Anodic Deprotonation of Polyaniline Films in Alcohol Solutions

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Polyaniline films immersed in alcohol solutions such as methanol, ethanol, 1-propanol, and 2-propanol are deprotonated by applying anodic potentials. The potential at which the deprotonation reaction is induced to occur is the most negative at methanol among the above four kinds of alcohols used, and ethanol, 1-propanol, and 2-propanol follow in this order. This finding is quantitatively discussed in terms of the difference of the affinity of the solvent for the protonated polyaniline. An equation to predict the potential at which the conductance of polyaniline is decreased to one-half of the highest conductance by the deprotonation is derived, and the validity of the equation is verified for results obtained both in aqueous solutions of different pH values and in the above alcohol solutions.

Introduction

Polyaniline films prepared by electrochemical oxidation of aniline possess high redox activities both in aqueous acidic and in nonaqueous solutions.[1-6] The high durability of the film against the redox cycling[2] opens applications of this material to electrochromic[2,7,8] and electronic[9,10] devices, and cathode-active materials of rechargeable lithium batteries.[11-13] Another interesting characteristics of polyaniline is that it is active for the protonation and deprotonation reactions in which hydrogen of the amino group of aniline molecules is involved. Such reactions are not seen in other conducting polymers. Polyaniline films prepared from acidic deposition baths are deprotonated by immersing them in aqueous neutral or alkaline solutions. The color of polyaniline in an oxidized state is then changed from green to blue, and simultaneously its electrical conductance[14-17] and redox activities[3,4] are decreased.

It has been reported in our previous paper[18] that the deprotonation reaction takes place even in weak acid solutions if anodic potentials are applied to polyaniline films of an oxidized state. We have discovered that similar deprotonation occurs in alcohol solutions, too. It is the purpose of this paper to report this finding in details. It will be shown that the potential at which the deprotonation commences to occur is influenced by the nature of alcohols used, and discussion will be made to correlate the deprotonation to the proton affinity of the solvent.

Experimental Section

Aniline was purified by distillation under reduced pressure. Methanol, ethanol, 1-propanol, and 2-propanol were distilled prior to use after storing in the presence of sodium metal. $LiClO_4$ used as an electrolyte was dried in vacuo at 140 °C for several hours. The 1 M $LiClO_4$ alcohol solutions prepared by these chemicals and used as the electrolyte solutions contained 0.015 wt % water as an impurity which did not disturb experimental results obtained in this study, because the deprotonation of polyaniline is quantitatively related to the acid dissociation constant of the alcohols used as the solvent, as will be shown below. Twice distilled water was used for the preparation of aqueous electrolyte solutions. Two-probe Pt films on a glass plate prepared by photolithography and used as the electrode substrate were donated by Matsushita Electric Works, Ltd. The size of each Pt film was 7 mm × 1 mm × 1 μm thickness, and they were arrayed on a glass plate with a narrow gap of 10 μm.

Polyaniline films were prepared by electropolymerization at 0.2 mA cm^{-2} of 1 mol dm^{-3} aniline dissolved in 2 mol dm^{-3} HCl. The conductance of polyaniline films was measured in situ under polarization in electrolyte solutions. For this purpose polyaniline was deposited with the deposition charge of 50 mC on the two-probe Pt films in such a way as to bridge them. After the deposition, the polyaniline film was rinsed several times with the solvent that was used for electrolyte solutions in the succeeding conductance measurements. The conductance measurements were made in such a way that one of the Pt probes was connected to a potentiostat (Hokuto HA-301) and both of them to an electrometer having a power source circuit (Advantest TR-8652).[19,20] After polarization of the film at desired potentials for 5 min, dc voltage of 10 mV was applied between the two Pt probes, and the resulting currents were measured.

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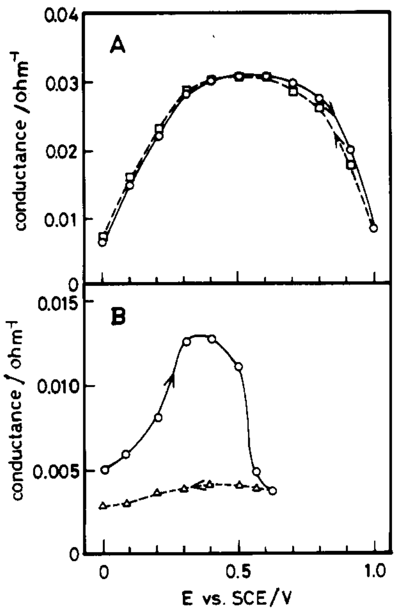

Figure 1. Changes in the conductance of a polyaniline film with changing applied potential to the film in acetonitrile (A) and methanol (B) containing 1 M $LiClO_4$. The direction of the potential change is given by arrows.

