

Influence of divalent cations on carboxylate surface interaction

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Interactions between organic molecules in aqueous environments are often affected by the cations present in the solution. However, the way in which these cations affect the water-organic interface is still not clear. We investigated how interactions between model self assembled monolayer (SAM) terminated by alkyl (-CH₃), acetate (-COO⁻) or malonate (-DiCOO⁻) are influenced by the presence of divalent cations Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺. We used atomic force microscopy (AFM) in chemical force mapping (CFM) mode to monitor changes in adhesion force between the functionalized tips and surfaces during exposure to solutions containing 0.5 M NaCl and 0.012 M of each divalent cation.

The number of carboxylates interacting and their molecular structure have an important impact on the adhesion forces (Fig.1). DiCOO⁻ geometrical rigidity decreases the tendency for ion bridging, leading to lower adhesion forces. Ca²⁺ and Sr²⁺ are more prone to form ion bridges with -DiCOO⁻ as a result of the positive geometric relationship between malonate spacings and their hydrated radii. The absence of carboxylates on the tip reduces considerably the possibility of ion bridging. Results indicate that charge separation and cooperative binding between carboxylates are critical factors for cation complexing.

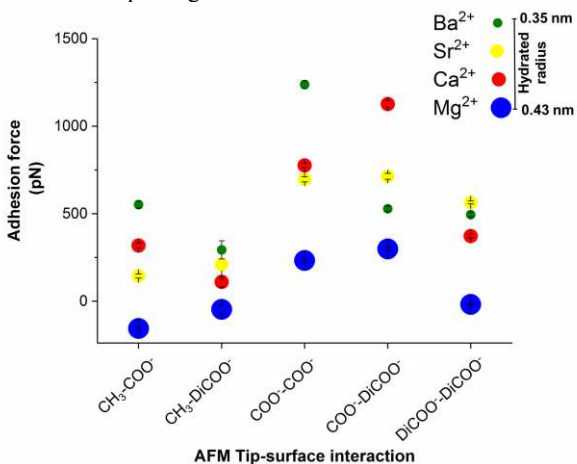


Figure 1. Average adhesion force measured for various carboxylate systems during exposure to solutions containing divalent cations.