Conducting polymers from aminobenzoic acids and aminobenzenesulphonic acids: influence of pH on electrochemical behaviour

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Abstract

The influence of pH on the electrochemical behaviour of conducting polymer films electrosynthesised from aminobenzoic acids and aminobenzenesulphonic acids was investigated by voltammetric and electrochemical impedance studies in sulphuric acid solution, acetate buffer and neutral phosphate buffer. The change in electrochemical behaviour with increasing pH is significantly less for poly(aminobenzenesulphonic acid)s and poly(aminobenzoic acid)s than for polyaniline. Polymer films made by electrosynthesis of mixtures of these monomers with aniline have also been analysed by the same techniques. Experimental results obtained over this pH range are interpreted in the light of previous studies carried out on these polymers in strong acid solution.
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1. Introduction

Due to their high environmental stability and ease of synthesis, polymers from aniline and its derivatives have attracted great interest in recent years. In particular, the importance of chain length and branching in determining the electronic, magnetic, optical, structural and mechanical properties of polyaniline have been stressed [1]. Potential applications include use as the cathode material for lithium batteries [2–5], in polymer light-emitting diodes [6–8], microelectronic devices [9], as conducting fibres [10], blends with Nafion® [11,12] or with cellulose esters [13], electrocatalytic material [14] or as sensors [15–25]. These include sensors for pH measurement [18,23,24], which exploit the change in conductivity and related properties with pH. For bioelectrochemical applications, it is important that the polymer film remains conductive at a pH value greater than 4, and although it is known that the conductivity of polyaniline is significantly reduced as the pH of the solution is increased, there has been some success reported concerning polyaniline electrodes modified by immobilised enzymes [17,20–22]. Co-polymerised aniline and 3-aminobenzoic acid have been employed for measuring ascorbate at pH 7.0 [25].

The variation in conductivity of polyaniline, and the factors that influence it, is extremely important in a number of applications. Thus, a number of studies have been undertaken concerning the influence of pH and of the variation of properties as a function of the counter-ions incorporated from the electrolyte both during synthesis and during characterisation [26–37]. Alternatively, the pH effect can be modified by external doping during synthesis or by introducing substituents in the aromatic ring of aniline. The latter has been explored in different ways and involves essentially three types of substituent. The first is electron-donating e.g. alkylated or alkoxy, such as in Refs. [38–42], and the second is electron-withdrawing, e.g. chloro or nitro groups such as in Refs. [38,43,44]; both of these types of substituent lead to lower conductivity than polyaniline itself. The third type of substituent involves introduction of acidic groups in the benzene ring, which directly influence the acidity constants of the amine groups and can lead to a

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decrease in the pH dependence. Important acidic group substituents studied include phosphonic [45], carboxylic [46–48] and sulphonic [47,49–52] acid substituents.

Another synthetic possibility is to polymerise mixtures of aniline and the substituted aniline, which has been investigated quite extensively [42,48,49,51–56], but often the influence of reaction conditions and the nature of the film formed has not been addressed in detail. This concern was addressed in Ref. [42] with regard to aniline and 2-methoxyaniline, in which regiospecific co-polyanilines were made by electropolymerisation of methoxy-substituted dimeric and trimeric oligoanilines. It was shown that such regiospecific polyanilines had a more crystalline and regular structure than random copolymers resulting from monomer mixtures, leading to higher film conductivities. In Ref. [49], probe beam deflection was employed to investigate the ion exchange properties of the film formed from mixtures of 2-aminobenzenesulphonic acid and aniline in the absence of supporting electrolyte, it being shown that the concentration of anions can be much smaller than that of the substituted aniline.

The electropolymerisation of carboxylate-substituted anilines (2-, 3- and 4-aminobenzoic acids (2-, 3- and 4-ABA, respectively)) [48] and sulphonate-substituted anilines (2- and 4-amino-benzene sulphonic acids (2- and 4-ABS, respectively)) [52] in sulphuric acid solution has recently been investigated by us. Polymer films were formed on glassy carbon substrates using cyclic potential sweep synthesis, and were characterised in sulphuric acid solution by cyclic voltammetry (CV). IR spectroscopy was carried out on the films after removal from the electrode substrates. Scanning electron microscopy was done using ITO electrodes, no difference being found in film growth between the two substrates. It was clearly demonstrated that coupling can occur in positions other than the position *para*- to the amine group on the aromatic ring. The rate of polymerisation of the substituted anilines was lower than that of aniline owing to inductive, mesomeric and steric effects and there was a tendency for formation of compact films containing short-chain polymers and of one- or two-dimensional growth.

Polymerisation of mixtures of aniline and the substituted aniline in different ratios was also carried out [48,52]. It was shown that aniline polymerisation dominates although the morphology of the films formed is changed from that of polyaniline alone by the presence of the substituted monomer and there is evidence from CV, chromatic properties and IR spectroscopic characterisation of the existence of both components. No direct experimental evidence was found for true co-polymerisation.

