



## Full Length Article

# Effect of polyvinylpyrrolidone at methane hydrate-liquid water interface. Application in flow assurance and natural gas hydrate exploitation



Nilesh Choudhary<sup>a</sup>, Subhadip Das<sup>b</sup>, Sudip Roy<sup>b</sup>, Rajnish Kumar<sup>a,\*</sup>

<sup>a</sup> Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Pune 411008, Maharashtra, India

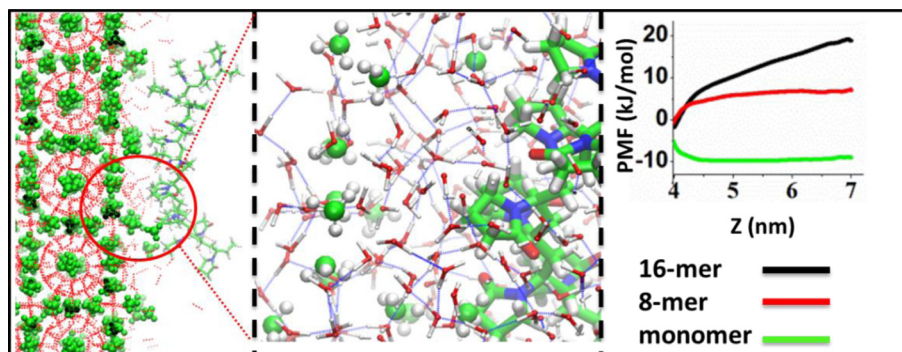
<sup>b</sup> Physical Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, Maharashtra, India

## HIGHLIGHTS

- This work illustrates the inhibition and decomposition mechanism of gas hydrate in presence of polyvinylpyrrolidone at molecular level.
- Free energy of binding of polyvinylpyrrolidone with hydrate surface was calculated.
- Higher molecular weight of polyvinylpyrrolidone has greater binding affinity with gas hydrate surface.
- Enhanced decomposition kinetics was observed in the presence of polyvinylpyrrolidone polymer.

## GRAPHICAL ABSTRACT

Images shows the engagement of atoms of 16-mer PVP inside water which are cages close to hydrate surface and graph is PMF (free energy) profiles of all three systems.



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## ABSTRACT

Polyvinylpyrrolidone (PVP) is one of the most studied low dosages hydrate inhibitor (LDHI), while its hydrate inhibiting effect is well known, its surface active properties by which PVP molecules alters the hydrate-liquid water interface has not been understood properly. In the present work, influence of PVP molecules at the hydrate-liquid water interface was studied at molecular level using molecular dynamics (MD) simulation. In addition, impact of various molecular weights (or chain length) of PVP molecules was also investigated. The force field parameters for PVP monomer ( $F_4$ ) and polymers were developed and validated against PVP physical properties. The free energy of binding of PVP with methane hydrate and methane hydrate decomposition kinetics was studied in presence of PVP at hydrate-water interface. Structural properties of hydrate were analyzed using four body order parameter and mutually coordinated guest order parameter (MCG-OP). The decomposition rate of methane hydrate in presence of PVP molecules (in bulk water near hydrate interface) was studied, it was observed that PVP polymer changes the surface properties of hydrate and enhances the hydrate decomposition rate.

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\* Corresponding author.

E-mail address: [k.rajnish@ncl.res.in](mailto:k.rajnish@ncl.res.in) (R. Kumar).

## 1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds; its formation requires supersaturated guest molecule-water mixture at suitable thermodynamic conditions. At favorable (thermodynamic) condition, gas hydrate stochastically nucleates and the crystal grows through enclathration of the guest molecules into hydrogen bonded water cages [1–4]. Enclathration of small gaseous molecules and lower hydrocarbons like methane, carbon dioxide, hydrogen sulphide, tetrahydrofuran etc. can stabilize the hydrate cages at suitable temperature and pressure through Van der Waals forces. Gas hydrates generally grows into different kinds of cubic and hexagonal structure, depending upon shape and size of the guest molecules, molecular interaction between the guests and host molecule and suitable thermodynamic conditions governed by surrounding temperature and pressure. Under temperature and pressure conditions prevalent on our planet, methane hydrates forms cubic structure I (sI) hydrate with a unit cell of two  $5^{12}$  (pentagonal dodecahedron) and six  $5^{12}6^2$  (hexagonal truncated trapezohedron) cages [1,2].

