Effects of Long-chain Surfactants, Short-chain Alcohols and Hydrolizable Cations on the Hydrophobic and Hydration Forces

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(ABSTRACT)

The DLVO theory states that the interaction between two lyophobic particles in aqueous media can be predicted by the sum of two surface forces, i.e., the electrical double-layer and van der Waals forces. This theory, which was developed 50 years ago, served as a backbone for colloid chemistry. However, various experiments conducted in recent years showed that it is applicable only to those particles whose advancing water contact angles (θ_a) are in the range of 15-60°. For example, direct surface force measurements conducted between silica substrates, whose θ_a values are less than 15°, exhibited the existence of repulsive hydration forces at relatively short separation distances. On the other hand, substrates, for which θ_a is greater than 60°, exhibit long-range attractive hydrophobic forces not considered in the DLVO theory . These extraneous attractive forces play important roles in many industrial applications. It is, therefore, the objective of the present study to measure the hydrophobic and hydration forces under different conditions. The measurements were conducted using both the Surface Forces Apparatus (SFA) and the Atomic Force Microscope (AFM). Mica and Silica were used as substrates, and the effects of dioctylammonium-hydrochloride (DOAHCl), octanol, methanol, ethanol, trifluoroethanol (TFE), pyridine, $CaCl_2$, $MgCl_2$ and sodium oleate were studied.

A Mark IV SFA was used to conduct force measurements between mica surfaces in aqueous solutions of DOAHCl, which is a secondary amine. At 7×10^{-6}M DOAHCl, the mica surfaces were rendered electrically neutral, and net attractive hydrophobic forces were observed. The measured forces can be represented by a double-exponential function with the larger decay length (D_2) of 5.1 nm. The measured hydrophobic forces are substantially stronger than those reported in literature between self-assembled monolayers of soluble single-chain surfactants such as dodeylammonium hydrochloride (DAHCl) and cetyltrimethylammonium bromide (CTAB).

Appearance of the strong hydrophobic forces is due to the likelihood that the double-chain cationic surfactant can create a higher hydrocarbon chain packing density than the single-chain cationic surfactants such as DAHCl and CTAB.

Force measurements were also conducted using the AFM between a silica plate and a glass sphere in aqueous solutions of methanol, ethanol, TFE and pyridine to study their effect on the hydration force. It was observed that in Nanopure water, silica surfaces exhibit a strong short-range hydration repulsion, which can be represented by a double-exponential function with its longer decay length (D_2) of 2.4 nm. In solutions containing 15% methanol, however, the hydration force disappears completely. This observation can be attributed to the displacement of the water molecules H-bonded to the silanol group by methanol, which in turn destroys the water structure in the vicinity of the silica surface. Methanol can displace water from the silanol group because it is more basic than the water. Ethanol, on the other hand, cannot cause the hydration forces to disappear, suggesting that it is less effective than methanol in displacing the H-bonded water molecules from the silanol groups, possibly due to steric hindrance. In the presence of triflouroethanol (TFE) and pyridine, hydration forces change little, which suggest that they are not effective in disturbing the water structure in the vicinity of silica.

Finally, an AFM was used to measure the hydrophobic forces between silica surfaces coated with oleate. Since this surfactant is anionic, and the silica surface is negatively charged in alkaline solutions, it was necessary to reverse the charge of the silica substrate. In the present work, $CaCl_2$ and $MgCl_2$ were used as activators. It was found that hydrophobic forces are observed at pHs where the $CaOH^+$ or $MgOH^+$ ion concentrations reach maximum, suggesting that the singly charged hydroxo-complexes are the activating species. A model developed in the proposed work suggests that a significant part of the free energy of adsorption comes from the lateral interactions between neighboring hydroxo-complexes on the surface. It is also suggested that oleate adsorbs on silica as basic calcium oleate and basic magnesium oleate. These species may be H-bonded to the silanol groups on surface.

The force measurements were also conducted between hydrophobic (silanated) silica surfaces in $CuCl_2$ solutions. The results show that the hydrophobic force decreases most

significantly at the pH where the concentration of the $CuOH^+$ ions reaches maximum, which suggests that the singly charged hydroxo-complexes are more surface-active than their unhydrolyzed counterpart. The driving forces for the adsorption of the $CaOH^+$ ions may include the electrostatic attraction from the surface and the lateral interaction between neighboring hydroxo-complexes on the surface.

ACKNOWLEDGEMENTS

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