Conducting polymers offer a number of potential advantages in electrochemical sensors, for example as electrode materials not subject to fouling or as substrates for enzyme immobilisation. Therefore, with a view to such future applications, in this paper the electrochemical behaviour of substituted polyanilines prepared from carboxylic and sulphonic substituted anilines and from their mixtures with aniline, has been investigated at different pH, principally using voltammetric techniques and electrochemical impedance—in highly acid pH, in weak acid and in approximately neutral aqueous solutions.

2. Experimental

Aniline (Riedel-de Haen), anthranilic acid (2-aminobenzoic acid) (Aldrich), 3-aminobenzoic acid (Aldrich), 4-aminobenzoic acid (Aldrich), 2-aminobenzenesulphonic acid (Aldrich), 4-aminobenzenesulphonic acid (Aldrich) were used as received, except for aniline which was distilled under a nitrogen atmosphere at reduced pressure, kept in the dark, and used within 3 days. The electrolyte for electrosynthesis was usually 0.5 or 1.0 M H_2SO_4, in some cases with the addition of Na_2SO_4 as will be detailed below. All other reagents were analytical grade and tridistilled water was used to make all solutions. Experiments were carried out at 25 ± 1 °C.

The electrochemical cell consisted of a glassy carbon disc working electrode (WE), diameter 0.5 cm, a Pt foil auxiliary electrode in a separate compartment connected by a glass frit and a Radiometer K401 saturated calomel reference electrode. Before use, the WE was polished with diamond lapping compound (Kemet International Ltd.) down to 1 μm particle size on a polishing cloth. The electrode was then held at a potential of +1.6 V versus SCE in H_2SO_4 electrolyte for 6 min and following this, cycled in the potential range -0.5 to $+1.5$ V at a sweep rate of 50 mV s^{-1} for 15 min. After this treatment a reproducible voltammogram of the GCE was obtained showing much reduced background currents.

Films were prepared on glassy carbon electrodes by cyclic potential sweep electropolymerisation as in Refs. [48,52] between potential limits to be specified below, for 30 cycles at a scan rate of 50 mV s^{-1}, using an analogue potentiostat constructed in this laboratory. For polymerisation of the aminobenzoic and aminobenzenesulphonic acids alone, a 0.05 M solution was used in 0.5 or 1.0 M H_2SO_4. The monomer solutions used for co-polymerisation experiments were 1:1 mixtures of the aminobenzoic or amino-benzenesulphonic acid with aniline of total concentration 0.1 M, again in 0.5 or 1.0 M H_2SO_4. The freshly coated electrodes were transferred to a H_2SO_4 electrolyte solution with the same composition as during electrosynthesis, but without any aniline derivatives, for characterisation. Three cycles of the film-electrode assembly were necessary to establish steady-state conditions, leading to cyclic vol-

tammograms the same as those after the 30 polarisation cycles.

Electrochemical impedance measurements were done with a PC-controlled Solartron 1250 frequency response analyser coupled to a Solartron 1286 electrochemical interface using ZPLOT software (Scribner Associates Inc.). An rms potential perturbation of 10 mV was applied over a frequency range from 65 kHz to 0.1 Hz logarithmically with five steps per frequency decade.

To investigate the changes occurring with an increase in pH, the cyclic voltammogram of each film was first measured in 1.0 M H_2SO_4 (pH ~ 0.2), then in 0.1 M H_2SO_4 (pH 1), in 0.2 M acetate buffer (pH 4.6) and in 0.2 M phosphate buffer (pH 6.2). Impedance spectra were also recorded.

3. Results and discussion

The influence of pH on the polyaniline films has been measured mainly through CV and electrochemical impedance studies. For many applications it is important to prepare a polymer that is still electroactive in weak acidic or neutral aqueous solutions.

3.1. Morphology and general characteristics

Although aniline can be electropolymerised even at pH 7, the polymer film formed shows little electroactivity in non-acidic media. However, the films are more compact at higher pH owing to the lower growth rate and scanning electron microscopy demonstrates that the fibrous open nature of films formed in strong acid solution is lost [35]. Nevertheless, on placing these films in acid solution, protons enter the film and they exhibit the normal electrochemical characteristics of polyaniline, despite the physical differences in the film. This reversible behaviour with respect to counterion and proton insertion has been observed on switching between sulphuric acid and acetate buffer solution in the presence of different counterions [35].

The films formed from substituted anilines also lead to compact films [48,52]. An example of the morphology of films formed by polymerisation of substituted anilines in sulphuric acid solution is given for poly(2-ABA) in Fig. 1. They show evidence of one- and two-dimensional growth patterns occurring from nucleation points with little evidence of branching in the polymer chains on the microscopic scale. Chemical microanalysis shows that all the substrate is covered by film. Although these micrographs were recorded using ITO substrates, the electrochemical behaviour of films formed on glassy carbon substrates was found to be the same, suggesting that under the polymerisation conditions employed, there is no difference between the two. This means that polymer growth is occurring mainly at the poly-
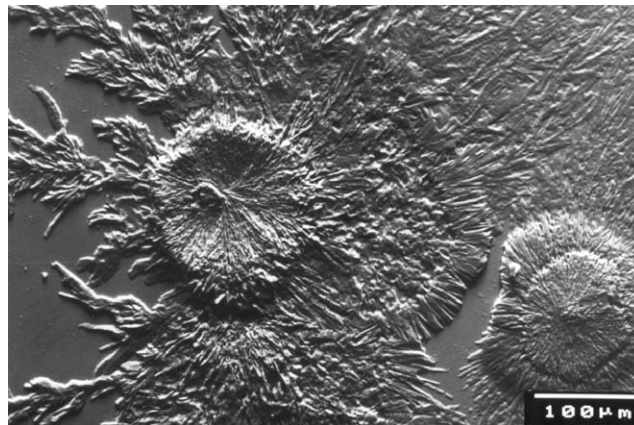

