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Co-adsorption of surfactants and water at inorganic solid surfaces†

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Computer simulations of the co-adsorption of water and methanoic acid at a range of surface features of calcite and fluorite minerals have shown that the relative adsorption energies for the two minerals are reversed when solvent effects are included in the calculations, a finding which is important in the search for effective surfactant reagents in flotation techniques, which are used extensively in the mining and pharmaceutical industries and in environmental remediation processes.

Fluorite (CaF_2), a major source of fluorine, and calcite ($CaCO_3$) are often found together in mineral deposits. As a result there is an active search for potentially selective surfactants for their extraction in mineral separation processes, such as flotation, a technique which is used extensively in the mining and pharmaceutical industries and in waste water and soil remediation processes. The technique is based on the selective adsorption of surfactants to the mineral of interest thus giving it a hydrophobic surface, after which these particles can be separated from the mixture. One major group of surfactants used in industrial flotation processes are carboxylic acids such as oleic acid,[1,2] which apart from the acid functional group has a simple hydrocarbon chain. As the major binding between mineral surface and surfactant molecule is *via* electrostatic interactions with the functional group,[3] we have concentrated in this work on methanoic acid as a representative of the carboxylic acid class of surfactants. Previous studies of organic adsorbates at mineral surfaces have often either neglected the presence of water[4] or studied adsorption of water and surfactant in separate calculations,[5] but we show in this article that the presence of solvent can neither be ignored nor treated in isolation, if the simulation results are to be useful in interpreting experiment.

Computational methods are well placed to calculate at the atomic level the geometry and adsorption energies of the adsorbate molecules at the solid surfaces. The approach we have used is to employ classical energy minimisation techniques to study the co-adsorption of methanoic acid and water at the dominant calcite (1014) and fluorite (111) surfaces. The computer simulation code used for the calculation of the surface and adsorbate structures and energies was METADISE,[6] employing established potential models for the calcite and fluorite crystals and adsorbate molecules.[5,7,8] The interactions between the methanoic acid and water molecules were derived for this work and fitted to the experimental hydration energy of methanoic acid (48 kJ mol^{-1}). As 'real' surfaces are never completely free from defects, we have included a collection of experimentally observed stepped surface sites in our calculations, as well as the ideal planar surfaces. We considered two different steps on the calcite surface, both found experimentally as growth steps or the edges of etch pits. They differ in the orientation of their carbonate groups which either lean backwards at an obtuse angle with respect to the underlying plane or forwards at an acute angle. A similar arrangement is seen for the F_2 groups in the steps on the fluorite (111) surface. As these lower-coordinated surface sites are often more reactive, we considered both adsorption sites on the terraces and at the step edges and calculated adsorption energies for a whole range of initial configurations and positions of the adsorbates.

We first considered adsorption of the surfactant molecules at the unhydrated calcite and fluorite surfaces and calculated the adsorption energies as the difference between the adsorbate/surface system compared to the surface and an isolated methanoic acid molecule. The adsorption energies are listed in Table 1, from which it is clear that for both materials binding of the surfactant to the stepped surface sites is more exothermic than onto the terraces, especially at the calcite step edges. The lattice spacing of the fluorite surface is smaller than that of the calcite surface and better suited to accommodating the surfactant molecules, hence the greater adsorption energy for the planar fluorite surface. However, this trend is reversed when we consider the stepped surfaces, where adsorption at the calcite steps is far more exothermic than at the fluorite steps. Fig. 1 shows the adsorption of a methanoic acid molecule at the acute step of the non-hydrated calcite surface. Due to the geometry of the step site, the surfactant molecule is able to form very strong interactions between the doubly bonded oxygen atom and a calcium ion on the terrace below the step (O–Ca 2.29 Å), while the other oxygen atom binds to calcium ions both at the edge and to the underlying terrace at longer distances of about 4 Å. The hydrogens also interact with ions both on the edge and the terrace, leading to a network of hydrogen-bonding between the surface and adsorbate. It is due to these multiple interactions that the surfactant adsorption at the stepped surfaces is more

