Adhesion attenuation and enhancement in aqueous solutions

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1. Introduction
When two surfaces confine water layers between them at the nanoscale, the behaviour of these confined water molecules can deviate significantly from the behaviour of bulk water, which affects the adhesion of such surfaces. This study assesses the role of confined water layers on the adhesion of hydrophilic surfaces, and how sensitive this adhesion is to the presence of contaminant solutes which can disrupt the hydrogen bonding network of water molecules between the surfaces.

2. Experimental

• Alumina-sputtered sphere-tipped cantilever, interacted versus an alumina single crystal, using atomic force microscopy.
• Solvent/solute concentrations tested over the range 0-100% organic.
• Measurements were performed under immersed conditions using (i) water, and mixtures of (ii) water/dimethylformamide, (iii) water/ethanol, and (iv) water/formamide.

3. Results

\[ W_{th} = -AR/6D \]

\[ A = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h\nu_0}{16\sqrt{2}} \left( \frac{n_1^2 - n_3^2}{n_1^2 + n_3^2} \right)^{3/2} \]

A = Hamaker constant, R = tip radius, D = separation distance, k = Boltzmann’s constant, T = temperature, \( \varepsilon \) = dielectric constant, h = Planck’s constant, \( \nu_0 \) = electron absorption frequency, n = refractive index

• The measured work of adhesion upon separation of the surfaces was greatly in excess of the theoretical value, \( W_{th} \), predicted by Eq. 1, assuming D = 1 nm.
• Low concentrations of dimethylformamide and ethanol increased the work of adhesion to values greater than the work of adhesion measured in water.
• Formamide and dimethylformamide exhibited differences in behaviour at high concentrations and for pure liquid.

4. Conclusions

• Number of possible hydrogen bonds which can be formed between surfaces strongly affects adhesion behaviour.
• Ability of atoms within the solute to act as hydrogen bond donors and acceptors is also important.
• For example, methyl hydrogen is a better donor than formyl hydrogen; the strength of a hydrogen bond depends on the specific binding environments involved.
• The number of water molecules in the primary solvation shell is important at low solute concentrations.
• Continuum theories describing adhesion between surfaces are not applicable when hydrogen bonding effects occur.
• When the two surfaces are at closest approach, the structure of the hydrogen bonded network requires further experimental and theoretical consideration.

Acknowledgements
The atomic force microscope used in this research was obtained through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and partly funded by the European Regional Development Fund (ERDF).

This poster is a summary of the paper published in Langmuir: ‘Adhesion of alumina surfaces through confined water layers containing various molecules.’ Langmuir 2012, 28, 4648-4653; DOI: 10.1021/la2045064
The URL can be obtained by scanning the adjacent QR code.