Fig. 1. Scanning electron micrograph of polymer film formed on ITO in sulphuric acid solution from 2-aminobenzoic acid (adapted from Ref. [48]).

mer | solution interface rather than at the substrate | solution interface, as generally occurs for aniline polymerisation [57].

3.2. Cyclic voltammetry

The effect of pH on the cyclic voltammograms of polymer films formed by electropolymerisation in acid solution is exemplified in Fig. 1, 2-ABS (Fig. 2a), and a 1:1 mixture of 2-ABS and aniline (Fig. 2b). Potential
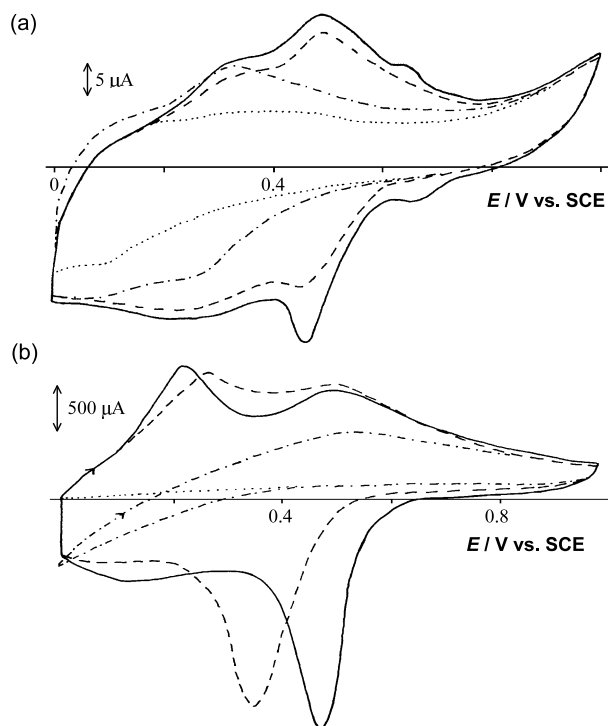

Fig. 2. Cyclic voltammograms of polymer films formed by electropolymerisation of: (a) 2-ABS; and (b) 1:1 mixture of 2-ABS and aniline. (——) in 1.0 M H_2SO_4, (----) 0.1 M H_2SO_4, (—·—·—·—) 0.2 M acetate buffer pH 4.6, (····) 0.2 M phosphate buffer pH 6.2.

limits used in electropolymerisation of substituted anilines were usually 0 and +1.0 V versus SCE. The most salient features are the progressive loss of the oxidation and reduction peaks associated with the conducting-insulating transitions, although it is clear that the relative effect of this change is less when mixtures of substituted aniline and aniline are used for electrosynthesis.

The influence of pH on the first oxidation peak current from cyclic voltammograms for polymers from the aminobenzoic acids, aminobenzenesulphonic acids and aniline is given in Fig. 3. With increasing pH the way in which the current diminishes as the polymer deprotonates is clearly demonstrated. All substituted anilines show very similar normalised currents at pH 1, higher than polyaniline. However, the differences between the various polymers become greater at higher pH values; the decrease in response of polymers made from ABS monomers is less than those from ABA. The peak current corresponding to polyaniline itself measured in pH 6.2 phosphate buffer was only 2% of its value in 1 M sulphuric acid, while for poly(2-ABA) it dropped to ca. 26% and for poly(2-ABS) it was still 53%. The substituent certainly reduces the influence of the pH value. The position of the peak potential is influenced by pH, and also by the counterion [35]. Between pH 0 and 1 this effect led, in general, to a shift in the first oxidation peak to a higher potential, while the second peak was shifted to a lower potential. For substituted anilines, these shifts were much smaller than in the case of polyaniline.

