presented for the studied monomers in Table 1. Vinyl-alcohol (ethanol) had the strongest interaction with water, followed by the monomers of PVCap, PNDMAm, PVP, and PNAm. Since ethanol is a known thermodynamic inhibitor (Sloan, 1990), this outcome is not very surprising.

Table 1. Interaction between water and monomers.

Monomer name	Final Running-average Energy, kcal/mole
vinylpyrrolidone	-7.86
vinylcaprolactam	-8.11
vinyl-N-dimethylacrylamide	-7.62
vinyl-N-acrylamide	-7.06
vinyl-alcohol (a.k.a. ethanol)	-8.57

From the monomer studies it was found that the strength of adsorption on sII {111} face varied with the surface distance (depth) from unit cell origin. A study of hydrate surface stability was done using Cerius<sup>2</sup> in order to determine the most stable hydrate surface for

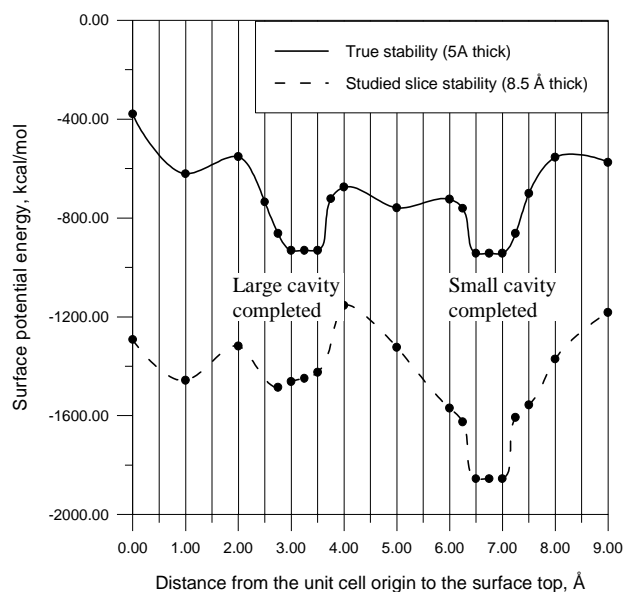


Fig. 1 Stability of sII {111} hydrate surfaces sliced at different depths from unit cell origin. Block thickness is kept constant. Potential values were not normalized by the number of water molecules in that surface.

polymer adsorption. A one-water-molecule-thick 5Å {111} slice of hydrate was cut from the sII unit cell at different positions, and the surface potential energy was calculated. We used DREIDING interaction parameters with hydrogen bonding potential well depth set to 5 kcal/mol and SPC Lennard-Jones and charge parameters for atoms in water. Two valleys were found at about 3Å and 7Å from the unit cell origin. These locations correspond to the surfaces where the large and the small cavities get completed (Figure 1). The same study was repeated for 8.5 Å thick slices of hydrate. The most stable slice was the one with its surface 7Å from the unit cell origin. This surface exhibits completed small  $5^{12}$  cavities and open  $5^{12}6^4$  cavities. The most stable surface was adopted for studying adsorption of polymers.

The same procedure was used to compare relative stabilities of {100}, {110}, and {111} hydrate surfaces of sII. It was found that in each of the three directions the number of water molecules falling into a 5Å-thick slab of hydrate varies, so the potential energies were normalized by the number of water molecules. The equilibrium shape of a crystal is that of its minimum energy. This is called the Wulff condition (Myerson, 1993). {111} planes show the most stability, which possibly explains why they are observed experimentally; same result was obtained for non-normalized surface energies.

