Surface Chemistry

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Approaches to the Design of Better Low-Dosage Gas Hydrate Inhibitors**

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Clathrate hydrates constitute a class of ice-like inclusion compounds formed from guest molecules (usually light hydrocarbon gases) and water.[1] The blockage of pipelines by the formation of natural gas hydrates is a serious problem for the energy industry. Traditionally, large volumes of chemicals such as methanol are employed as thermodynamic hydrate inhibitors. Recently, low-dosage hydrate inhibitors (LDHIs) have also been investigated.[1–3] We have previously shown that antifreeze proteins (AFPs) have higher inhibition activities than the commercial LDHI poly(*N*-vinylpyrrolidone) (PVP).[4,5] Remarkably, active AFPs also demonstrated the novel ability to eliminate the "memory effect" (that is, faster reformation of hydrate after melting), while PVP did not.[4,5] The results suggest that a better understanding of the inhibition mechanism of natural AFPs can help in the design of more efficient synthetic LDHIs.

Since PVP and AFPs appear to have little effect on the homogeneous nucleation of clathrate hydrates,[4] the proposed inhibition mechanism needs to focus on the effect of the LDHI on heterogeneous nucleation and subsequent growth of hydrate crystals. In effect, the inhibition of the growth of hydrate crystals by LDHIs through specific adsorption to certain face(s) of the hydrate crystals has been studied.[4,6] The observation that LDHIs all retard the formation of clathrate hydrates but affect the "memory effect" in different ways indicates that these macromolecules act in distinct ways during the heterogeneous nucleation of clathrate hydrates,[1–4] which has not been studied in detail previously. It is well-known that a suitable contaminant or "sympathetic" surface is needed to induce heterogeneous nucleation.[7] Thus, it is reasonable to propose that a good inhibitor of heterogeneous nucleation can adsorb and deactivate the nucleation sites,[7] including impurities such as hydrated oxides of Si or Fe, or even hydrophilic container walls. As a consequence, the probability of subsequent formation of ice/clathrate hydrate is reduced. Thus, the adsorption of these inhibitors on silica was examined to explore this possibility,.

The adsorption of LDHIs onto silica was determined using a quartz crystal microbalance (QCM) equipped to determine the energy loss or dissipation factor (*D*).[8,9] Our previous studies revealed that an AFP from fish (winter flounder, wfAFP, MW ≈ 4000) had weaker inhibition activity than an insect AFP (*Choristoneura fumiferana* (CfAFP), MW ≈ 9000).[4] On the basis of the adsorb-and-deactivate mechanism,[7] an inhibitor with a larger adsorption mass on the nucleator surface should theoretically show stronger inhibition activity for heterogeneous nucleation. Our QCM-*D* analysis showed that CfAFP had a higher adsorption mass (*m*) than wfAFP at all three concentrations tested (Figure 1 A). However, the results also showed that PVP (Mw ≈ 40 000) had a higher adsorption mass than wfAFP on silica at each concentration tested (Figure 1 B), even though wfAFP is a better inhibitor of heterogeneous nucleation than PVP.[4] Therefore, it is important to also consider the status of the adsorbed macromolecular film.

In QCM-*D* analysis, the *m* value represents the adsorption mass, while the *D* value (dissipation factor) represents the

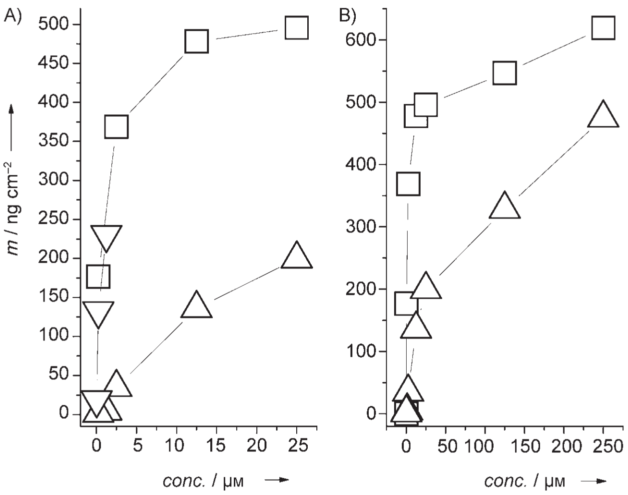

Figure 1. A) Adsorption mass (*m*) of wfAFP (△), CfAFP (▽), and PVP (□) versus concentration on the silica surface. B) Adsorption mass *m* of PVP and wfAFP over a broader concentration range.