3.3. Impedance

Some typical impedance spectra of poly(2-ABS) in 1.0 M H_2SO_4 solution are shown in Fig. 4a after electro-
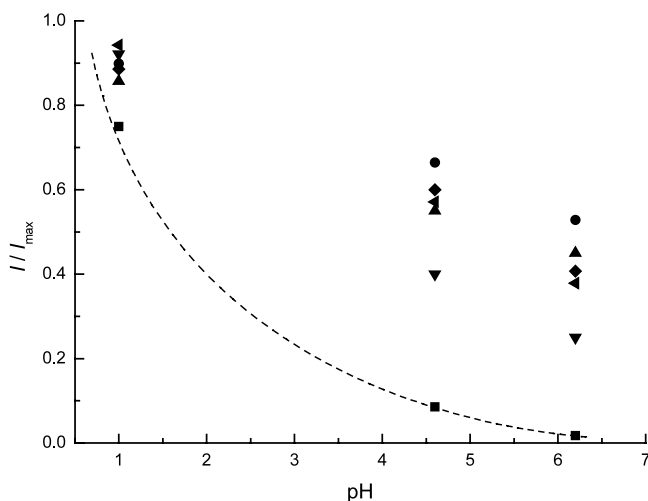

Fig. 3. Plot showing effect of pH on normalised peak current of first oxidation peak for polymers from: ■, aniline; ▼, 2-ABA; ◆, 3-ABA, ◀, 4-ABA, ●, 2-ABS, ▲, 4-ABS. The dotted curve refers to polyaniline.

synthesis for 30 cycles. They exhibit a predominantly capacitive behaviour at 0.0 and 0.4 V, charge transfer becoming evident at 0.9 V versus SCE, corresponding to full oxidation. At high pH—pH 6.2 phosphate buffer (not shown)—the impedance values increase by a factor of around 5 and the spectra are similar in form to that at 0.9 V in Fig. 4a.

Fig. 4b shows spectra of the polymer formed from a 1:1 mixture of 2-ABS and aniline. These are similar to those measured for aniline, i.e. very small values at 0.0 and 0.4 V (at the beginning and in the middle of the electronically conducting zone) and larger values with resistive behaviour at 0.9 V versus SCE.

Detailed studies on polyaniline in strong acid solution [58–63] have been carried out. In Ref. [58] the variation of conductance and capacitance with applied potential was monitored, showing the larger values expected in the conducting zone from ∼0.2 to 0.8 V versus SCE and a direct correlation between the variation of the two parameters, also demonstrated in Ref. [59]. In Ref. [60] it was shown by potential modulated transmittance measurements that the capacitance is associated entirely with charge transfer. It was demonstrated that the impedance can be described to a reasonably good approximation by a Randles-type circuit at low potentials, modelling ion-exchange phenomena at the film | solution interface, in series with a capacitance representing the film itself; at more positive potentials a double nested RC parallel combination can be used. Nevertheless, the possible equivalent circuits depend on a number of experimental factors. For example, when a very high positive switching potential is used in electropolymerisation and there is formation of benzoquinone side products, a more complex circuit with negative capacitance has to be employed [64], or when there is only partial coverage of the electrode substrate [65].

For the case of the substituted polyanilines studied here, there are not clearly defined conducting and nonconducting zones. It is therefore difficult to apply the equivalent circuits described above. For this reason, comparisons are made between film capacitance values derived from spectra such as those in Fig. 4 which reflect principally the properties of the film itself. At higher potentials where a semicircle feature appears for some combinations of polymer and pH, the C value from fitting to an RC parallel combination is employed. Although approximate, this is able to illustrate the trends occurring. In order to make the comparison more meaningful, capacitance values have been normalised with respect to the film thickness obtained with polyaniline.

