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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

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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.

Keywords: benzoic acid · graphite · polyethylene glycol · polymers · thermodynamic parameters

Introduction

Modified carbon materials play an important role in catalysis, analytical and biotechnological applications. Free radical grafting methods, either via the electrochemical reduction of diazonium salts, or the electrochemical oxidation of aryl acetates and aromatic amino compounds, respectively, at carbon electrode surface have recently provided efficient route for the modification of carbon surfaces.[1–14]

In the present study we first modified the surface of graphite powder with benzoic acid groups using methodology developed in this laboratory.[15] To this end graphite powder was modified with 4-carboxyphenyl groups via the chemical, as opposed to electrochemical, reduction of 4-carboxybenzenediazoniumtetrafluoroborate using hypophosphorous acid. Jeffamine (bis(3-aminopropyl) terminated polyethylene glycol) was then coupled onto the graphite surface by the formation of an amide bond linkage to the benzoic acid modified carbon (BAcarbon). The evaluation of the acid/base properties of these modified species is important because the physical and chemical properties of surface-immobilised molecules are often different from those in the bulk solution and is an important consideration in the further development of possible synthetic strategies. This effect has been observed for a wide number of relevant systems, for example, phenyl carboxylic acids on glassy carbon electrodes[7,16] azo dyes,[17] self assembled monolayers of thiols[18–21] and thioctic acids[22] on gold electrode surfaces, fatty amines in phosphatidylcholines[23] and amines on gold electrodes.[24] The reasons for the shifts in pK_a are not fully understood, but have been attributed to a variety of factors. These include such considerations as whether the interface is charged or not, the nature of the surface such as its hydrophobicity, lateral interactions between adsorbed species for example, hydrogen bonding, electronic interactions between surface bound species and the bulk solid electrode and dif-

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fering molecular environments (such as solvation shell, solvent accessibility etc.).[25] In our work graphite powder covalently modified with Jeffamine groups exhibits significantly large changes in the measured pK_a values of the protonated species compared to protonated Jeffamine in solution (pK_a = 7.1 and 9.7, respectively, at 25 °C). The changes in the surface pK_a value of the Jeffamine-modified carbon (Jcarbon) from that of Jeffamine in solution were studied between the temperature range of 25–40 °C. This then allowed us to determine the thermodynamic parameters associated with this process such as the enthalpy, entropy and Gibbs energy change upon protonation of the Jeffamine amine group. The observed pK_a values of protonated Jcarbon are found to be shifted by more than two pK_a units to lower values at 25 °C.

The enthalpic contribution in both cases is found to be negligibly small, indicating that lateral interactions and/or hydrogen bonding are not responsible for these changes. However the change in surface pK_a value is found to be controlled by the entropy change upon protonation of the Jeffamine amine groups. This is interpreted as being due to a change in solvent ordering/disordering at the interface.[15] As the entropic process influences the observed pK_a value this is taken to imply that the end groups of the long chain Jeffamine molecules are oriented on the graphite surface rather than extending into the bulk solution.

Thermodynamic Analysis

Jeffamine is a weak base which reacts with an acid according to Equation (1).

$$RNH_2 + HA \rightleftharpoons RNH_3^+ + A^- \tag{1}$$

The pH of the solution depends on both the acid dissociation constant, K_a, and the concentration of the protonated Jeffamine and deprotonated Jeffamine remaining in solution, described by Equation (2).

$$\mathrm{pH} = \mathrm{p}K_a + \log\left[\frac{[RNH_2]}{[RNH_3{}^+]}\right] \tag{2}$$

If the concentration of protonated Jeffamine and Jeffamine are known (or can be calculated) then the pK_a of the species under consideration can be determined from the intercept of the appropriate plot of pH versus the log term in Equations (2). Having obtained the ionisation constant, K_a, one can then determine the value of the thermodynamic parameters such as the change in entropy, enthalpy and Gibbs energy for the dissociation of protonated Jeffamine via the integral form of the Van't Hoff Isochore [Eq. (3a)] and standard thermodynamic relationships given by the following Equations (3b–c).