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viscoelastic properties of the adsorbed molecules (an example is given in Figure 2 A).[8,9] It is notable that during the measured time scale (about 1 h), no desorption was observed (Figure 2 A). The relationship between the change of dissipation factor with adsorption mass (R) is calculated as $R = \Delta D/\Delta m$ and represents the status of the adlayer on the surface. A change in the value of R comes from three factors: the adsorbed layer, the trapped liquid, and the bulk solution.[8,9] A large R value indicates a porous, flexible adlayer with more trapped liquid. The observed change in the R values of wfAFP and PVP suggests a rearrangement occurred as adsorption progressed,[10] and the final R value (R_2) represents the final status of the adsorbed film on the silica surface. The very low R_2 value of wfAFP indicates the presence of an adlayer that is more compact and rigid with little trapped water. In contrast, the much larger R_2 value for PVP indicates a porous layer with more trapped liquid (Figure 2 B–D). Note that the D versus m curves for wfAFP and CfAFP are similar (Figure 2 B,C), thus indicating that both AFPs form a rigid film on silica. At 0.25 µм, CfAFP showed an adsorbed mass comparable to that of wfAFP at a 100-fold higher concentration (140 versus 191 ng cm^{-2}, see Figure 1 and Figure 2 B,C), while wfAFP at 0.25 µм did not give a detectable adsorbed mass. These results suggest that more of the nucleator surface was covered by CfAFP at a lower concentration. This finding is in agreement with the observation that a low concentration of CfAFP showed higher inhibition activity for the heterogeneous nucleation of clathrate hydrates than did wfAFP.[4]

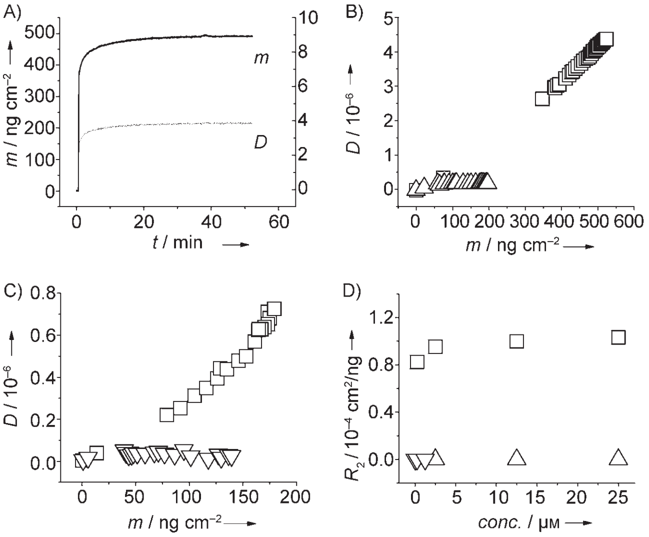

Figure 2. Adsorption behaviors of LDHIs on silica in terms of mass (m) and dissipation factor (D) of: A) PVP at 12.5 µм. B) wfAFP (△) and PVP (□) at 25 µм; C) CfAFP (▽) and PVP (□) at 0.25 µм; D) R_2 value versus concentration for wfAFP, CfAFP, and PVP.