Values of film capacitances, calculated in this way, are summarised in the plots in Fig. 5 for polymerisation of the substituted anilines alone and of Fig. 6 for 1:1 mixtures of polymers from substituted aniline and aniline, in both cases for pH ∼0.2 and 6.2.
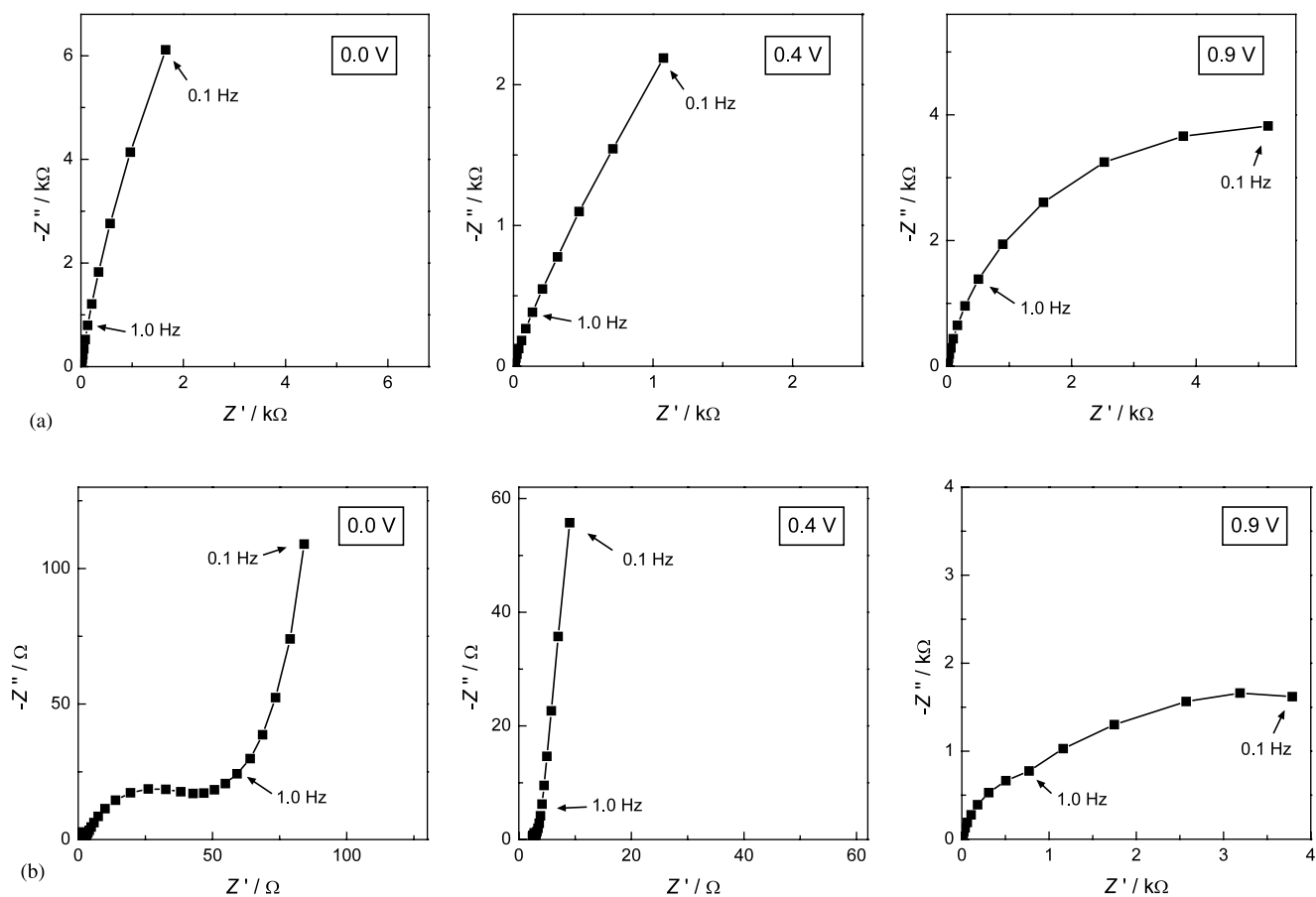
Fig. 4. Complex plane impedance spectra in 1.0 M H$_2$SO$_4$, recorded at different applied potentials for polymer films formed from: (a) 2-ABS; and (b) a 1:1 mixture of 2-ABS and aniline.
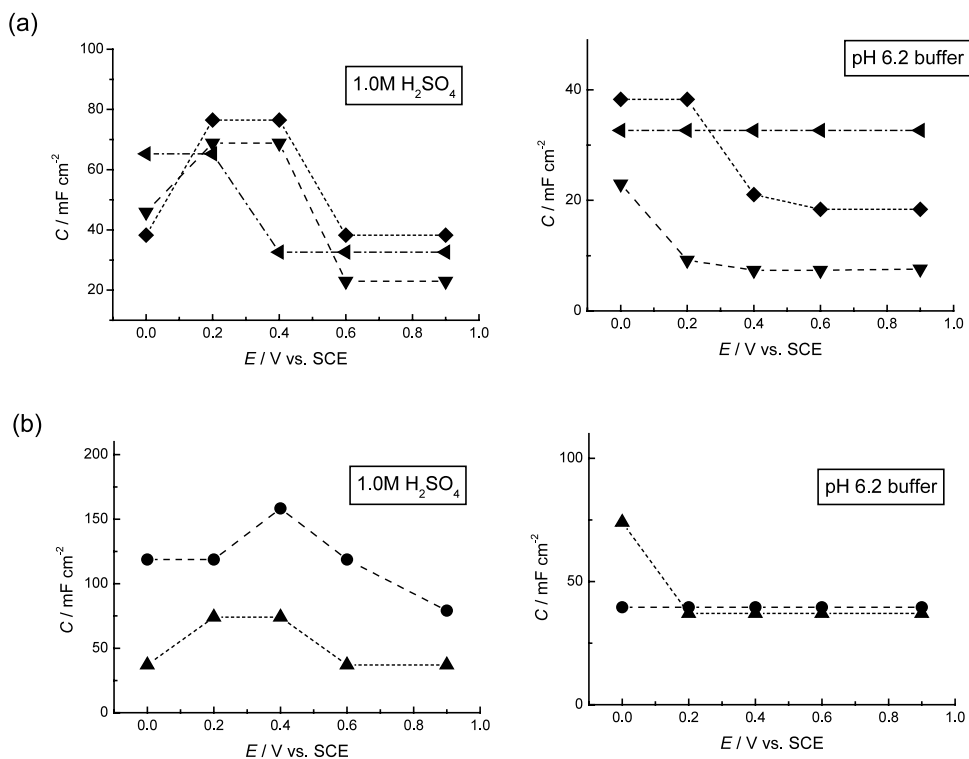