Results and Discussion

It has been found that the deprotonation of polyaniline is induced to occur by anodic polarization not only in aqueous solutions but also in alcohol solutions. A quantitative evaluation of the deprotonation was attempted by utilizing the characteristic feature that the conductance decreases with increasing the degree of the deprotonation of polyaniline.[14-17] Figure 1 shows changes in the conductance of the polyaniline films as a function of the anodic potentials taken in acetonitrile and methanol solutions both of which contained 1 M $LiClO_4$ as a supporting electrolyte. The measurements were first made from 0 V vs SCE with ascending anodic potentials. At 0 V vs SCE, the film is in a reduced state having a low conductivity.

The conductance measured in the acetonitrile solution increases with positive shifts of the applied potential up to 0.5 V due to oxidation of the reduced form of the polyaniline film, while beyond 0.5 V vs SCE it decreases. Similar behaviors are observed in cases of high anodic polarization of polyaniline films in strong acid solutions where polyaniline exhibits the highest conductivity in a medium oxidation state.[9,21] When the direction of the applied potential was switched at 1.0 V toward the negative direction, the conductance change made a good trace on that obtained with the positive shift of the applied potentials from 0 V vs SCE, indicating that any irreversible reaction such as deprotonation and decomposition of polyaniline did not occur with polarization of the film between 0 and 1.0 V vs SCE in the acetonitrile solution.

In contrast, a little different behavior of the conductance changes was observed in the methanol solution. The highest conductance was achieved at 0.3 V vs SCE, being less positive than that obtained in the acetonitrile solution, and with further increase in the anodic polarization up to 0.6 V vs SCE, the conductance steadily decreased. The film color was changed from green to blue in that case. The negative shift of the applied potentials from 0.6 V did not recover the decreased conductance in that case, indicating that an irreversible reaction of the polyaniline film took place at around 0.6 V vs SCE in the methanol solution. It was found that blue films having the decreased conductance were changed quickly into green ones by immersing them in strong acid solutions such as 2 mol dm^{-3} HCl. It is suggested from this finding that the decrease in the conductance caused by anodic polarization of polyaniline in the methanol solution must result from deprotonation.

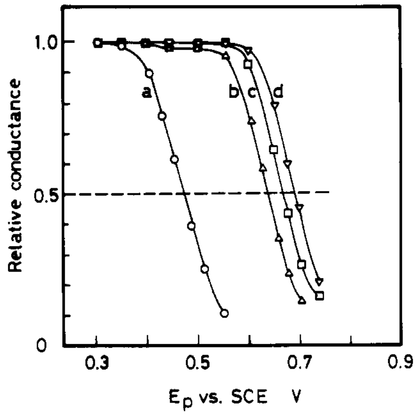

Figure 2. Ratio of irreversibly changed conductance of polyaniline films caused by anodic polarization at E_p to the maximum conductance obtained at 0.3 V. The irreversibly changed conductance was measured at 0.3 V vs SCE after polarization at E_p for 5 min. The solutions were methanol (a), ethanol (b), 1-propanol (c), and 2-propanol (d) containing 1 M $LiClO_4$ in all cases.

The conductance of the polyaniline film is influenced both by the oxidation state[9,21] and by the degree of the deprotonation[14-17] of the film. To evaluate changes of the film conductance caused by the deprotonation at various anodic potentials separating from those caused by changes in the oxidation states, the following measurements were performed: (1) An as-grown polyaniline film was immersed in an electrolyte solution and its initial conductance (ρ_0) was measured at 0.3 V vs SCE which gives the highest conductance of the protonated films. (2) The films was then polarized at an arbitrary potential (E_p) for 5 min, by which both the oxidation state and the degree of protonation are changed. (3) The applied potential was returned to 0.3 V vs SCE, and the film conductance (ρ) was measured. If there is any difference in the film conductance measured in the steps 1 and 3, the difference is attributable to the deprotonation caused by anodic polarization at E_p. These measurements were repeated for various E_p using a freshly prepared polyaniline film in every time.

