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Preparation and characterization of surface modified electrodes from hydroxyanthraquinones

S. I. BAILEY*, I. M. RITCHIE, N. SEARCY†, P. SINGH

School of Mathematical and Physical Sciences, Murdoch University, Murdoch, Western Australia

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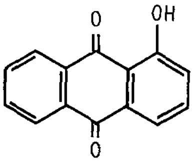
The preparation of polyphenylene oxide polymer films has been extended to the anthraquinone series. Potentiostatic and cycled potential procedures have been utilized in the anodic polymerization of several hydroxy-substituted anthraquinones producing surface modified electrodes incorporating the quinone moiety. The electrochemical response of such electrodes was investigated in aqueous media and the stability of the films was evaluated under moderately harsh testing conditions, simulating the environment of a lead–acid battery electrolyte.

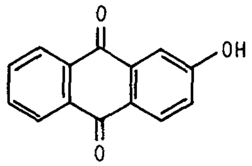
1. Introduction

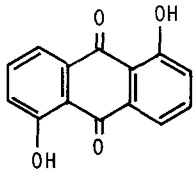
One strategy in attempts to detect the state of charge of a lead–acid battery involves the preparation of a surface modified electrode (SME) which is responsive to pH, stable, and durable in strongly acid media. Quinones in aqueous solution exhibit redox potentials dependent upon the solution pH [1, 2] and the incorporation of quinones into various forms of SME has recently been reviewed [3].

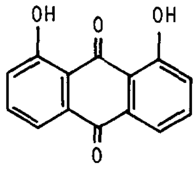
Quinonoid SMEs are often prepared by dip coating polymers with pendant quinone groups and this has already been accomplished for pendant anthraquinone groupings [4–11]. Such SMEs suffer from questionable chemical stability in aggressive media due to various reactive functional linkages of monomer units and between pendant groups and the polymer backbone. Lack of adherence to the electrode surface may also become a problem over extended periods.

An alternative procedure for preparing polymeric SMEs involves the electrooxidation of a phenolic monomer to give an integral polyphenyleneoxide polymer film [12–34]. This method allows greater control of the polymer coating and produces adherent films. Such films prepared from simple phenols have been employed as protective coatings against corrosion [15–19], and as coatings to improve the surface properties of carbon fibres [20, 21]. Chemical doping has produced a conducting polymer [22], albeit of relatively low conductivity, whilst copolymerization with pyrrole yields a polymer of considerably greater conductivity [23]. The polymerization of more complex substituted phenols provides anchors for functional groups which may later be reacted to bind pendant electroactive species [24–28], and ligands to bind metal ions forming metal complex-based SMEs [29–31]. Recently 5-hydroxynaphthoquinone (5HNQ), which contains both a phenolic function and the electroactive quinone centre, has been employed to prepare an integral SME of this type [32–34]. To our knowledge only monocyclic and bicyclic phenols have been studied previously. In order to obtain greater chemical stability we have chosen to consider the tricyclic anthraquinone nucleus, which has all quinonoid double bonds protected [2]. In this work we report the preparation and characterization of SMEs based on tricyclic hydroxy-substituted anthraquinones which combine the stability of the anthraquinone nucleus with the phenolic function. The quinones chosen were:

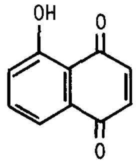

1-hydroxyanthraquinone
1HAQ


2-hydroxyanthraquinone
2HAQ


1,5-dihydroxyanthraquinone
15DHAQ


1,8-dihydroxyanthraquinone
18DHAQ

The films prepared from these hydroxyanthraquinones were then compared with films from 5HNQ [32].


5-hydroxynaphthoquinone
5HNQ

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* Author to whom correspondence should be addressed.
† Deceased.