For trimer, pentamer and octamer adsorption the conformations were: 1) laying flat with the backbone parallel to the surface (train), 2) with some part of the

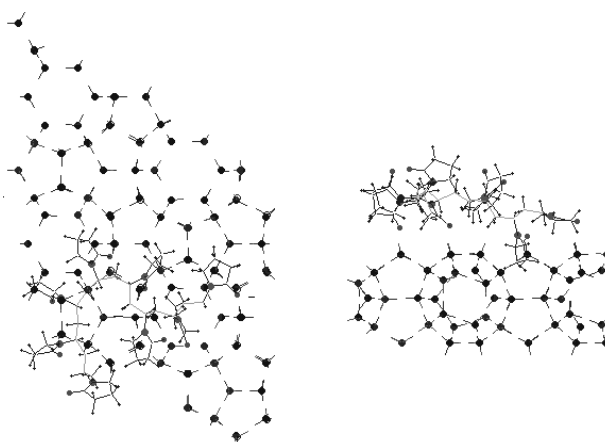


Fig 2. PVP octamer on {111} sII viewed along  $\langle 111 \rangle$  and  $\langle \bar{1}10 \rangle$  directions. One side group is adsorbed into an open  $5^{12}6^4$  cavity.

chain adsorbed and the other part not adsorbed (tail), and 3) with two ends of the chain adsorbed (loop). The preferred conformation was a train for most short polymers (Figure 2). It was found that known inhibitor polymers (PVP and PVCap) adsorbed stronger than non-inhibitors (PVA). Kvamme (1997) found that PVCap adsorbed stronger than PVP. Strongly adsorbing impurities are expected to have a greater effect on the growth rate of crystals than impurities that adsorb weakly (Myerson, 1993).

Simulations of methane adsorption on hydrate surface with a pre-adsorbed inhibitor were performed to study the hypothesis that inhibitors sterically block the diffusion of methane to the hydrate surface. The runs were performed for a range of temperatures from 100 K to 400 K in 50 K increments. Length of simulations included 50,000 equilibration cycles and 50,000 run cycles. Each simulation was repeated 4 to 8 times, and the results were averaged.

It was found that the adsorption of methane in hydrate cavities had changed with the presence of a polymer on the hydrate surface (Figure 3). Different polymers had different effects on the methane adsorption. The largest decrease in methane adsorption was caused by PVCap, followed by PVP and PVA.

The curves in the Figure 3 are only meaningful up to the temperature of ice melting. The empty hydrate lattice was artificially fixed in place and could not melt. Shape of the curves in Figure 3 is attributable to the nature of methane interaction with the hydrate surface and/or the adsorbed polymer. Without polymer on the surface at 100K methane condenses and doesn't move out of a hydrate cavity. The number of cycles which methane spent outside hydrate cavities increased with temperature.

In presence of a polymer at 100 K temperature methane condensed on the polymer and spent less time

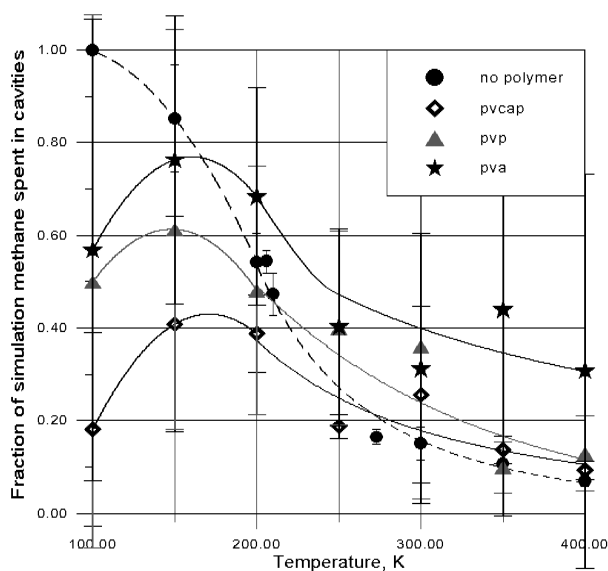


Fig. 3. Adsorption of methane on bare sII {111} hydrate surface and with octamers of PVCap, PVP and PVA.

in hydrate cavities. This results in low adsorption of guest into open cavities. At 150 K there is a peak in adsorption curves. Methane, which mostly adsorbed on polymer at 100 K is now able to desorb from the polymer and reach the hydrate surface. The temperature is still sufficiently low for methane's thermal motion to overcome the attraction of hydrate cavities. Methane mostly remains adsorbed in hydrate cavities. This results in a peak in adsorption curves. At 200 K methane doesn't adsorb in cavities as often because of a higher temperature and its higher thermal motion. At temperatures above 200 K methane adsorbs less on hydrate and moves in and out of hydrate cavities. The fraction of methane adsorption on hydrate is higher with polymers present than on a bare surface because polymer creates additional attraction for methane towards the hydrate.