Figure 2 shows the ratio of the conductance measured at 0.3 V vs SCE after polarization at E_p to the initial conductance measured at 0.3 V vs SCE as a function of E_p for several kinds of alcohol solutions. The results obtained in aqueous solutions of various pHs are given in Figure 3. When the conductance of the polyaniline films becomes decreased, the contribution of the conductance of the electrolyte solution must become serious. To eliminate any contribution of the conductance of the electrolyte solution, a relative conductance greater than 0.1 was chosen, as shown in Figures 2 and 3. It is seen in both figures that the conductance is decreased linearly with positive shifts of E_p. In the case of aqueous solutions, the potential at which the deprotonation commences to

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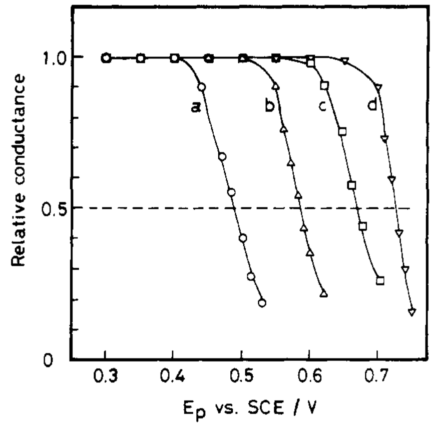

Figure 3. As in Figure 2 but for 2 mol dm^{-3} phosphate buffer solutions adjusted to pH 3 (a), 2 (b), 1 (c), 0 (d).

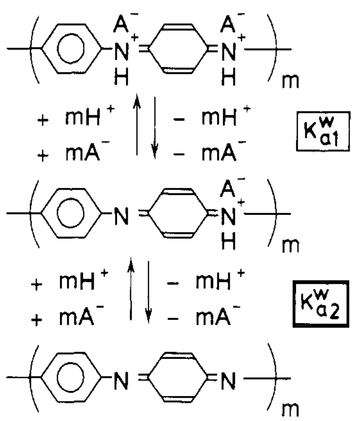

Figure 4. Schemes for protonation–deprotonation reactions of polyaniline in aqueous solution under open-circuit conditions, proposed by Huang et al.[22]

occur becomes negative with an increase in the pH of the solution, as expected.[18] In the case of the alcohol solutions, that potential is the most negative at methanol, and with changing the solvent to ethanol, 1-propanol and 2-propanol, it shifts positively in this order.

MacDiarmid and co-workers proposed the mechanism for the protonation-deprotonation of polyaniline in aqueous solutions under no external bias, as shown in Figure 4.[22] This reaction scheme seems valid as long as the oxidation state of polyaniline is unchanged. They determined the dissociation constants of K^W_{a1} and K^W_{a2} for the reactions given in Figure 4 to be 8.91×10^{-2} mol dm^{-3} and 2.82×10^{-3} mol dm^{-3}, respectively, based on measurements of relationships between the electrode potentials of polyaniline films under open-circuit conditions and pH values of immersion baths. However, for the case of the anodic deprotonation of polyaniline in protic solvents (S) such as water and alcohols, different reaction schemes as shown in Figure 5 seems valid, because the oxidation state as well as the degree of protonation of polyaniline are changed, as discussed in our previous paper for the use of weak acidic aqueous electrolyte solutions.[18]

The chemical state of a partially oxidized polyaniline film having the highest conductance is given by Ox(P) in this figure. If it is further oxidized to give a fully oxidized form, a chemical state will be changed into that given by Ox(F1). Then the deprotonation commences to occur, finally giving a state given by Ox(F3). The easiness of the deprotonation of polyaniline must be influenced by the proton affinity of the solvent of the electrolyte solution, and the greater the proton affinity, the potential at which the deprotonation reactions commences to occur must become more negative, because the proton relase from polyaniline can occur in that case with a less extent of accumulation of positive charges in polyaniline.

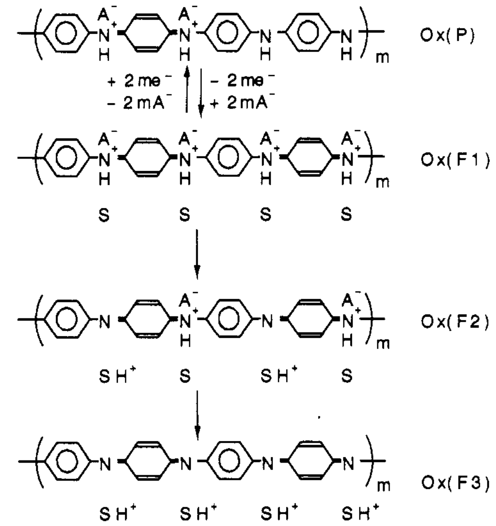

Figure 5. Schemes for anodic deprotonation reactions of polyaniline. S = solvent molecule.