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2. Experimental details

2.1. *Hydroxyanthraquinones*

1-Hydroxyanthraquinone (1HAQ) and 2-hydroxyanthraquinone (2HAQ) were prepared from the corresponding sulfonates [2] by autoclaving with barium hydroxide and water at 180° C, similar to the literature procedures [35]. After recrystallization the authenticity of the products was confirmed by melting point, UV–VIS spectroscopy and IR spectroscopy [35–37]. 15DHAQ and 18DHAQ were purchased from T.C.I., Kasei, Tokyo.

2.2. *Electrochemical polymerization*

Solutions of the various hydroxyquinones in organic solvent containing sodium hydroxide were polymerized electrochemically onto a glassy carbon disc electrode by two methods:

2.2.1. Potentiostatic method. The electrode was held at a constant potential throughout the polymerization process. In addition to investigating the effect of using different potentials, other variables studied were the time of polymerization and the effect of electrode rotation.

2.2.2. Cycled potential method. The potential of the electrode was cycled between upper and lower limits at a constant rate as in cyclic voltammetry. Many permutations of potential sweep rate and cycle limits are possible, so a standard method was established. The procedure adopted was closely analogous to that of Pham *et al.* [32]: the potential was cycled between 0 and 3 V at 50 mV s^{-1} for 10 cycles. All potentials are quoted relative to the saturated calomel electrode (SCE).

2.3. *Characterization of anodic films*

After polymerization, the electrode was rinsed first with pure solvent and then with water before being transferred to an aqueous electrolyte solution for assessment of any electroactive polymer by cyclic voltammetry. Measurement of the anodic peak current density of any surface quinonoid redox couple provided a means for comparing the effectiveness of polymerizations carried out under differing conditions. A sweep rate of 100 mV s^{-1} and potential limits -0.4 to $+0.3$ V in 1 M aqueous H_2SO_4 were chosen as standard conditions for such comparisons. To permit 'conditioning' of the film, the anodic peak current density on the tenth cycle was selected as the 'film activity', I_A. This gives a measure of the film thickness, but only the (useful) electroactive portion is detected.

2.4. *Assessment of film stability*

Two procedures were used to investigate the stability of the polyquinone films in acidic media.

2.4.1. Redox cycling stability. The film activity was monitored as a function of the time for which the electrode had been subjected to repetitive potential cycling in 1 M H_2SO_4. The potential was cycled continually from -0.3 V to $+0.2$ V vs SCE at 100 mV s^{-1} and the film activity measured at suitable intervals.

2.4.2. Chemical durability. The electrode was immersed in 30% by weight aqueous H_2SO_4 at 40° C, and periodically tested for film activity.

2.5. *Equipment*

Electrochemical experiments were carried out with a PAR 173 Potentiostat and a PAR 175 Programmer using glassy carbon disc electrodes, and cells according to earlier descriptions [2]. Spectra were recorded on a Hewlett Packard 8450A UV/VIS Spectrophotometer and a Pye Unicam SP 2000 Infrared Spectrophotometer.

3. Results and discussion

3.1. *Choice of solvent*

The preparation of quinone SMEs by oxidative electropolymerization requires a high concentration of monomer in an electrolyte solution. It was not possible to prepare sufficiently concentrated solutions (*ca* 0.1 M [32]) of the hydroxyanthraquinones in most of the common solvents. The phenolic substituents on the quinone monomers are weakly acidic and can be ionized in alkaline solution, as indicated by the changes shown in the UV–VIS spectrum (colour) shown in Table 1. The ionization increases the solubility in polar solvents, so solubility tests were carried out for both neutral and alkaline solutions of the hydroxyquinone monomers. The solvents tested include water, methanol, ethanol, 1-propanol, 2-propanol, acetone,

Table 1. Characterization of hydroxyquinone monomers by spectral maxima in neutral and alkaline DMA solutions. The results in neutral DMA solutions are comparable with those in alcoholic solutions [36] above approximately 270 nm, below which DMA absorbs strongly

Quinone	*Neutral DMA*		*DMA/NaOH*	
	λ_{max} *(nm)*	*log* ε	λ_{max} *(nm)*	*log* ε
1HAQ	269	4.12	271	4.19
	318	3.67	532	3.42
	387	3.65		
2HAQ	275	4.49	273	4.33
	354	4.01	371	3.96
			550	3.63
15DHAQ	269	4.25	284	4.09
	415	3.97	329	3.84
			396	3.65
			558	3.86
18DHAQ	283	3.89	285	4.44
	332	3.62	321	4.39
	430	4.00	550	4.21

acetonitrile, propionitrile, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide (DMA) and dimethylsulfoxide (DMSO).

