

# Anion specific effects in weak polybasic brushes

Professor Erica J. Wanless

The University of Newcastle, Newcastle, Australia

erica.wanless@newcastle.edu.au

The anion-specific solvation and conformational behaviour of weakly basic poly(2-dimethylamino)ethyl methacrylate) brushes together with the increasingly hydrophobic poly(2-diethylamino) and poly(2-diisopropylamino) analogues have been investigated using *in situ* ellipsometric and quartz crystal microbalance with dissipation measurements.[1,2]

In the osmotic brush regime, as the concentration of salt is gradually increased the brushes osmotically swell by the uptake of solvent as they become charged and the attractive hydrophobic inter- and intra-chain interactions are overcome. With increased ionic strength, the brushes move into the salted brush regime where they desolvate and collapse as their electrostatic charge is screened. Here, as the brushes collapse they transition to more uniform and rigid conformations, which dissipate less energy than similarly solvated brushes at lower ionic strength.

Significantly, in these distinct regimes brush behaviour is not only ionic strength-dependent but is also influenced by the nature of the added salt based on its position in the well-known Hofmeister series; with potassium acetate, nitrate and thiocyanate investigated. The strongly kosmotropic acetate anions display low affinity for the hydrophobic polymers and the largely unscreened electrosteric repulsions allow the brushes to remain highly solvated at higher acetate concentrations. The mildly chaotropic nitrate and strongly chaotropic thiocyanate anions exhibit a polymer hydrophobicity-dependent affinity for the brushes. Increasing thiocyanate concentration causes the brushes to collapse into uniform and rigid conformations at lower ionic strength than for the other two anions. This study is unprecedented for weak polyelectrolyte brushes and demonstrates the importance of all ion, solvent and polymer interactions.

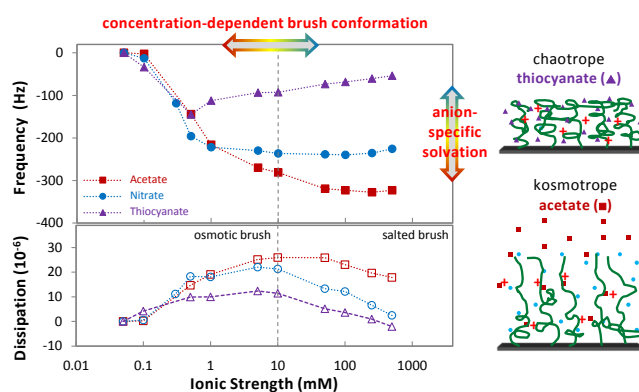


Figure 1. Specific anion effects evident within the salt-induced conformation of a poly(2-dimethylamino)ethyl methacrylate) brush.

[1] J.D. Willott, T.J. Murdoch, B.A. Humphreys, S. Edmondson, G.B. Webber, E.J. Wanless, *Langmuir* **30**(7) 1827 (2014). DOI: 10.1021/la4047275

[2] J.D. Willott, T.J. Murdoch, B.A. Humphreys, S. Edmondson, E.J. Wanless, G.B. Webber, *Langmuir*, *in press* (2015). DOI: 10.1021/acs.langmuir.5b00116