Fig. 5. Plots showing the values of capacitance, C, at various applied potentials from impedance spectra of polymer films grown electrochemically from: (a) ABA monomers: ▼, 2-ABA; ♦, 3-ABA; ◄, 4-ABA; and (b) ABS monomers: ●, 2-ABS; ▲, 4-ABS. Values have been normalised by film thickness, using polyaniline as reference.
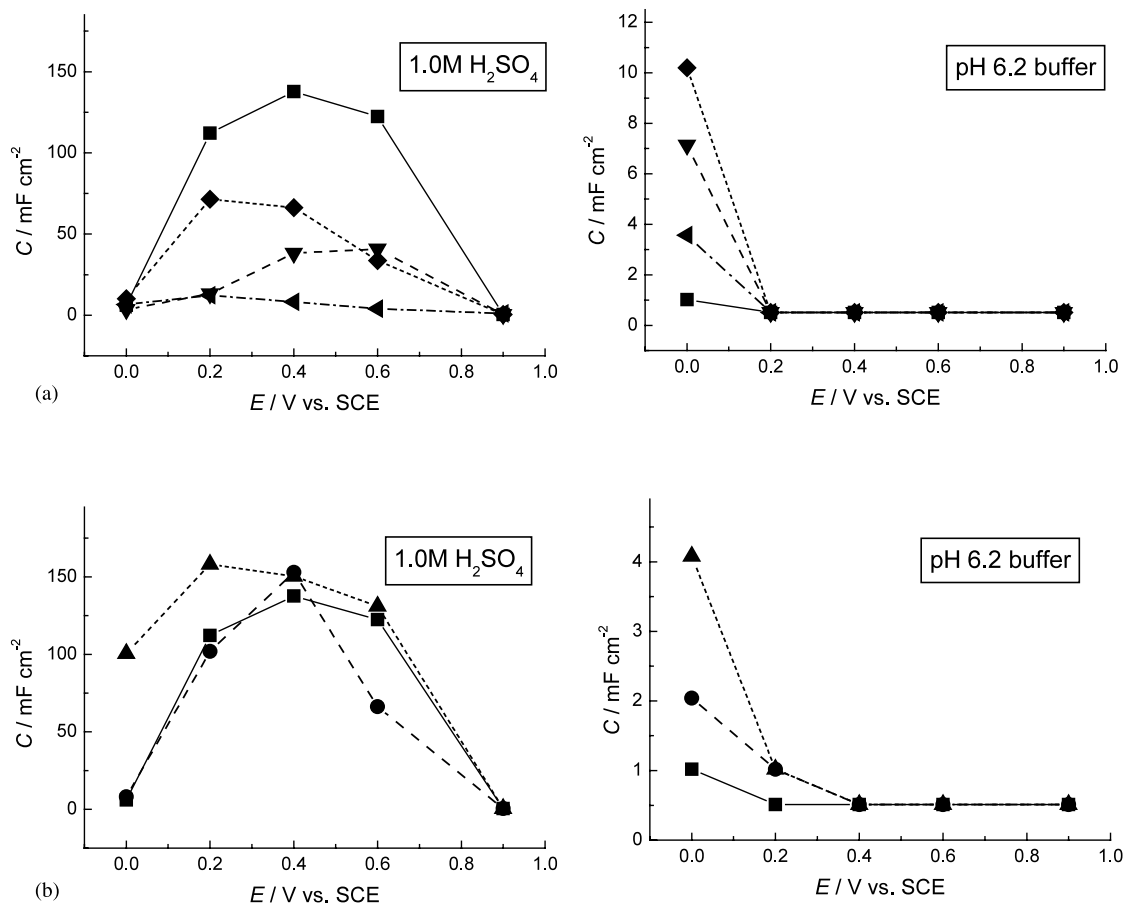
Fig. 6. Plots showing the values of capacitance, C, at various applied potentials from impedance spectra of polymer films grown electrochemically from 1:1 mixtures of aniline with: (a) ABA monomers: ▼, 2-ABA; ▲, 3-ABA; ◄, 4-ABA; and (b) ABS monomers: ●, 2-ABS; ▲, 4-ABS. ■ represents aniline. Values have been normalised by film thickness, using polyaniline as reference.

For films made from either ABA or ABS monomers, the normalised capacitance values are around 80 mF cm^{-2}, becoming lower at pH 6 by a factor of 2 or 3. The trend with variation of potential is for capacitance to be larger in the more conducting zone in the middle of the potential range and lower at 0.0 and 0.9 V—in agreement with studies on polyaniline [63], where an equivalent observation was made in terms of an 'impedance pit' i.e. the modulus of the impedance measured at fixed frequency was found to decrease at such potentials. Additionally in acid solution, capacitance values are larger for the 2-substituted anilines than for the 4-substituted aniline, which do not show the variation in the conducting zone similar to the others. Interestingly, in the case of aminobenzenesulphonic acids, both 2- and 4-ABS show a similar profile to 2- and 3-ABA, i.e. here there is not a different behavioural trend with applied potential when *para*-coupling is impeded.