Of all these solvents listed only alkaline DMA and alkaline DMSO were able to dissolve sufficient monomer.

3.1.1. Monomer solution stability. The choice of solvent was completed by comparing the stability of solutions of 18DHAQ in alkaline solutions in DMSO and DMA. The solution in DMSO deteriorated rapidly, depositing a brown sludge, and so DMA was chosen as most suitable. The best results were obtained by stirring 0.1 M hydroxyquinone monomer and DMA with excess solid NaOH to give 0.1 M monomer solution in 'NaOH-saturated DMA'. Titration with standard acid indicated that $[OH^-] = 0.13$ M. This solution also proved to be unstable over a period of days. Monitoring the monomer concentration by UV–VIS spectroscopy at the characteristic wavelengths given in Table 1 indicated a decrease of phenoxide monomer concentration over several days. This decay was confirmed by the observation of a decrease in polymerization efficiency using a solution stored for several days. In order to avoid any problems from monomer solution deterioration, freshly prepared solutions were used for all further experiments.

3.2. *Potentiostatic polymerization*

A fixed potential (potentiostatic) polymerization incorporates greater control over the primary variables involved – the potential and duration (time) of polymerization. Rotation of the electrode was also possible to establish the importance of mass transport. After subjecting the electrode to the chosen polymerization regime, the film activity was evaluated as described in Section 2.3.

An illustrative cyclic voltammogram (CV) of a film prepared from 18DHAQ is shown in Fig. 1. This CV, recorded in 1 M aqueous H_2SO_4, is independent of electrode rotation and shows $E_{1/2} = -0.20$ V. The peak currents were linearly dependent on the scan rate as expected for a surface redox couple. When the electrolyte pH was changed the $E_{1/2}$ value shifted by approx. -63 mV pH unit^{-1}, consistent with the behaviour of a two proton/two electron quinonoid redox couple.

Assessment of the CVs of films formed from 18DHAQ, as shown above, indicated that there was little variation in film activity, I_A, within the range of $+0.5$ V to $+2.5$ V polymerization potential. An optimal value of $+1.20$ V was chosen, as higher potentials failed to generate superior films. The polymerization time had a more dramatic effect on I_A. As shown in Fig. 2, I_A increased rapidly at first, but reached a limiting value at times greater than 5 min. No strong trend in film activity resulted from variation of the electrode rotation speed. Results were variable, but overall a small increase occurred as the rotation speed was increased. Similar results were obtained for the other hydroxyquinones.

3.3. *Cycled potential polymerization*

In contrast to the potentiostatic method where the current merely decays slowly, the variation of current with time (or equivalently, with potential) exhibits

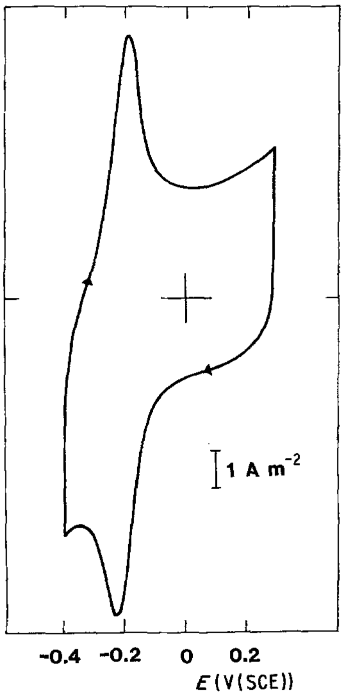

Fig. 1. A cyclic voltammogram of a 18DHAQ film in aqueous 1 M H_2SO_4, sweep rate 100 mV s^{-1}. The film was prepared from 0.1 M 18DHAQ in DMA/NaOH by the potentiostatic method at 1.20 V and 100 rpm for 10 min.

