

Towards Improved Zinc Corrosion Inhibitors - Understanding the Role of Silanes on ZnO

Researchers at the University of Vienna have used Materials Studio® to study the binding of silane molecules on the surface of zinc oxide¹⁻³. Zinc oxide forms as a thin film under atmospheric conditions on the surface of zinc. The simulations revealed how the polarity of the tail group and the presence of solvent can effect the configurations the molecules adopt on the oxide surface. These findings will lead to the design of improved coatings and zinc corrosion inhibitors.

The behavior of molecules on oxide surfaces, in particular silanes, has been widely studied using computational chemistry techniques. Industrial applications include corrosion inhibition, adhesives, paints, self assembled monolayers, and catalysis.

The scientists used MS Modeling's Amorphous Cell to create solvent-silane cells which are placed on the oxide substrate (Fig. 1). The behavior of three different silane molecules - octyltrihydroxysilane, aminopropyltrihydroxysilane, and thiolpropyltrihydroxysilane (Fig. 2) on the surface was studied using molecular dynamics simulations and the COMPASS forcefield.

These silanes were studied as the degree of polarity on the tail varies and hence can be used to understand the role of the tail on the dominant configurations found on the surface. The simulations were run for 1 ns using approximately ten different starting configurations.

The results show that when these systems came to equilibrium two types of configurations exist; the A position where only the silane head group binds to the surface and the B configuration where both the head and tail are in contact with the surface (Fig. 3a,b).

There is a strong correlation between the polarity of the tail group with the dominant configuration adopted by the molecule on the ZnO surface. The very polar aminopropyl molecule prefers the B configuration, while the non-polar octyl molecule prefers the A configuration. The intermediate thiol group shows a slight preference for B over A. An important point to note is that such

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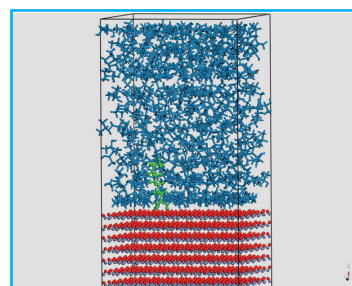
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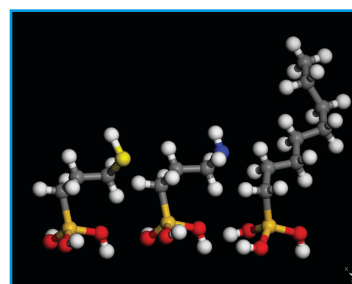
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▲ Fig. 1 The amorphous cell containing the ZnO substrate, the solvent molecule (blue) and the silane (green).



▲ Fig. 2 Silanes used in the study; thiolpropyltrihydroxysilane (left), aminopropyltrihydroxysilane (center) and octyltrihydroxysilane (right).

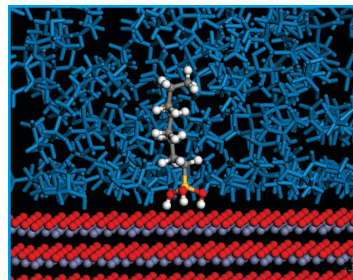
effects are only seen in the presence of solvent, without the solvent, the B configuration is the most dominant for all of the silanes. The adsorption energies show that the strongest binding energies to the ZnO surface correspond to the degree of polarity; amino > thiol > octyl.

Conclusion

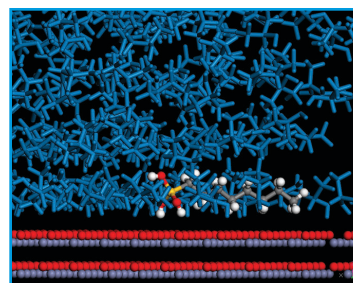
This study is unique in that the simulation included the presence of an isopropanol solvent; traditionally the solvent has been ignored to save computational time. The work is a good example of how computational chemistry can not only be used as a screening tool to test several different molecules, but more importantly to develop an understanding on the behavior of different systems as a function of their molecular characteristics. This reduces the number of experiments required and allows one to do more intelligent experiments.

References

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▲ Fig. 3(a) The A configuration of the silane. Solvent is blue.



▲ Fig. 3(b) The B configuration of the silane molecule. Solvent is blue.