Table 1 Adsorption energies (kJ mol^{-1}) for methanoic acid in the absence and presence of a co-adsorbed water layer

Surface sites	Dehydrated surface	Hydrated surface
Calcite		
Planar	−37.5	−38.7
Acute step	−168.0	+141.3
Obtuse step	−108.1	+335.6
Fluorite		
Planar	−56.3	−75.9
Acute step	−90.8	−68.6
Obtuse step	−79.5	−295.0

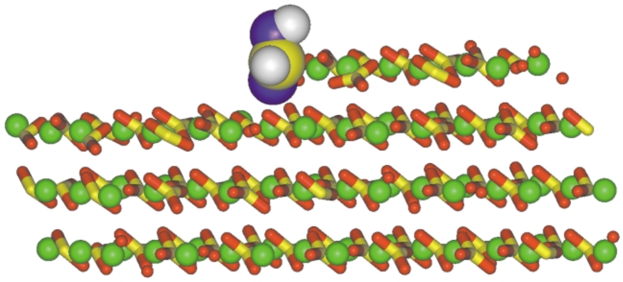

Fig. 1 The acute step on the dehydrated calcite surface with adsorbed methanoic acid; Ca = green, O = red, O_{meth} = purple, C = yellow, H = white.

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exothermic than on the planar surfaces. Adsorption at the calcite steps is now preferred as these sites are more open than the step sites of fluorite and the surfactant fits in the hollow between the step wall and terrace.

We next considered the more realistic process of surfactant adsorption at the same calcite and fluorite surfaces in the presence of water, where the adsorption energies for the surfactant were now calculated with respect to the hydrated surface and a solvated methanoic acid molecule. The data listed in Table 1 show that on the planar surfaces, the presence of water does not significantly alter the adsorption energies or indeed the preference of surfactant adsorption onto fluorite rather than calcite. The reason that the co-adsorption of water does not appreciably affect the surfactant adsorption energies becomes clear if we compare the adsorption pattern of the surfactant with that of water at the same surface sites. The methanoic acid only replaces one adsorbed water molecule at the surfaces and although on the fluorite surface the adsorbate is stabilised to some extent by the formation of hydrogen-bonded interactions to neighbouring water molecules, the adsorption pattern of the water is not disturbed on either surface by the presence of the surfactant. In addition, hydration of the planar calcite and fluorite surfaces releases an average energy per water molecule of 30.7 and 38.5 kJ mol^{-1}, respectively, which is not very different from the adsorption energy of methanoic acid and hence there is little competition between the two adsorbate species. Furthermore, the intermolecular interactions between the water molecules themselves (43 kJ mol^{-1}) or with the methanoic acid (40 kJ mol^{-1}) are very similar, hence negating any preference the water molecules might have for interacting with either the surfactant or each other. As a result, even though methanoic acid is a stable adsorbate at both planar surfaces, there is no significant change in the adsorption energies due to the co-adsorption of water.

However, as we can see from Table 1, at the stepped surface sites the co-adsorption of water radically changes the surfactant adsorption energies. Surfactant adsorption at the stepped calcite sites becomes very endothermic indeed, while adsorption at the obtuse fluorite step is aided considerably by the presence of water. Again, the reason is twofold, based on both the geometry of the surface sites and the relative adsorption energies of the surfactant and the water molecules. Although the adsorption of water at the calcite step sites releases less energy per molecule (80–125 kJ mol^{-1}) than adsorption of one surfactant molecule, the geometry of these sites is such that the methanoic acid would be replaced by two or more water molecules instead of one as was the case on the terrace sites of the planar surface. Due to the high reactivity of these stepped calcite sites, a layer of water is formed at the surface surrounding the steps, when no methanoic acid is present. However, the presence of the surfactant molecule prevents the formation of an orderly pattern of adsorbed water, even away from the step, leading to an energetically unfavourable configuration. In addition, as the water molecules prefer to adsorb to the surface rather than interact with the surfactant molecule, the methanoic acid is forced away from the surface and the water molecules do not form a proper solvation shell around the surfactant molecule and hence its adsorption to the surface becomes less energetically favourable than solvation in bulk water.

