Contrasting pKa of Protonated Bis(3-aminopropyl)-Terminated Polyethylene Glycol "Jeffamine" and the Associated Thermodynamic Parameters in Solution and Covalently Attached to Graphite Surfaces

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Abstract

The pKa 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 pKa 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 pKa 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 pKa 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.