$$\ln K_a = -\left(\frac{\Delta H_a^\circ}{RT}\right) + \mathrm{const} \tag{3a}$$

$$\Delta G^\theta = -RT\ln K_a \tag{3b}$$

$$\Delta G^\theta = \Delta H^\circ - T\Delta S^\circ \tag{3c}$$

Results and Discussion

XPS Characterization: Unmodified graphite, benzoic acid modified graphite and Jeffamine modified graphite were characterized using XPS (see Figure 1). Two peaks could be observed with binding energies of about 285.6 and about 534 eV corresponding to photoelectrons emitted from C_{1s} and O_{1s} levels, respectively. Two further spectral features are observed at about 746 and 998 eV corresponding to the O_{KLL} and C_{KLL} Auger emissions. Furthermore for Jcarbon a broad peak is observed at about 401 eV corresponds to emission from the N_{1s} level in both the terminal amine and amide bond linkages confirming modification of Jeffamine onto the graphite surface. For BAcarbon the atomic percentage of oxygen on the surface, as measured using the spectral peak areas, the O_{1s} signal increased by 16.7 %. Thus the introduction of benzoic acid onto the graphite powder accounts for about 8.35 % of the total oxygen-containing functionality on the surface. The atomic percentage of oxygen on the surface of Jcarbon was found to further increased by 12.54 %. Thus the introduction of Jeffamine onto the graphite powder accounts for about 12.5 % of the total oxygen-containing functionality on the surface (Table 1). A crude calculation using the molecular dimensions of Jeffamine and the lattice parameters for a perfect sheet of graphite indicate that this is equivalent to an almost monolayer coverage of Jeffamine on the graphite surface (10^{-10} mol cm^{-2}).

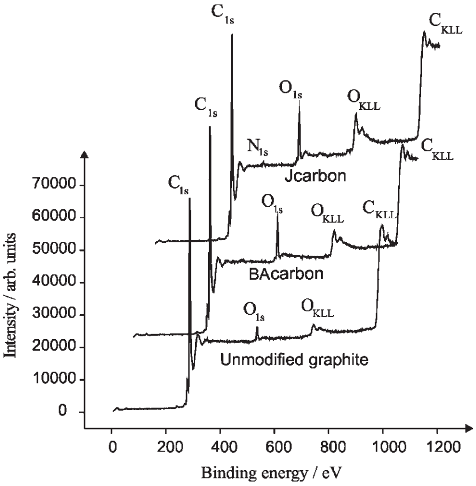


Figure 1. XPS spectra (wide scans 0–1296 eV) of blank graphite BAcarbon and Jcarbon (offset for clarity) for comparison.

Table 1. Tabulated percentage values of each elements present in the blank and modified carbon samples determined by the Gaussian fit to their XPS spectra.

Carbon sample	C [%]	O [%]	N [%]
Unmodified graphite	91.8	8.2	91.8
BAcarbon	74.5	24.9	0.5
Jcarbon	61.4	37.4	1.1

Potentiometric titration of molecular Jeffamine and Jcarbon powder: The potentiometric titration of Jeffamine (described in the Experimental Section) produced a sigmoidal plot of pH against volume of HCl (Figure 2). The exact concentration of Jeffamine initially present in solution was calculated from the equivalence point volume of HCl, where stoichiometric amount of reactants have been mixed together. After each addition of HCl, the concentration of Jeffamine cations formed by the protonation, and hence the concentration of Jeffamine remaining in solution, was obtained from the concentration of hydroxonium ions, as determined by the solution pH, and the amount of HCl added. The pK_a of Jeffamine was determined graphically using equation 2 and it was found to be 9.7 at 25 °C (Figure 3b) consistent with the literature values for the range of pK_a values of primary amines.[31]

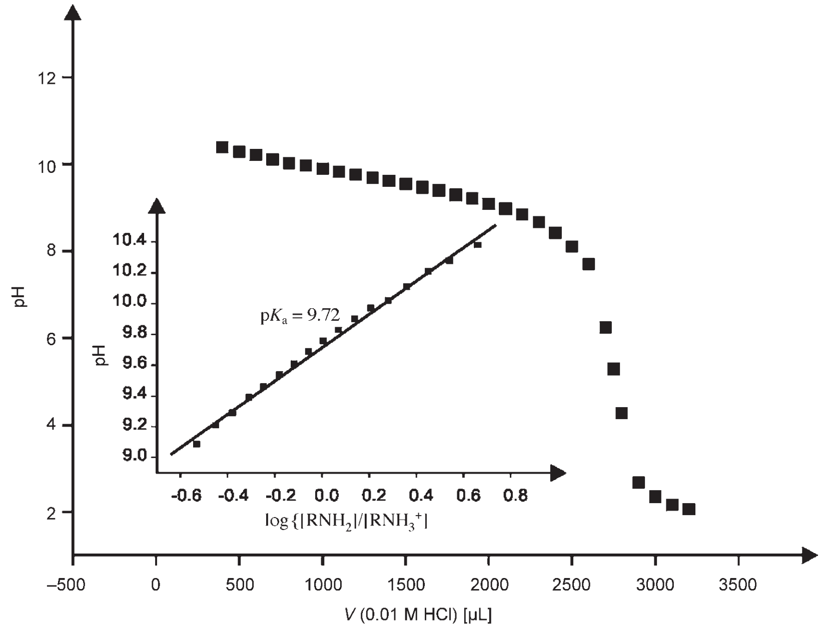


Figure 2. Plot of pH versus volume of HCl added and the corresponding plot of pH versus log{[RNH_3^+]/[RNH_2]} at 25 °C for 0.01 M Jeffamine in solution.