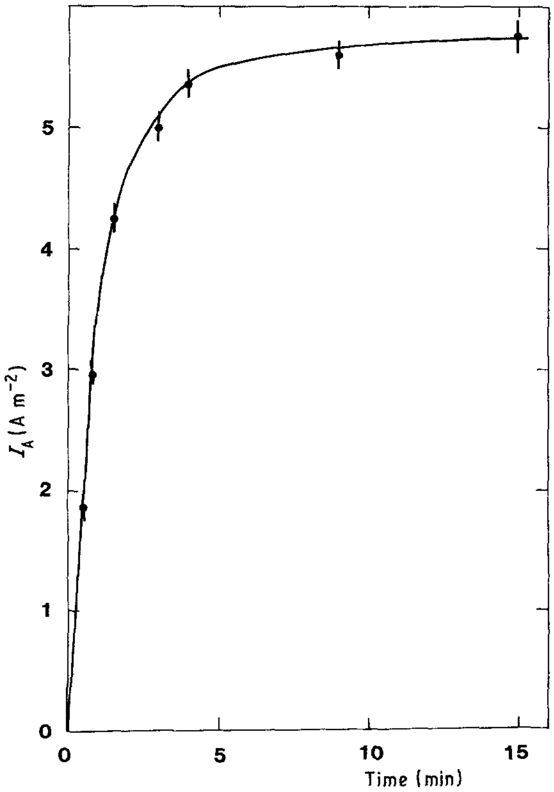

Fig. 2. The dependence of film activity I_A on polymerization time for films prepared from 0.1 M 18DHAQ in DMA/NaOH at 1.20 V.