The capacitance values for the 1:1 mixtures calculated directly from the experimental impedance spectra are much higher owing to the presence of aniline, which increases the rate of polymer growth and the difference

between pH ~ 0 and 6.2 is much more striking. However, in the normalised plots of Figs. 5 and 6 the trends are similar to those obtained from the polymerisation of the substituted anilines alone. As discussed previously [48,52], there is good evidence for incorporation of polymer chains of the substituted monomer with polyaniline chains. Nevertheless, although aniline shows higher capacities than the films formed from aniline plus aminobenzoic acid monomers in acid solution this is not the case for aminobenzenesulphonic acids. Indeed, it was noted [52] that the peak currents obtained for the first oxidation peak from mixtures of aniline and aminobenzenesulphonic acids are larger than for aniline itself, which is a confirmation of these results. This suggests that there may be some true co-polymerisation, or at the very least that there is interaction between the poly(ABS) and polyaniline chains. In fact, at pH 6.2 the capacitance of all mixed polymer films is essentially the same, except at 0.0 V when aniline is clearly worse than the substituted aniline polymers; however, the values of capacitance are slightly larger than the corresponding values in Fig. 5.

Although polymerisation of a mixture of aniline and substituted aniline (in an attempt to improve conductivity and increase film thickness) leads to differences in morphology of the film formed with respect to polyaniline, comparison of Figs. 5 and 6 shows clearly that the behaviour at neutral pH is certainly dominated by aniline. Therefore, for applications which are not in strong acid solution, such as in film sensors for biological matrices, it is preferable to use the substituted monomer electropolymerisation strategy without polymerisation of mixtures with aniline.

4. Conclusions

The studies described in this paper have demonstrated that polymers made by electrosynthesis of aminobenzoic acids and of aminobenzenesulphonic acids lead to a lesser variation of electrochemical behaviour with pH than aniline itself. Sulphonic acid substituents appear to offer particular advantages. Interesting changes in behaviour can also be obtained by mixing these monomers with aniline, where the presence of aniline dominates the behaviour at weak acid and neutral pH values. For sensor applications it thus seems that it is better to polymerise the substituted anilines, carrying out the synthesis for a longer period of time in order to achieve the necessary film thickness. The exploitation of these characteristics will be the object of future studies.