Next a potentiometric titration of the Jcarbon powder was performed at 25 °C, which also produced sigmoidal titration curve, as shown in Figure 3. Interestingly the surface pK_a value for Jcarbon was found to be 7.1 at 25 °C using Equation (2) (Figure 3). This value is significantly lower than that of Jeffamine in solution. In our previous work when benzoic acid was modified onto a graphite surface the observed pK_a values were found to shift by more than two pK_a units to higher values, whereas in this report pK_a values were found to shift by more than two pK_a units to lower values. This can interpreted as being due to a change in solvent ordering/disordering at the interface upon ionization of benzoic acid and protonation of Jeffamine onto the graphite surface. This implies that the orientation of the Jeffamine in Jcarbon should be on the surface of the carbon as an end group, even though Jeffamine is a long chain polymer.

These results reveal that the graphite powder to which the Jeffamine is covalently attached plays a role in changing the surface pK_a value. To investigate this effect further, a series of potentiometric titrations were carried out on Jeffamine and Jcarbon powder over a temperature range of (25–40 °C). The pK_a values for each case were calculated at each temperature studied as described above and were found to decrease with increasing temperature. These results were used to calculate the standard enthalpy, entropy and Gibbs energy of the protonation of Jeffamine with the aid of Equations (3a–c). The enthalpy change, ΔH^0, for the ionization of protonated Jeffamine and Jcarbon was determined by plotting lnK_a versus $1/T$. In both cases the plots were linear, with an R^2 value not less than 0.999. The enthalpy changes were found to be negligibly small at 0.9 and 0.7 kJ mol^{-1} respectively. Tables 2 and 3 detail the Gibbs energy and entropy change for the deprotonation of Jeffamine in solution Jcarbon powder, respectively. In the case of the Jcarbon the entropy change upon deprotonation is significantly lower than that of Jeffamine in solution. In our previous work in the case of benzoic acid modified onto the graphite surface entropy change upon ionisation was significantly greater than that of benzoic acid in solution, where the pK_a value was shifted to higher value for the benzoic acid modified onto graphite surface from its solution value. One possible explanation for this is that the BAcarbon deprotonation leads to a charged surface whereas for Jcarbon deprotonation leads to a neutral surface. Therefore the shift of pK_a value is controlled by the entropic factor which is also responsible for the large shifts in the surface pK_a values of Jcarbon. The negligibly small enthalphic changes indicate that the lateral interactions and/or hydrogen bonding do not play a significant role in altering the pK_a value. The entropic factor most likely reflects a change in the solvent ordering around the

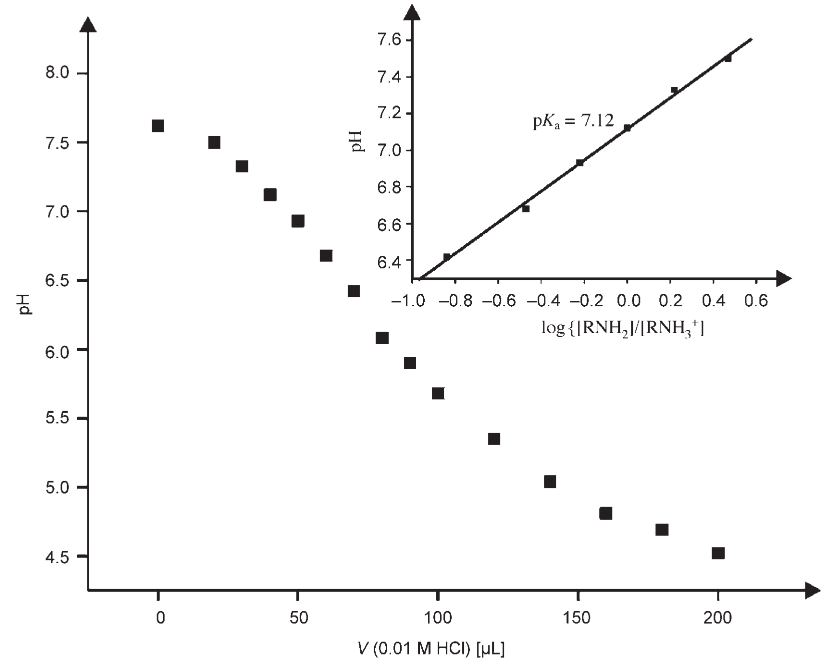


Figure 3. Plot of pH versus volume of HCl added and the corresponding plot of pH versus log{[RNH_3^+]/[RNH_2]} at 25 °C for Jcarbon.