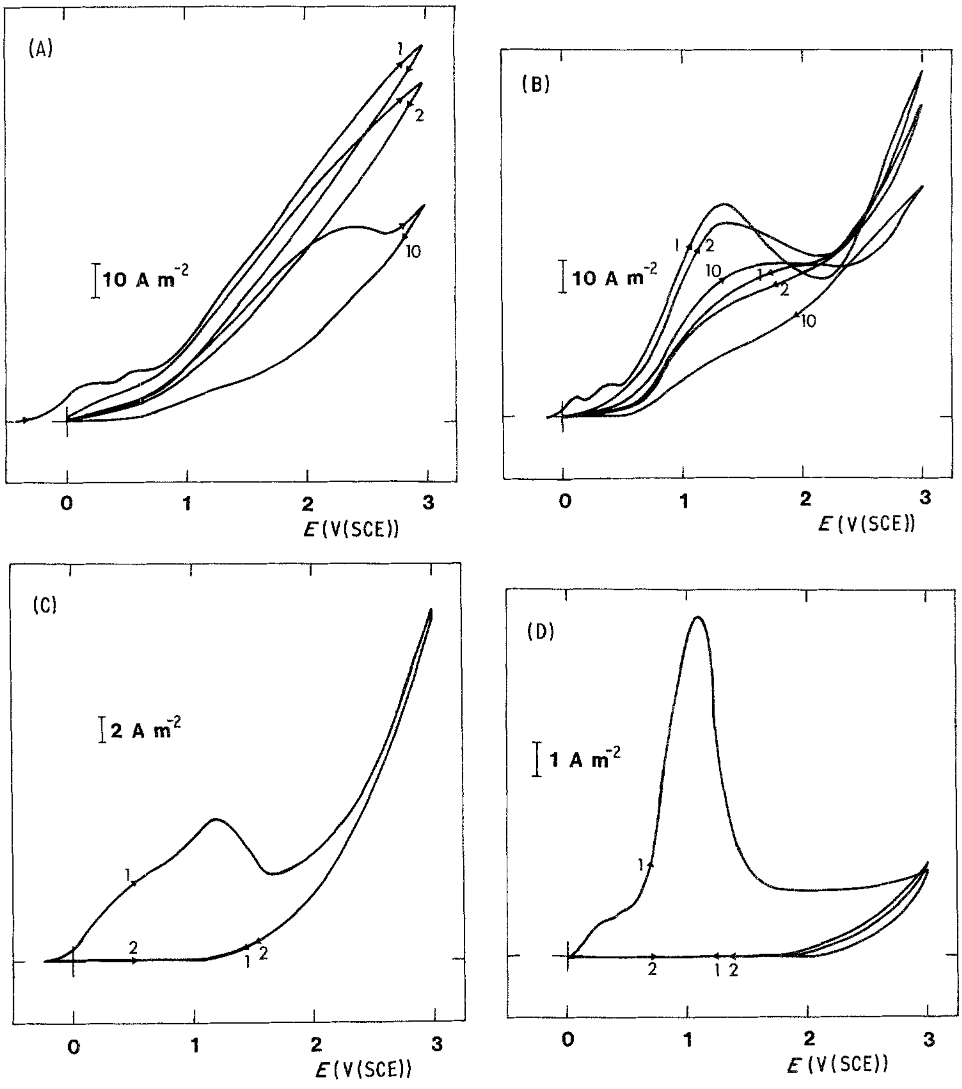

Fig. 3. Cyclic voltammograms of the cyclic polymerization of the quinones as 0.1 M solutions in DMA/NaOH, sweep rate 50 mV s^{-1}. (A) 1HAQ and (B) 2HAQ show the first, second and tenth cycles, whereas (C) 15DHAQ and (D) 18DHAQ show only the first and second cycles since strong passivation occurs. Cycle numbers are shown near arrows on the voltammogram indicating the direction of the scan.

interesting and informative features. Some CVs of the polymerization process for the individual hydroxyanthraquinones as 0.1 M solutions in DMA/NaOH are shown in Figs 3A–D and salient features are as follows.

1HAQ: The first cycle of the polymerization gave two small peaks at +0.25 V and +0.57 V followed by an almost linearly rising current. In subsequent sweeps these peaks were undetectable. The origin of these peaks is uncertain and no further attempt has been made to identify it. Little passivation was evident (*cf.* 15DHAQ, 18DHAQ), although the current did drop slowly and an indistinct peak had evolved by the tenth cycle. Clearly, the entire irreversible anodic current is not expended in the production of polymer film. This suggests that the polymerization may be inefficient or that low molecular weight products may be lost from the electrode surface. The gradual evolution of the peak does, however, suggest that there is a slow build-up of polymer.

2HAQ: As with 1HAQ, two minor and unidentified peaks appeared in the first polymerization cycle of this quinone at +0.12 V and +0.42 V. A major peak followed at +1.35 V. The smaller peaks were absent, while the major peak decreased slowly, on subsequent cycles. The current on the tenth cycle had only decreased to 60% on the first cycle – showing little sign of passivation, and again suggesting a slow build-up of polymer similar to 1HAQ.

15DHAQ: This monomer was not completely soluble (to 0.1 M), so a saturated solution was used. The polymerization gave a peak at 1.24 V on the first scan, followed by rapid passivation (i.e. the current was suppressed to almost zero on all subsequent scans).

18DHAQ: The first cycle showed a large peak at 1.08 V, dropping rapidly to a much lower value, followed by essentially complete passivation on all subsequent scans.

There is a clear trend in the CVs of the polymerization process that the two dihydroxyanthraquinones undergo rapid and profound passivation when compared with the monohydroxyanthraquinones. This is presumably due to the existence of two polymerizable substituent groups: despite the structural similarity in the position of substitution, 1HAQ does not behave in the same manner, but rather is quite similar to 2HAQ.