According to our results, the inhibition of hydrate growth by kinetic LDHI is affected by inhibitor adsorption on hydrate and by inhibitor prevention of guests from reaching open hydrate cavities by interacting with the guest molecules. By adsorbing on the hydrate crystal, the polymer forces the crystal to grow around and between the polymer strands, with a small radius of crystal curvature. This effect was discussed by Larsen (1997) and Rider (1999). Other variables that may affect kinetic inhibition include inhibitor copolymer ratio and inhibitor concentration (Cingotti et al., 2000), as well as hydrate structure and absolute pressure (Svartaas et al., 2000). The mechanism of kinetic inhibition was described as inhibitor adsorption on a hydrate by Edwards (1994), Carver et al. (1995, 2000), Kvamme (1997), Freer and Sloan (2000), and other researchers.

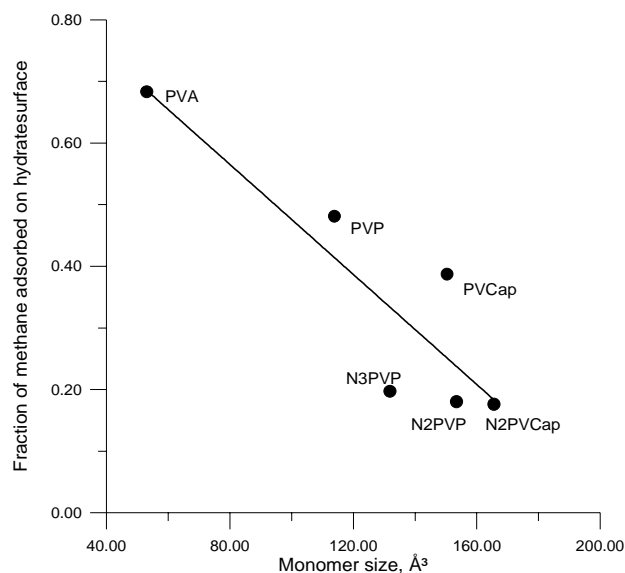


Fig. 4. Methane blocking performance of chemicals sampled at 200 K is proportional to the monomer size.

Molecules of gas and water diffuse to the hydrate surface and adsorb on hydrate crystal according to Makogon (1997). Shortage of either gas or water near the crystal will decrease the rate of hydrate surface growth. Figure 4 shows that methane is blocked from entering the hydrate lattice more effectively by chemicals with larger monomers. However, the effectiveness reaches a limit around 160 Å<sup>3</sup>. A similar method relating the monomer size to inhibitor effectiveness was described (Talley, et al. 1999) in a patent.

The results of neutron scattering study by King et al. (2000) showed that the studied kinetic inhibitor polymers adsorbed to the hydrate-crystal surface. This work also showed additional scattering, possibly indicating a polymer-propane interaction prior to crystal formation. These data support our hypothesis that kinetic inhibitors interact with guest molecules and thus limit the diffusion of guests to the hydrate surface.

According to the information in Figure 1, completion of cavities represents an energetically favorable conformation of water molecules in hydrate. We suggest that the completion of hexagonal faces is the rate limiting step in surface buildup for two reasons: for sII hydrate hexagonal faces are located in the slowest growing {111} plane, and the {111} surface with an open large cavity is more stable. Since water molecules are normally bonded with four hydrogen bonds, each molecule can assume one of six orientations. The time to change this orientation is about 8-9 ps (Bertolini, et al. 1982). Since each of the six water molecules in the hexagonal ring can assume any of the six orientations, the number of possible orientations equals a factorial of six, or 720, yet only

one will result in a continued hydrate growth. Thus the time to form one hexagonal ring is about  $9 \times 720 = 6.48$  ns.