Table 2. Tabulated values of the change in Gibbs energy and entropy for the ionization of Jeffamine in solution from 25 to 40 °C.

T [°C]	ΔG^o [kJ mol^{-1}]	ΔS^o [J K^{-1} mol^{-1}]
25	55.4	−183
30	54.6	−177
35	54.0	−172
40	53.9	−169

Table 3. Tabulated values of the change in Gibbs energy and entropy for the ionization of Jcarbon powder from 25 to 40 °C.

T [°C]	ΔG^o [kJ mol^{-1}]	ΔS^o [J K^{-1} mol^{-1}]
25	40.6	−134
30	39.8	−129
35	39.4	−125
40	39.2	−123

interface, implying that it is the relative hydrophobicity/hydrophilicity of the graphite surface that is the major factor influencing the changes in surface pK_a values.

Conclusion

Graphite powder covalently modified with Jeffamine via coupling to benzoic acid species on the carbon surface exhibits significantly large changes in the measured pK_a values compared to Jeffamine in solution. Potentiometric titration revealed that the pK_a of the amino terminated Jeffamine on the surface of graphite powder is shifted to by more than two pK_a units lower than Jeffamine in solution.

The thermodynamic parameters such as the Gibbs energy, enthalpy and entropy of the protonation of the Jeffamine on the graphite surface, as well as Jeffamine in solution have been determined. The enthalphic contribution to this process was negligibly small, indicating that any lateral interactions on the carbon surface and/or hydrogen bond formation were not responsible for the observed changes in pK_a. Instead the different surface pK_a values were found to be controlled by the entropic term. This has been attributed to the relative ordering/disordering of solvent molecules at the interface between the carbon substrate and the solution. Thus the orientation of Jeffamine molecules on the surface of graphite can be inferred by the variation in the observed pK_a values and suggests these long chain molecules are lying that on the graphite surface rather than existing into bulk solution.

Experimental Section

Reagents and equipment: All reagents were obtained from Aldrich (Gillingham, UK) and were of the highest grade available and were used without further purification. All solutions and subsequent dilutions were prepared using deionized water from Millipore (Vivendi, UK) UHQ grade water system with a resistivity of not less than 18.2 MΩ cm at 25 °C. The synthetic graphite powder (Aldrich) consisted of irregularly shaped particles 2–20 μm in diameter. pH measurements were performed using a Hannah pH 213 pH meter. In order to calibrate the pH meter at elevated temperatures, a two-point calibration was made prior to each experiment using IUPAC standard buffer solutions (0.5 M sodium acetate + 0.5 M acetic acid, pH 4.6 at 25 °C; 0.05 M disodium tetraborate, pH 9.2 at 25 °C) which have a known pH at each temperature studied.[26]

X-ray photoelectron spectroscopy (XPS) was performed on a VG Clam 4 MCD analyzer system at the OCMS Begbroke Science Park, University of Oxford, UK using X-ray radiation from the $Mg_{K\alpha}$ band ($h\nu$ = 1253.6 eV). All XPS experiments were recorded using an analyzer energy of 100 eV for survey scans and 20 eV for detailed scan with a take-off angle of 90°. The base pressure in the analysis chamber was maintained at not more than 2.0×10^{-9} mbar. Each derivatised carbon sample studied was mounted on a stub using double sided adhesive tape and then placed in the ultra-high vacuum analysis chamber of the spectrometer. Analysis of the resulting spectra was performed using Origin 7.0. Assignment of spectral peaks was performed using the UKSAF[27] and NIST[28] databases.