At the fluorite step sites, however, the opposite effect is found. Hydration of the fluorite steps is not as exothermic as the calcite steps (30–50 kJ mol^{-1} on average) and indeed very similar to the planar fluorite surface (average ~ 38 kJ mol^{-1}). In addition, unlike the stepped calcite surfaces, the pattern of water adsorption away from the steps is not significantly disturbed by the presence of the surfactant. Even in the presence of water the methanoic acid remains closely bound to the step site and stabilising interactions with the surrounding water molecules lead to very favourable adsorption energies, especially at the obtuse step, which is shown in Fig. 2. The water molecules away from the step adsorb in a regular pattern while others in the step region cluster round the surfactant molecule, which also smoothens the transition from the upper to the lower terrace.

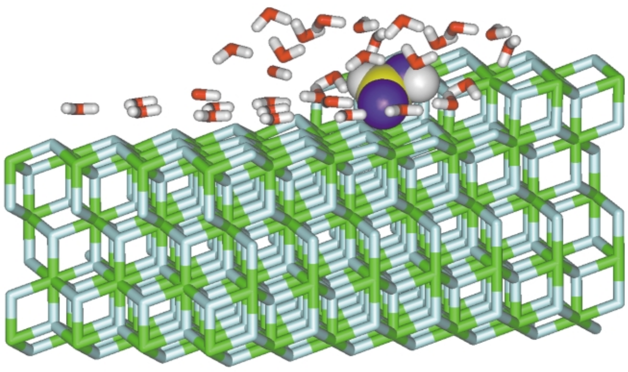

Fig. 2 Co-adsorption of water and methanoic acid at the obtuse step on the fluorite surface, where the fluorite crystal is shown in blue, Ca = green, F = blue, O_{meth} = purple, C = yellow, H = white, O_{water} = red.

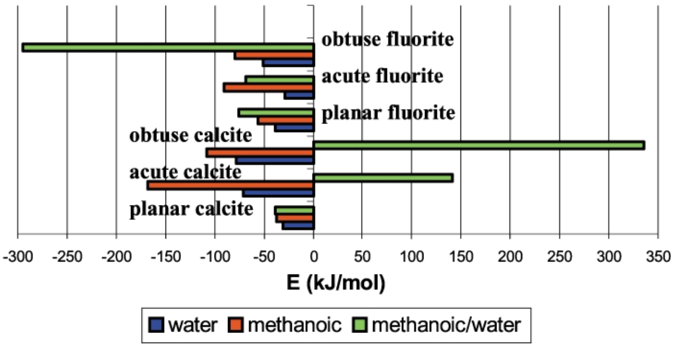

Fig. 3 Adsorption energies of water, methanoic acid and methanoic acid in the presence of water, at planar and stepped calcite and fluorite surfaces.

In summary, we have shown that it is not sufficient to calculate the interactions of surfactant molecules with mineral surfaces in isolation as the presence of solvent in the calculations makes a significant contribution to the final adsorption energies, shown in Fig. 3. Carboxylic acid surfactants are known to adsorb to fluorite in preference to calcite, which finding is only reproduced once we model systems which include both realistic surface defects, such as low-coordinated steps, and solvent in the simulations. Without the presence of water, we would expect from Fig. 3 that the surfactant interactions with calcite outweigh those with fluorite, but under aqueous conditions, the opposite is very clearly the case. Future work will include adding hydrocarbon chains to the carboxylic acid group to investigate whether the presence of a hydrophobic group, which all experimental surfactants contain, leads to different adsorption behaviour.

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