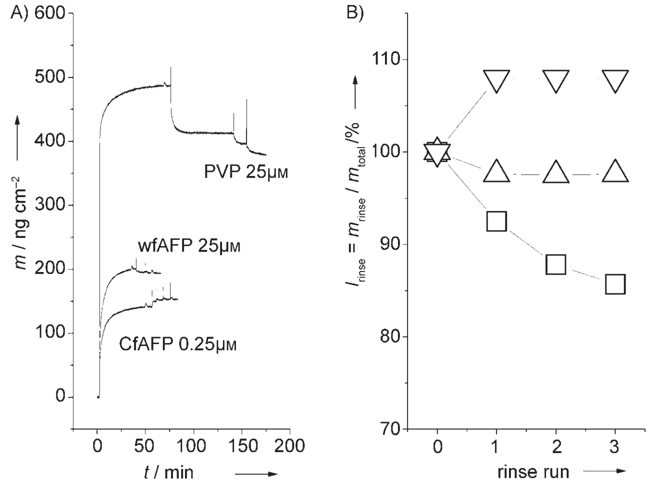

Figure 3. The effect of rinsing the silica surface on the adsorption of wfAFP (25 µм, △), CfAFP (0.25 µм, ▽), and PVP (25 µм, □). A) The adsorption onto the silica surface after rinsing (3×0.5 mL) with pure water and B) the percentage of adsorption mass loss ($m_{\text{rinse}}/m_{\text{total}}$) at each rinse.

AFPs have the unique ability to eliminate the “memory effect” during the melting and reformation of clathrate hydrates.[4] In the present study, the effects of rinsing the adsorbed AFPs and PVP were examined to further elucidate the different behaviors of these macromolecules on the “memory effect”. After the adsorbed crystal had been rinsed with ultrapure water (1.5 mL), the adsorption mass on the wfAFP-covered silica surface decreased by about 2–3 %. Conversely, the apparent adsorption mass of CfAFP increased by about 8 %, thus indicating that there was no loss. It is possible that additional CfAFP molecules, originally trapped in the loops of the QCM-D instrument, were then able to adsorb onto the silica surface. Strikingly, however, rinsing removed almost 25 % of the PVP from the silica surface (Figure 3). It is known that in bulk solutions in which clathrate hydrates are formed, hydrophilic impurity particles, such as silica, are virtually unavoidable. Thus, if AFP or PVP were present in solution, the impurity surface would be partially covered by AFP or PVP, with the AFP molecules forming a rigid and compact film and PVP molecules forming looser films. As a result, different inhibition activities are observed under hydrate-forming conditions. When the clathrate hydrate is decomposed at modest conditions, the potential nucleating silica surfaces are essentially “rinsed” because of the movement of the melted solution. Since the silica surface remains effectively covered by AFPs, and additional AFP molecules may also adsorb to the impurity surface during the melting, the kinetics of clathrate hydrate inhibition do not change appreciably during the reformation of the hydrate in the presence of these proteins.[4,5] In contrast, in the absence of AFPs, a large area of the impurity surface is exposed to the solution after the rinsing or melting, with the result that the heterogeneous nucleation of clathrate hydrates would occur more readily. This situation gives rise to the frequently observed “memory effect”,[4,5] which is a particular problem in pipelines.[1] Compared with wfAFP, CfAFP showed an even stronger resistance to the effect of rinsing at a 100-fold lower concentration. This finding possibly explains why CfAFP eliminates the memory effect at low concentrations while wfAFP is effective at higher concentrations.[4]

Previous studies on LDHIs have emphasized the effects of LDHIs on the growth of clathrate hydrate crystals. The present study shows that the interaction between LDHIs and the nucleating surface is also important. It suggests that there are three important factors to be considered in the design of future LDHIs, namely, the status of the adsorption layer, adsorption mass, and resistance to rinsing (or adsorption strength). A good LDHI should have the ability to form a rigid adlayer film with a large adsorption mass and a high resistance to rinsing at low concentrations. Thus, we advocate the use of QCM-*D* as a fast and efficient technique that offers promise for large-scale screening and design of potential LDHIs. In addition, it would be worthwhile considering other factors such as the effect of the molecular weight of the macromolecule on adsorption. It is also important to further investigate the structures of the LDHIs on the nucleating surface, that is, the change(s) in the secondary structure of the macromolecules upon adsorption to the surface. Therefore, other surface-analysis techniques such as circular dichroism[11] or the use of a fluorescent probe[12] would further illuminate the adsorption-and-inhibition mechanism and provide useful guidance for the design of better synthetic LDHIs.

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