Synthesis of 4-carboxybenzenediazonium tetrafluoroborate:[16] 4-Aminobenzoic acid (0.01 mol) was dissolved in warm HCl (2 M; 18 mL), after which the solution was cooled to 0 °C and a solution of sodium nitrite

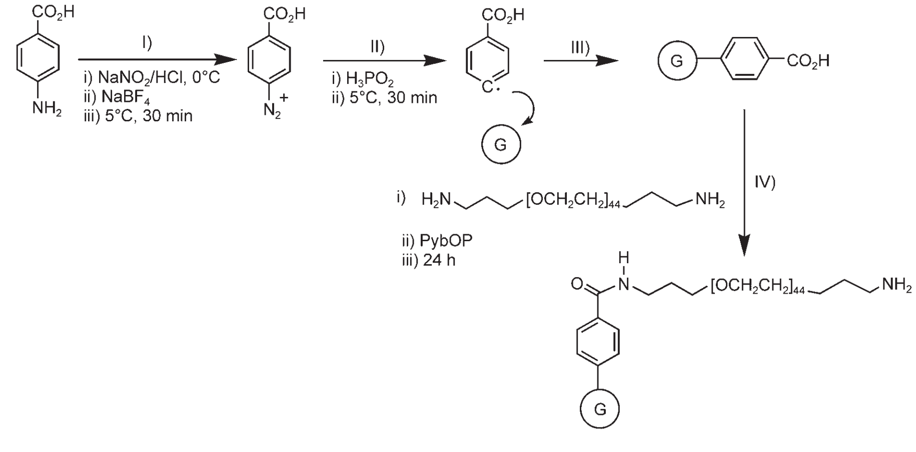
(0.011 mol in 4 mL water) was added drop wise for 20 minutes with stirring. The solution was filtered and sodium tetrafluoroborate (1.48 g, 0.013 mol) was added in several small portions to the filtrate which was stirred for a further 15 minutes. After this time the solution was filtered by suction and washed with ice water and cold ether. The powder was dried and recrystallised from a mixture of acetonitrile and ether. The resulting 4-carboxy-benzenediazonium salt was stored under vacuum in a desiccator over dry alumina.

Derivatisation of graphite powder with 4-carboxybenzenediazonium tetrafluoroborate to form BAcarbon: The chemically activated derivatisation of graphite powder was achieved by the following method.[29,30] First graphite powder (0.5 g) was stirred into a 0.1 M solution of 4-carboxybenzenediazonium tetrafluoroborate (10 mL) prepared using pure water to which hypophosphorous acid (H_3PO_2, 50 % w/w in water; 25 mL) was added. Then the solution was allowed to stand at 5 °C for 30 min with gentle stirring. After that the solution was filtered under suction and washed with deionised water to remove any excess acid and finally with acetonitrile to remove any unreacted diazonium salt. The experiment was carried out again using the above protocol with benzoic acid modified carbon (BAcarbon) replacing the graphite powder to get maximum derivatisation. The BAcarbon was then air-dried by placing inside a fume hood for a period of 12 h prior to use.[29,30]

Synthesis of Jcarbon powder: BAcarbon (500 mg), benzotriazol-1-yl-oxy-tripyrrolidinophosphonium hexafluorophosphate[32] (PyBop, 0.5 g, 1 mmol) and Jeffamine (400 mg, 0.2 mmol) were placed in a round bottomed flask. Dioxane (8 mL) and ethyl diisopropylamine (1.7 mL, 10 mmol) were added to the reaction mixture as solvent and base, respectively. The reaction mixture was stirred under argon at room temperature. After 24 h the mixture was filtered and the solid washed with methanol and acetonitrile. The solid was dried in *vacuo* to afford a black powder consisting of Jeffamine coupled to the benzoic acid modified carbon surface via an amide bond linkage (see Scheme 1).

Potentiometric titration of Jeffamine and Jcarbon powder: An aqueous 0.01 M solution of Jeffamine (25 mL) was pipetted into a 20 mL double-walled glass cell connected to a temperature controlled water bath and allowed to come to thermal equilibrium. After which the initial pH was recorded using a potentiometric glass pH meter. The solution was then titrated using aliquots of a known volume of 0.01 M HCl. The pH of the solution was measured thirty seconds after each addition of HCl.

The potentiometric titration of Jcarbon powder was performed using the modified carbon powder (0.5 g) stirred into pure water (10.0 mL) for 2 min prior to titration against HCl. Again the suspension was stirred for 30 s after each addition of HCl. The pH of the suspension was then recorded. Note that the pH meter was calibrated at each temperature before taking readings using two IUPAC standard buffers which have a known pH at each temperature studied. The pH probe was not affected by poly-electrolytes or carbon particles. This was confirmed by performing the above experiment with unmodified blank graphite.



Scheme 1. Schematic diagram for the derivatisation of Jcarbon.

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