The Nernst equation for the redox reactions between Ox(P) and Ox(F1) is given by

$$E = E_0 + \frac{0.059}{n} \log \frac{[\mathrm{Ox(P)}]}{[\mathrm{Ox(F1)}]} \tag{1}$$

where n is the number of electrons involved in the redox reaction. The dissociation constants for the two stages of the deprotonation reactions of the polyaniline in a nonaqueous solution are given by

$$K_{a1} = \frac{[\mathrm{Ox(F2)}][\mathrm{SH^+}]}{[\mathrm{Ox(F1)}][\mathrm{S}]} \tag{2}$$

$$K_{a2} = \frac{[\mathrm{Ox(F3)}][\mathrm{SH^+}]}{[\mathrm{Ox(F2)}][\mathrm{S}]} \tag{3}$$

where [S] denotes the concentration of the solvent molecules involved in the deprotonation reaction, and [SH$^+$] is that of the protonated solvent molecule. The total concentration of the fully oxidized polyaniline ([Ox(FT)]) is given by

$$[\mathrm{Ox(FT)}] = [\mathrm{Ox(F1)}] + [\mathrm{Ox(F2)}] + [\mathrm{Ox(F3)}] \tag{4}$$

To obtain the Nernst equation concerning the deprotonation reaction with use of [Ox(FT)] and not of [Ox(F1)], eqs 2–4 are substituted into eq 1, followed by rearrangements. The result obtained is

$$E = E_0 - \frac{0.059}{n} \log \frac{[\mathrm{Ox(P)}]}{[\mathrm{Ox(FT)}]} - \frac{0.059}{n} \log \frac{[\mathrm{SH^+}]^2 + K_{a1}[\mathrm{S}][\mathrm{SH^+}] + K_{a1}K_{a2}[\mathrm{S}]^2}{[\mathrm{SH^+}]^2} \tag{5}$$

The dissociation constant of the protonated solvent such

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[22] Huang, W. S.; MacDiarmid, A. G.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* 1987, 1784.

as H_3O^+ and $CH_3OH_2^+$ is given by

$$K_{SH} = [S][H^+]/[SH^+] \quad (6)$$

By using this equation, the dissociation constants of polyaniline in aqueous solution (K_{a1}^w, K_{a2}^w) are correlated to those in nonaqueous solution (K_{a1}, K_{a2}) as given by

$$K_{a1}^w = [Ox(F2)][H^+]/[Ox(F1)] = K_{a1}K_{SH} \quad (7)$$

$$K_{a2}^w = [Ox(F3)][H^+]/[Ox(F2)] = K_{a2}K_{SH} \quad (8)$$

By applying the values of K_{a1}^W and K_{a2}^w mentioned above to these equation, it is suggested that polyaniline in aqueous neutral solutions are almost completely deprotonated to give the state given by Ox(F3).

The electrode potential of polyaniline (E_m) under the condition of [Ox(P)] = [Ox(FT)] is evaluated from eq 5. By substituting K_{a1} and K_{a2} of eq 5 with K_{a1}^w and K_{a2}^w, respectively, using eqs 7 and 8, we obtain

$$E_m = E_0 - \frac{0.059}{n}\log\frac{K_{SH}{}^2[SH^+]^2 + K_{a1}^w K_{SH}[SH^+][S] + K_{a1}^w K_{a2}^w[S]^2}{K_{SH}{}^2[SH^+]^2} \quad (9)$$

Then eq 5 is transformed into eq 10 by using E_m:

$$E = E_m - \frac{0.059}{n}\log\frac{[Ox(P)]}{[Ox(FT)]} \quad (10)$$

As shown in Figures 2 and 3, the decrease in the relative conductance caused by positive shifts of the applied potential gave roughly the same slope regardless of the kind of the electrolyte solutions used, whereas the potential at which the conductance begins to decrease was different among the electrolyte solutions used. The obtained behaviors of the film conductance seem to reflect the Nernst equation expressed by eqs 9 and 10, from which it is suggested that changes in some parameter of the electrolyte solution must largely affect the E_m value without changing the relative concentration of Ox(P) caused by the positive potential shifts. There is a possibility that the film conductance bears a linear relationship to the concentration of Ox(P). If it is assumed that the film conductance is entirely proportional to the amount of positive charges of the Ox(P) form, the conductance of the polymer which is polarized at E_m must become one-half of the highest conductance, because in such cases the polarization of the film at E_m oxidizes one-half of the amount of polyaniline to give Ox(F1), and the resulting Ox(F1) looses its positive charges in the successive conversion into Ox(F3) via Ox(F2). However, the assumption that the potential at which the film conductance is one half of the highest conductance gives E_m is not always valid. Nevertheless, the E_m values evaluated with this assumption are useful, because considering that the relative conductance obtained in different solutions parallels to each other, there seems to be no marked difference between the use of one-half of the highest conductance and other value of the relative conductance. Differences in the E_m values evaluated for different solutions seem to be almost the same between the two.