Nerheim (1992) reported the critical nuclei sizes between 5 and 30 nm. Octahedral shape of sII hydrate crystal was reported by Smelik and King, (1997), Larsen (1997), Makogon et al. (1997c). A 30 nm octahedral crystal contains 3476 unit cells, each having 16 unique (not shared) hexagonal rings. Such sII crystal could form in 0.36 ms. For a sI hydrate the shape is a rhombic dodecahedron, containing some hexagonal faces in the slowest growing {110} planes. This shape can be approximated with a sphere. A sI crystal could form in 0.318 ms. The faster formation of a sI hydrate is supported by data from Montfort et al. (2000) and Svartaas et al. (2000).

When an inhibitor fails, hydrate will gradually consume all water. The growth rate is likely to be diffusion-limited, defined by the solubility of gas in water at in-situ conditions, rather than heat-transfer limited.

This simple mechanistic approach may be used to estimate the induction time of hydrate inhibitors through the surface potential at the inhibited hydrate-water interface. Surface tension can be measured either through shear at the hydrate-water interface or through a contact angle of a water drop on a solid hydrate in a temperature controlled cold room.

The mechanism of anti-agglomerant LDHI could be different. An additive that allowed hydrate crystals to flow in suspension within the fluids was described by Behar et al. (1991). A hypothetical mechanism for anti-agglomerant hydrate inhibitors could be due to a distorted hydrate lattice formation. According to Makogon (1974, pg.8), a tertiary-butyl amine hydrate has a cubic symmetry and a  $19 \text{ \AA}$  unit cell, which is larger than a sII unit cell size of  $17.3 \text{ \AA}$ . The distorted hydrate nuclei promote the formation of hydrate, but limit the size of hydrate particles as crystal defects make further growth energetically unfavorable. Simultaneously, the hydrocarbon radicals of anti-agglomerants form an oleophilic barrier on the crystal and block the diffusion of water to the hydrate crystal. If this hypothesis is correct, one should be able to control the hydrate particle size distribution with the concentration of anti-agglomerant inhibitor. Some substantiation is seen from Monfort et al. (2000). Molecular simulations of this class of chemicals by Storr and Rodger (2000) showed preferred adsorption locations for quaternary ammonium sulfonate zwitterions and proposed a lock-and key mechanism for these inhibitors.

## Conclusion

We proposed a mechanism of kinetic inhibitors based on our computer model that seems to be supported by recent data from other laboratories. By adsorbing on the hydrate crystal, the polymer forces the crystal to grow around and between the polymer strands, with a small radius of

crystal curvature. Simultaneously, inhibitors block the diffusion of gas to the hydrate surface. Anti-agglomerant inhibitors are hypothesized to promote distorted hydrate crystals leading to reduced crystal size and to form an oleophilic layer that blocks water and disperses crystals in oil.

The presented inhibition mechanism was purposely simplified. Additional experimental evidence may provide additional data on the location and type of inhibitor adsorption on hydrate crystals.

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## References

- Behar, E., Bourmayer, P., Sugier, A., Thomas, M. (1991). Proceedings Seventh Annual Convention GPA, San Antonio, March 11-12, pp.115-120.
- Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., Hermans, J. (1981). in *Intermolecular Forces*, B.Pullman, Ed., Reidel Dordrecht, the Netherlands.
- Bertolini, D., Casserati, M., Salvetti, G. (1982). The dielectric relaxation time of supercooled water. *J. Chem. Phys.*, 76: 3285.
- Carver, T.J., Drew, M.G, Rodger, P. M. (1995). Inhibition of crystal growth in methane hydrate. *J. Chem. Soc. Faraday Trans.*, 91(19), 3449-3460.
- Carver, T.J., Drew, M.G, Rodger, P. M. (2000) Configuration-biased Monte Carlo simulations of poly(vinylpyrrolidone) at gas hydrate crystal surface. *Annals of the New York Academy of Sciences* 912, 658-668.
- Cingotti, B., Siquin, A., Durand, J.P., Palermo, T. (2000). Study of Methane hydrate inhibition mechanisms using copolymers. *Annals of the New York Academy of Sciences* 912, 766-776.
- Edwards, A.R. (1994) A molecular modeling study of the winter flounder antifreeze peptide as a potential kinetic hydrate inhibitor. *Annals of the New York Academy of Sciences* 715, 543-544
- Freer, E.M., Sloan E.D., Jr. (2000). An engineering approach to kinetic inhibitor design using molecular dynamics simulations. *Annals of the New York Academy of Sciences* 912, 651-657.
- Jorgensen, W.L., Chandrasekhar, J.D., Madura, J.D., Impey, R.E., Klein, M.L. (1983). Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.*, 79: 926.
- Kvamme, B. (1997). Characterization of kinetic hydrate inhibitors by molecular dynamics simulations.