Discovery of naturally occurring gas hydrates under the sea bed and in the permafrost ensures a potential fossil energy source for future. Recovery of methane from natural gas hydrates, however, is not trivial as its chemical and physical properties are sensitive to pressure and temperature conditions, which are attributed mostly to their complex structures and non-bonded interactions between the hosts and the guests molecules [1,5]. In oil and gas industries gas hydrate plug formation is quite common in production and transmission pipelines. Therefore, various flow assurance options are being used to inhibit solid hydrate formation in the production and transmission pipelines to maintain consistent flow and seamless operations [6,7]. Gas hydrate formation in such cases is controlled by addition of suitable additives that operates by ensuring either thermodynamic phase boundary shift or by altering the kinetics of nucleation and growth. Depending on the water cut, as much as 40 wt% of thermodynamic hydrate inhibitors (THIs) like methanol and glycol are used to shift the phase boundary of hydrate formation. Thus, use of THIs for hydrate inhibition is not only expensive it also leads to environmental and other operational challenges [7,8]. In comparison, the low dosage (0.1–1 wt %) hydrate inhibitors (LDHIs) slows down the kinetics of nucleation, growth and agglomeration of hydrate crystals by changing the surface property thereby maintaining sustained hydrocarbon flow [9,10]. Polymers like Polyvinylpyrrolidone (PVP) and Polyvinylcaprolactam (PVCap) are some of the common LDHIs used in the industry. Multiple literature points towards use of more expensive but supposedly green chemicals like anti-freeze proteins (AFPs) and other novel materials as LDHI and their efficiency has been compared with PVP and PVCap [9,11–14]. There is need of more effective and environment friendly LDHIs drives research towards understanding the mechanism of such inhibition.

Various studies have reported that LDHIs can alter the formation as well as decomposition kinetics of gas hydrate. The inhibiting effect of such additives on hydrate nucleation and growth is well documented, however not much have been done to understand the mechanism of gas hydrate inhibition [9,15–19]. In one such experimental work Daraboina et al. [15] concludes that few LDHIs were capable of inhibiting hydrate formation and also enhancing the kinetics of hydrate decomposition. On the contrary, Bruusgaard et al. [16] studied gas hydrate formation as well as decomposition experiments on water droplet by using AFP, PVP and PVCap as LDHIs and concluded that LDHIs acts as hydrate preserving agent by showing higher memory effect and slow decomposition rate in comparison with pure water system. Thus, study of hydrate decomposition kinetics in presence of such

additives might help in understanding the mechanism by which certain additive changes the surface property of water-hydrate interface. Multiple studies exist in literature where hydrate formation/decomposition kinetics have been studied in presence of different LDHIs, nature of its interaction with liquid water, free gas and, solid gas hydrate surface has been studied [13,20–23]. Anderson et al. [21] have proposed that the LDHIs disrupt hydrate structure if they have higher free energy of binding with the gas hydrate surface. More recently Yagsaki et al. [23] have showed the stabilization PVCap monomer on gas hydrate surface by certain free energy cost. Bagherzadeh et al. [20] have studied the action of AFP (Winter Flounder) on hydrate surface and concludes that pendent methyl groups of AFP adsorbs on empty hydrate cages which discontinue further hydrate growth. The authors proposed three plausible mechanisms of hydrate inhibition; (1) modification of the local structuring of water molecule by LDHI resulting in inhibition of hydrate nucleation. (2) Prevention of the local organization of guest and host molecule in presence of LDHI thus increasing the nucleation barrier. (3) Attachment of LDHIs on the nucleated surface, which prevents further hydrate growth.

In the present work, we have carried out all atomistic MD simulation to look into the effect of a common industrial inhibitor, PVP polymer and its monomer on the hydrate surface and hydrate decomposition kinetics at molecular level. Understanding of methane hydrate decomposition kinetics in presence of such additives on the interface is very relevant for maintaining flow assurance in oil and gas pipelines. Moreover, experimental evidence exists in the literature where presence of such additives helps enhance the decomposition kinetics of methane hydrate at certain temperature and pressure condition. Thus, use of such additives would be essential for exploitation of natural gas hydrate reservoir for methane recovery [24]. MD simulation study as presented in the current work is the most widely used method to get detailed information regarding the molecular level interactions as well as providing valuable input on the free energy of binding of the additive to the hydrate and its effect on the hydrate decomposition kinetics [25–30]. Depending upon PVP molecular weight from monomer to polymer, PVP may have different conformation at the hydrate water interface which may lead to difference in free energy of binding. Free energy landscape between PVP and hydrate were calculated using steered molecular dynamic (SMD) simulation and umbrella sampling (US) simulation [26,31,32]. Decomposition of gas hydrates is influenced by various factors like mass transfer, heat transfer and presence of additives in the flow stream. We wanted to identify, with other operating conditions remaining same how addition of an additive like PVP in the bulk aqueous phase affects the hydrate decomposition kinetics.

## 2. Computational details

All atomistic MD simulations were performed using Gromacs 4.6.3 [33]. Multicomponent systems were used for simulation which contained methane (in hydrate phase), water (in liquid and hydrate phase) and PVP (monomer or polymer solvated in liquid water phase). The crystallographic structure of one unit cell of sI methane hydrate was obtained and it was replicated in the form of supercell of  $3 \times 3 \times 6$  and  $6 \times 6 \times 6$  form of supercell (in X, Y and Z directions) [27,30,34]. Details about the construction of simulation box are given in simulation procedure. Tetrahedral rigid methane potential parameters were used as proposed by Murad et al. [35] and Alavi et al. [30]. The extended simple point charge (SPC/E) water model was used for liquid and hydrate water which is optimal water model for calculating property of interest [27–29,36–38]. Suitability of SPC/E water model for decomposition kinetics has been proved by multiple studies in literature

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