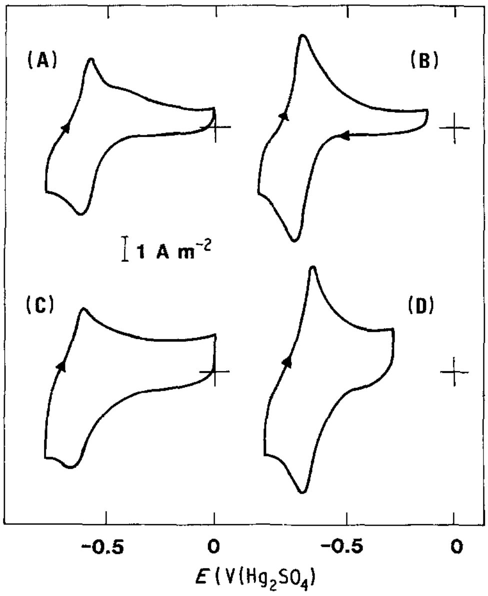

Fig. 4. Cyclic voltammograms in aqueous 1 M H_2SO_4 of the films prepared by the cyclic method, sweep rate 100 mV s^{-1}. (A) 1HAQ; (B) 2HAQ; (C) 15DHAQ; (D) 18DHAQ. A mercury(I) sulfate references electrode was used for these measurements.

Despite the differences in polymerization CVs, the films produced all showed similar CVs in 1 M aqueous H_2SO_4, as illustrated in Fig. 4. The $E_{1/2}$ values and film activities are compared in Table 2. All film activities are similar, irrespective of the fact that the currents passed during the polymerization process of the monohydroxyanthraquinones are higher than the currents for the dihydroxyanthraquinones by an order of magnitude. It would seem that the lower polymers from the monohydroxyanthraquinones are more soluble, perhaps because there is less opportunity for cross-linking.

3.4. *Film stability*

In order to evaluate the long-term stability of the quinone films, severe test conditions were employed. The films were subjected to cyclic voltammetric cycling as described in Section 2.4.1. Each cycle of the redox cycling test corresponds to complete reduction of the quinone units to the hydroquinone form, followed by re-oxidation back to the quinone form, in a total time of 10 s. A typical result showing the loss of electroactivity of a film prepared from 18DHAQ is shown in Fig. 5. It can be seen that around 70% of the initial level of redox response remains after over 8000 complete cycles, demonstrating very good redox stability.

Table 2. Properties in aqueous 1 M H_2SO_4 of films formed by cyclic polymerization

Quinone	$E_{1/2}$ (*V*)	*Film activity* I_A (*A m*$^{-2}$)
1HAQ	−0.23	5.3
2HAQ	−0.23	6.2
15DHAQ	−0.24	2.4
18DHAQ	−0.19	5.4

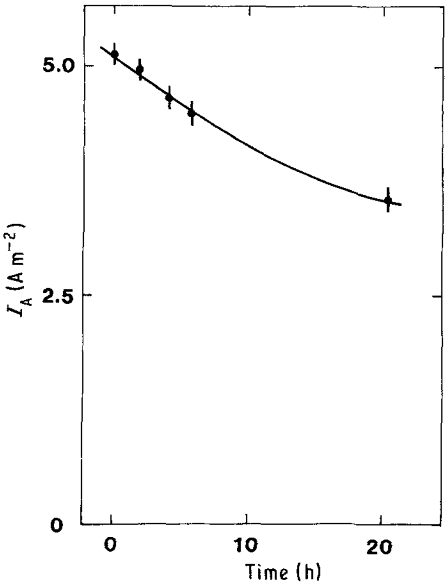

Fig. 5. The change in film activity, I_A, with time, of a 18DHAQ film subjected to the redox cycling stability test.

