

Contrasting pK_a of protonated bis(3-aminopropyl)-terminated polyethylene glycol "Jeffamine" and the associated thermodynamic parameters in solution and covalently attached to graphite surfaces

Abiman, P.¹, Wildgoose, G.G.¹, Crossley, A.², Jones, J.H.³ and Compton, R.G.¹

¹ Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, United Kingdom

² Materials Department, University of Oxford, Parks Road, Oxford, United Kingdom

³ Chemical Research Laboratory, University of Oxford, Mansfield Road, Oxford, United Kingdom

Abstract

The pK_a value of protonated Jeffamine (bis(3-aminopropyl) terminated polyethylene glycol) in solution and attached as a monolayer to graphite surfaces has been determined using Potentiometric titration. The protonated Jeffamine was found to have a pK_a value of 9.7 in solution at 25°C, whereas this value decreases to 7.1 when it is attached to a graphite surface. Potentiometric titrations from 25 to 40°C allowed us to determine the surface pK_a of the protonated Jeffamine at each temperature studied and hence to determine the enthalpy, entropy and Gibbs energy changes associated with the deprotonation of the amino-terminated surface bound Jeffamine groups. It was found that the enthalpic contribution is negligibly small and the evaluation of these thermodynamic parameters controlling the shift in surface pK_a value indicates that this process is controlled by entropic contribution arising from the ordering/disordering of solvent molecules at the carbon-water interface. This suggests that the long chain Jeffamine molecules are oriented on the carbon surface rather than existing in the bulk solution.

Author keywords

Benzoic acid; Graphite; Polyethylene glycol; Polymers; Thermodynamic parameters

Indexed keywords

Engineering controlled terms: Enthalpy; Entropy; Gibbs free energy; Graphite; Polyethylene glycols; Polymers; Titration

Engineering uncontrolled terms: Enthalpic contribution; Potentiometric titrations; Protonated Jeffamine; Thermodynamic parameters

Engineering main heading: Carboxylic acids