- Proceedings Thirteenth Symposium on thermophysical properties, June 22-27, Boulder, Colorado
- Larsen, R. (1997). Clathrate hydrate single crystals: growth and inhibition. Ph.D. Thesis, Norwegian University of Science and Technology, Trondheim, Norway.
- Lederhos, J.P., Long, J.P., Sum, A.K.W., Christiansen, R.L., Sloan E.D., Jr. (1996) Effective kinetic hydrate inhibitors for natural gas hydrates. *Chemical Engineering Science*, 51
- Madras, N., Sokal, A. D. (1988). The pivot algorithm: a highly efficient Monte Carlo method for the self-avoiding walk. *J. of Statist. Phys.* 50: 109.
- Makogon, Y.F. (1974). *Hydrates of Natural Gases*, Nedra, Moscow. (in Russian); (1981), Pennwell, Tulsa (in English).
- Makogon Y.F. (1997). *Hydrates of Hydrocarbons*. PennWell, Tulsa
- Makogon Y.F. and Holditch S.A. (2001). Gas Hydrates formation and dissociation with inhibitors, *Oil & Gas Journal*, Feb.5, 2001
- Makogon, T. (1997b). Experimental and computer study of the effect of kinetic inhibitors on clathrate hydrates. PhD Dissertation, Colorado School of Mines, Golden, Colorado
- Makogon, T.Y., Larsen, R., Knight C.A., Sloan, E.D., Jr. (1997c) Melt growth of tetrahydrofuran clathrate hydrate and its inhibition: Method and first results. *J. Crystal Growth*. 179, 258-262.
- Mayo, S. L., Olafson, B. D., Goddard, W. A. (1990). DREIDING: a generic force field for molecular simulations. *J. Phys. Chem.* 94: 8897.
- MMS (1994). *Dispersed Oil Toxicity Tests with Biological Species Indigenous to the Gulf of Mexico*. MMS Publication 94-0021
- Monfort, J.P., Jussaume, L., Hafaia, T.El, Canselier, J.P. (2000) Kinetics of gas hydrates formation and tests of efficiency of kinetic inhibitors. *Annals of the New York Academy of Sciences* 912, 753-765
- Myerson, A. S (1993). *Handbook of industrial crystallization*. Butterworth-Heinemann: New York 37.
- Nerheim, A.R., Svartaas, T.M., Samuelson, E.J. (1992), Investigation of hydrate kinetics in the nucleation and early growth stage by laser light scattering. In *Proceedings of the Second International Offshore and Polar Engineering Conference*. 1. 620-627.
- Reid, R. C., Prausnitz, J. M., Poling, B. E. (1987). *The properties of gases and liquids*, 4th ed. McGraw-Hill.
- Rider, K.T. (1999). *Hydrate single crystals : morphology, inhibition, and pipeline flow assurance*. M.S. Thesis, Colorado School of Mines, Golden, Colorado
- Rodger, P.M. (1994). The stability of gas hydrates. *J. Phys. Chem.*, 94: 6080.
- Sloan E.D., Jr. (1990) *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York.
- Smelik, E.A., King, H.E., Jr. (1997). Crystal growth studies of natural gas clathrate hydrates using a pressurized optical cell., *American Mineralogist*, 82, 88.
- Storr, M.T., Rodger, P.M. (2000). A molecular dynamics study of the mechanism of kinetic inhibition. *Annals of the New York Academy of Sciences* 912, 669-677
- Svartaas, T.M., Kelland, M.A., Dybvik, L., (2000) Experiments related to the performance of gas hydrate kinetic inhibitors. *Annals of the New York Academy of Sciences* 912, 744-752
- Talley, L.D., Oelfke, R.H. (1999) Method for predetermining a polymer for inhibiting hydrate formation. U.S. patent 5,900,516