The chemical durability test provided additional information simulating the harsh conditions of a lead–acid battery electrolyte. The films from the dihydroxyanthraquinones were found to be more durable than those from the monohydroxyanthraquinones. This is consistent with the proposal in Section 3.3 that polymers from the monohydroxyanthraquinones are more soluble. Of the dihydroxyanthraquinones, 18DHAQ gave the more durable films. Overall, the resistance of the quinone films to this rather aggressive acid medium was unsatisfactory for the use of such materials in long-term applications. Even the most stable films from 18DHAQ completely lost their electroactivity within approximately 15 days when subjected to this test, as shown in Fig. 6.

Naphthoquinone films have previously been prepared from the related 2-ring quinone 5HNQ [32–34]. For comparison with our results on anthraquinone films, a film was prepared from 5HNQ

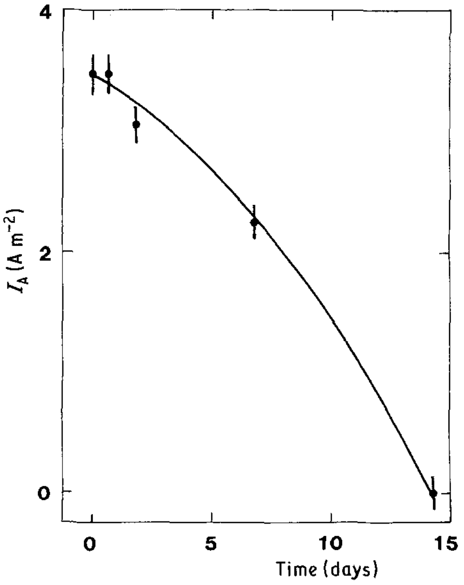

Fig. 6. The loss of film activity with time for a 18DHAQ film subjected to the chemical durability test.

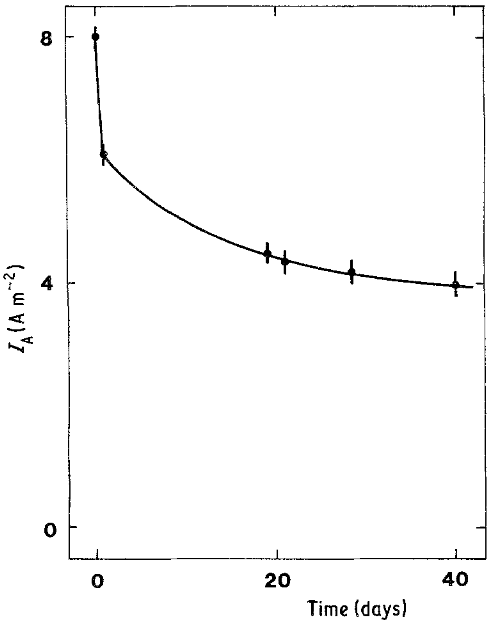

Fig. 7. The change in film activity with time for a 5HNQ film subjected to the chemical durability test.

according to the literature method [32] and tested under the same conditions. Figure 7 shows that these naphthoquinone films have much superior durability. Although a considerable drop in activity occurred in the first few days, the amount of material detected then levelled off at around 50% of the initial quantity.

This observed greater stability of naphthoquinone films compared with anthraquinone films is the reverse of expectations based on monomer stability. Degrand and Miller [4, 5] experienced similar degradation of polyanthraquinone films, but those films are fundamentally different since they contain amide functional linkages. Loss of material may then occur through hydrolysis of these linkages, but this is not possible with polyhydroxyquinone films. It is possible, then, that steric constraints may have led to less effective polymerization with the larger anthraquinone-based monomers unable to adopt suitable orientations to form high molecular weight stable polymer.

4. Conclusions

A number of hydroxy-substituted anthraquinones have been tested for the preparation of SMEs by anodic polymerization. Quinone films were produced and these were evaluated for suitability as pH sensors. It was found that the films were not sufficiently stable over long periods of time, or under harsh conditions. Further investigations should clarify the effect of the position of hydroxy-group substitution on the polymerization, and examine the possibility of using less conformationally restricted polymer backbones in order to increase molecular weight and stability.

Acknowledgement

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