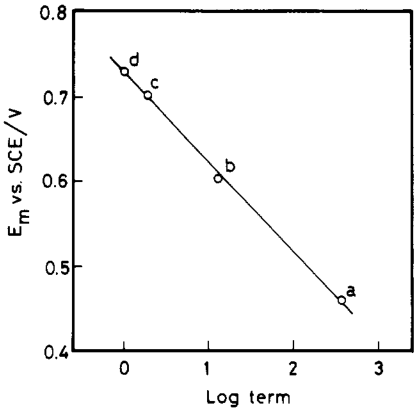

Figure 6. Relationships between E_m values estimated from Figure 3 and the log term values in the right-hand side of eq 9. E_m is the electrode potential at which one-half of the amount of polyaniline is partially oxidized, as given by Ox(P) in Figure 5 and the other one-half is totally oxidized as given by Ox(F1), Ox(F2), and Ox(F3) in the same figure.

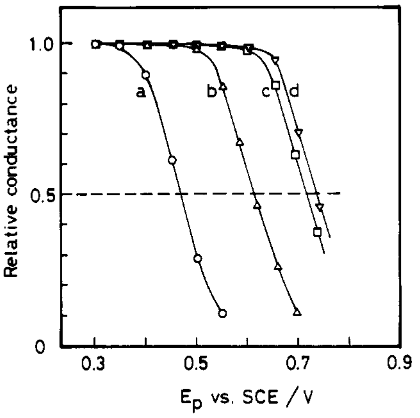

Figure 7. As in Figure 2, but for methanol solutions containing 1 mol dm^{-3} $LiClO_4$ and 0 (a), 10^{-5} (b), 10^{-4} (c), 10^{-3} (d) mol dm^{-3} CF_3SO_3H.

Then the following discussion must be valid except for the estimation of E_0 which is given in eq 9. If the E_m values obtained at one half of the highest conductance are plotted against log term values of the right-hand side of eq 9, Figure 6 is obtained. In making the plots, $K_{SH} = 1.80 \times 10^{-2}$,[33] [S] = 55.5 mol dm^{-3}, and $[SH^+] = 10^{-pH}$ were used together with K_{a1}^w and K_{a2}^w evaluated by MacDiarmid et al.[22] It is seen that a linear relationship is established between the two, which is formulated by

$$E_m = 0.73 - 0.112(\log \text{term}) \quad (11)$$

The obtained slope of 0.112 gives n = ca. 2 of eq 9, supporting the reaction scheme shown in Figure 5 where it is shown that oxidation of one aniline unit with two electrons induces deprotonation of four aniline units.

The effect of the concentration of protons in methanol solutions on the anodic deprotonation of polyaniline films is given in Figure 7, where relationships between the relative conductance and E_p are shown. The value of E_m becomes positive with increasing the concentration of the sulfonic acid, as in aqueous solutions.

The dissociation constant (K_a) and autoprotolysis constant (K_W) of methanol are given by eqs 12 and 13, respectively.[23-25]

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(23) Jencks, W. P.; Regenstein, In *Handbook of Biochemistry and Molecular Biology*; Fasman, G. D., Ed.; CRC Press: Cleveland, 1976; Vol. 3, p 305.

(24) Schaal, R.; Teze, A.; *Bull. Soc. Chim. Fr.* **1961**, 1783.