Acknowledgements

References

[1] A.G. MacDiarmid, Y. Zhou, J. Feng, Synth. Met. 100 (1999) 131.
[2] C. Barbero, M.C. Miras, B. Schnyder, O. Haas, R. Kötz, J. Mater. Chem. 4 (1994) 1775.
[3] L. Yang, W. Qiu, Q. Liu, Solid State Ionics 86–88 (1996) 819.
[4] W. Qiu, R. Zou, L. Yang, Q. Liu, Solid State Ionics 86–88 (1996) 903.
[5] H. Tsutsumi, S. Yamashita, T. Oishi, J. Appl. Electrochem. 27 (1997) 477.
[6] S. Karg, J.C. Scott, J.R. Salem, M. Angelopoulos, Synth. Met. 80 (1996) 111.
[7] S.-A. Chen, K.-R. Chuang, C.-I. Chao, H.-T. Lee, Synth. Met. 82 (1996) 207.
[8] E. Harlev, T. Gulakhmedova, I. Rubiniovich, G. Aizenshtein, Adv. Mater. 8 (1996) 994.
[9] E.W. Paul, A.J. Ricco, M.S. Wrighton, J. Phys. Chem. 89 (1985) 1441.
[10] S.N. Bhadani, S.K. Sen Gupta, G.C. Sahu, M. Kumari, J. Appl. Polym. Sci. 61 (1996) 207.
[11] D. Orata, D. Buttry, J. Electroanal. Chem. 257 (1988) 71.
[12] C. Barthet, M. Guglielmi, Electrochim. Acta 41 (1996) 2791.
[13] A.P. Marques, C.M.A. Brett, H.D. Burrows, A.P. Monkman, B. Retimal, J. Appl. Polym. Sci., 86 (2002) 2182.
[14] Z. Mandic, L. Duic, J. Electroanal. Chem. 403 (1996) 133.
[15] J. Ye, R.P. Baldwin, Anal. Chem. 60 (1988) 1982.
[16] J. Yano, Curr. Top. Electrochem. 3 (1994) 93.
[17] M. Shaolin, K. Jinqing, Electrochim. Acta 40 (1995) 241.
[18] X. Zhou, H. Cha, C. Yang, W. Zhang, Anal. Chim. Acta 329 (1996) 105.
[19] I.G. Casella, R.I. Tommaso, A. Guerruri, E. Desimoni, Anal. Chim. Acta 335 (1996) 217.
[20] Y. Yang, S. Mu, J. Electroanal. Chem. 415 (1996) 71.
[21] H. Sangodkar, S. Sukeerthi, R.S. Srinivasan, R. Lai, A.Q. Contractor, Anal. Chem. 68 (1996) 779.
[22] A.A. Karyakin, O.A. Bobrova, L.V. Lukachova, E.E. Karyakina, Sens. Actuators B 33 (1996) 34.
[23] E. Pringsheim, E. Terpetschig, O.S. Wolfbeis, Anal. Chim. Acta 357 (1997) 247.
[24] U.W. Grummt, A. Pron, M. Zagorska, S. Lefrant, Anal. Chim. Acta 357 (1997) 253.
[25] D.-M. Zhou, J.-J. Xu, H.-Y. Chen, H.-Q. Fang, Electroanalysis 9 (1997) 1185.
[26] W.W. Focke, G.E. Wnek, Y. Wei, J. Phys. Chem. 91 (1987) 5813.
[27] T. Hirai, S. Kuwabata, H. Yoneyama, J. Chem. Soc., Faraday Trans. I 85 (1989) 969.
[28] E.M. Geniès, J.F. Penneau, E. Vieil, J. Electroanal. Chem. 283 (1990) 205.
[29] G. Inzelt, G. Horanyi, Electrochim. Acta 35 (1990) 27.
[30] W.E. Rudzinski, L. Lozano, M. Walker, J. Electrochem. Soc. 137 (1990) 3132.
[31] G.E. Asturias, G.-W. Jang, A.G. MacDiarmid, K. Doblhofer, C. Zhong, Ber. Bunsen-Ges Phys. Chem. 95 (1991) 1381.
[32] L. Duic, Z. Mandic, J. Electroanal. Chem. 335 (1992) 207.
[33] R. Saraswathi, S. Kuwabata, H. Yoneyama, J. Electroanal. Chem. 335 (1992) 223.
[34] J. Backsai, V. Kertesz, G. Inzelt, Electrochim. Acta 38 (1993) 393.
[35] C.M.A. Brett, A.M. Oliveira Brett, J.L.C. Pereira, C. Rebelo, J. Appl. Electrochem. 23 (1993) 332.
[36] K. Fraoua, M. Delamar, C.P. Andrieux, J. Electroanal. Chem. 418 (1996) 109.
[37] Z. Ping, G.E. Nauer, H. Neugebauer, J. Theiner, J. Electroanal. Chem. 420 (1997) 301.
[38] L.H. Dao, M. Leclerc, J. Guay, J.W. Chevalier, Synth. Met. 29 (1989) E377.
[39] W.A. Gazotti, Jr., R. Faez, M.A. De Paoli, J. Electroanal. Chem. 415 (1996) 107.
[40] W.A. Gazotti, Jr., T. Matencio, M.A. De Paoli, Electrochim. Acta 43 (1998) 457.
[41] L.G. Xu, S.C. Ng, H.S.O. Chan, Synth. Met. 123 (2001) 403.
[42] A.E. Pullen, T.M. Swager, Macromolecules 34 (2001) 812.
[43] X.-H. Wang, L.-X. Wang, X.-B. Jing, F.-S. Wang, Synth. Met. 69 (1995) 335.
[44] M. Ranger, M. Leclerc, Synth. Met. 84 (1997) 85.
[45] S.C. Ng, H.S.O. Chan, H.H. Huang, P.K.H. Ho, J. Chem. Soc., Chem. Commun. (1995) 1327.
[46] N. Toshima, H. Yan, Y. Gotoh, M. Ishiwatari, Chem. Lett. (1994) 2229.
[47] A.A. Karyakin, A.K. Strakhova, A.K. Yatsimirsky, J. Electroanal. Chem. 371 (1994) 259.
[48] C. Thiemann, C.M.A. Brett, Synth. Met. 123 (2001) 1.
[49] C. Barbero, R. Kötz, Adv. Mater. 6 (1994) 577.
[50] A.A. Karyakin, I.A. Maltsev, L.V. Lukachova, J. Electroanal. Chem. 402 (1996) 217.
[51] H. Tang, T. Yamashita, A. Kitani, S. Ito, Electrochim. Acta 43 (1998) 2237.
[52] C. Thiemann, C.M.A. Brett, Synth. Met. 125 (2001) 445.
[53] J.Y. Lee, C.Q. Cui, J. Electroanal. Chem. 403 (1996) 109.
[54] P.A. Kilmartin, G.A. Wright, Synth. Met. 88 (1997) 153, 163.

[55] H. Tang, A. Kitani, S. Ito, Electrochim. Acta 42 (1997) 3421.
[56] T.-C. Wen, C. Sivakumar, A. Gopalan, Electrochim. Acta 46 (2001) 1071.
[57] H.N. Dinh, V.I. Birss, J. Electrochem. Soc. 147 (2000) 3775.
[58] S.H. Glarum, J.H. Marshall, J. Electrochem. Soc. 134 (1987) 142.
[59] I. Rubinstein, E. Sabatini, J. Rishpon, J. Electrochem. Soc. 134 (1987) 3078.
[60] R.S. Hutton, M. Kalaji, L.M. Peter, J. Electroanal. Chem. 270 (1989) 429.
[61] P. Fiordiponti, G. Pistoia, Electrochim. Acta 34 (1989) 215.
[62] G. Sandí, P. Vanýsek, Synth. Met. 64 (1994) 1.
[63] K.-H. Lubert, L. Dunsch, Electrochim. Acta 43 (1998) 813.
[64] W.-C. Chen, T.-C. Wen, A. Gopalan, Synth. Met. 128 (2002) 179.
[65] C.-C. Hu, C.-H. Chu, J. Electroanal. Chem. 503 (2001) 105.