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$$\mathrm{CH_3OH} \overset{K_a}{\rightleftarrows} \mathrm{CH_3O^-} + \mathrm{H^+}$$

$$K_a = [\mathrm{CH_3O^-}]/[\mathrm{CH_3OH}] = 8.5 \times 10^{-16}\ \mathrm{mol\ dm^{-3}} \quad (12)$$

$$2\mathrm{CH_3OH} \overset{K_W}{\rightleftarrows} \mathrm{CH_3OH_2^+} + \mathrm{CH_3O^-}$$

$$K_W = [\mathrm{CH_3OH}][\mathrm{CH_3O^-}] = 2.0 \times 10^{-17}\ \mathrm{mol^2\ dm^{-6}} \quad (13)$$

The dissociation constant of protonated methanol ($CH_3OH_2^+$) is correlated to K_a and K_W, as follows:

$$K_{SH} = [\mathrm{CH_3OH}][\mathrm{H^+}]/[\mathrm{CH_3OH_2^+}] = K_a[\mathrm{CH_3OH}]^2/K_W = 2.6 \times 10^4\ \mathrm{mol\ dm^{-3}} \quad (14)$$

By assuming that [SH^+] is equal to the concentration of the sulfonic acid used and by inserting [S] = 24.8 mol dm^{-3} and K_{SH} given by eq 14 into eq 9, E_m and the log term values given by eq 9 are calculated. The relation obtained here is given in Figure 8, which shows good accordance with that obtained for aqueous solutions. The filled circle (a) given in this figure is a relation obtained for methanol solution containing $LiClO_4$ alone and not containing CF_3SO_3H. The potential of E_m in that case is 0.48 V vs SCE. The log term value of eq 11 in methanol is then determined to be 2.48, from which [$CH_3OH_2^+$] = 1.1 × 10^{-6} mol dm^{-3} is obtained. This value is ca. 3 orders of magnitude greater than the concentration of [$CH_3OH_2^+$] generated by the autoprotolysis of methanol (4.5 × 10^{-9} mol dm^{-3}). The difference is then a matter of discussion.

Since 100 mL of solution was used for the conductance measurements, the total amount of protons in the methanol solution must be 1.1 × 10^{-7} mol based on the concentration of [$CH_3OH_2^+$] derived above. The polyaniline film prepared with 50 mC is in the emeraldine form and contains doped anions in the molar ratio of ca. 0.5 to aniline units.[4,17,26] Therefore, the total amount of aniline unit of the prepared polymer film is estimated to be 0.05/2.5F = 2.07 × 10^{-7} mol. Considering that when this polyaniline film is polarized at E_m one-half of aniline units of polyaniline are deprotonated, the amount of the released protons must be 1.035 × 10^{-7} mol, which agrees well with the amount of $CH_3OH_2^+$ estimated from analysis of eq 11.

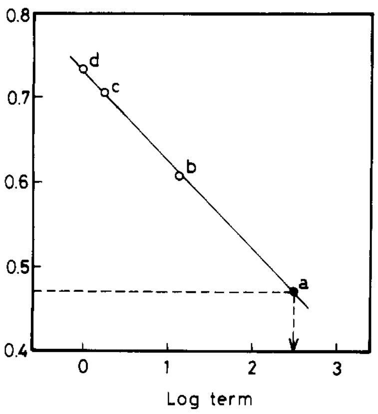

Figure 8. As in Figure 6, but for the results obtained from Figure 7. The solid line is the relationship between E_m and the log term value given by eq 11.

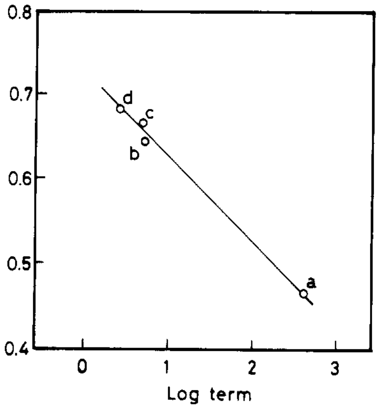

Figure 9. As in Figure 8, but for methanol (a), ethanol (b), 1-propanol (c), and 2-propand (d) containing 1 mol dm^{-3} $LiClO_4$.

If it is assumed that [SH^+] of methanol ([SH^+] = 1.1 × 10^{-6} mol dm^{-3}) is applicable to the other alcohol solutions used, because it is eventually determined by the deprotonation of polyaniline, then the log term value of each alcohol is evaluated with the use of K_{SH} of ethanol, 1-propanol, and 2-propanol, which are estimated by applying K_a and K_W values of each alcohol solution[23-25] to eq 14. The estimated K_{SH} values are 5.6 × 10^5, 5.3 × 10^5, and 2.9 × 10^6 mol dm^{-3} for ethanol, 1-propanol, and 2-propanol, respectively. The plots of the determined E_m against the log term values obtained in this way are shown in Figure 9, which satisfies eq 11, suggesting that deprotonation of polyaniline is given by eq 9, regardless of the kind of solvents used for electrolyte solutions.

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