

# Membrane-Properties of Polymer Films: The Acid-Doping Reaction of Polyaniline

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The protonation/deprotonation reaction of polyaniline in the emeraldine oxidation state (PANI-E) is discussed on the basis of membrane-equilibrium considerations. The important role of the partitioning of  $H^+$  between the polymer and the bathing solution is pointed out. The concentration of (free)  $H^+$  in the polymer phase is used as a parameter in formulating the dissociation equilibrium of the Brønsted acid (PANI-E) $H^+$ . It is shown that the  $pK_a$  value determined for this dissociation equilibrium,  $pK_a \approx 5$ , is practically constant for all experimental conditions considered in this work. However, the pH of the bathing solution which leads to a defined protonation state of the PANI-E may vary widely depending on the partitioning equilibrium for  $H^+$ . This fact is demonstrated experimentally, and the experimental findings are shown to agree with theoretical predictions based on estimated and experimentally determined Donnan potentials.

## Introduction

The "conducting polymers", (polypyrrole, polyaniline, etc.) can be reversibly oxidized and reduced. During oxidation, radical cation sites ("polarons") are normally formed on the polymer chains. To fulfill the condition of electro-neutrality in the polymer, this process is associated with the incorporation of anions. It has been well established by a number of different experimental methods (e.g., measurement of the ionic mobility [1] or via Volta-potential measurements [2]) that these counter ions are mobile in the polymer matrix. Thus, an unmodified conducting polymer in the oxidized state will normally resemble an anion exchanger.

The membrane properties of such conducting polymers can be modified by introducing redox-inactive fixed ions, in particular anions, into the polymer matrix. This may be achieved by preparing the polymer from a substituted monomer (e.g., N-sulfopropyl-pyrrole [3,4]) or by incorporating an anionic polyelectrolyte (e.g., polyvinylsulfonate, PVS [5,6]) into the matrix. If the concentration of fixed anions is larger than the maximum concentration of radical cations, the polymer constitutes a cation exchanger at all oxidation states [3].

In the case of polyaniline ("PANI" [7,8]) the situation is complicated by the fact that the imine ( $N-H$ ) $^+$  formed in the oxidation process acts as a (Brønsted-) acid. In the current work we consider one particular oxidation state of PANI, known as "Emeraldine", the deprotonated (base) form, "PANI-E", and the protonated form, "(PANI-E) $H^+$ ", of which are given in Fig. 1 [8].

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The acid-base equilibrium of emeraldine (Fig. 1) may be represented schematically as:



where  $H_{poly}^+$  are the free protons in the polymer phase. Furthermore, one may define the dissociation constant  $K_a$ :

$$\frac{[PANI-E][H_{poly}^+]}{[(PANI-E)H^+]} = K_a \quad (2)$$

where the concentrations of the species are indicated by the brackets.

The protonation/deprotonation reaction, Eq. (1), corresponds to the transition between the electronically conducting and the insulating states of PANI-E. Thus it is of considerable interest to study this transition experimentally. This may be done by equilibrating the polymer with electrolytes of defined pH values, i.e., containing defined concentrations of protons,  $[H_{sn}^+]$ . In order to determine  $[H_{poly}^+]$  the partitioning equilibrium of the protons between the solution and the polymer



along with possible ion-exchange equilibria must be evaluated. The situation is illustrated in Fig. 2 for PANI-E in contact with an acidic electrolyte. We have included schematically the equilibrium potential drop across the interface between the polymer and the electrolyte, i.e., the Donnan potential  $\Delta\phi_D$ , which will largely determine the partitioning of the protons into the polymer.

Since  $\Delta\phi_D$  is a function of the ionic strength of the electrolyte we expect the value of  $[H_{sn}^+]$ , which is required to transform PANI-E into the conducting (PANI-E) $H^+$  form,

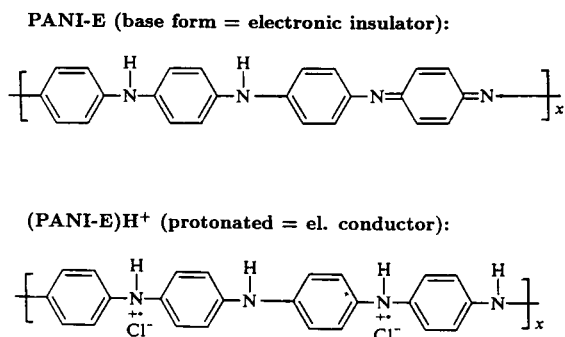


Fig. 1  
The acid- and base forms of polyaniline in the emeraldine oxidation state (PANI-E)

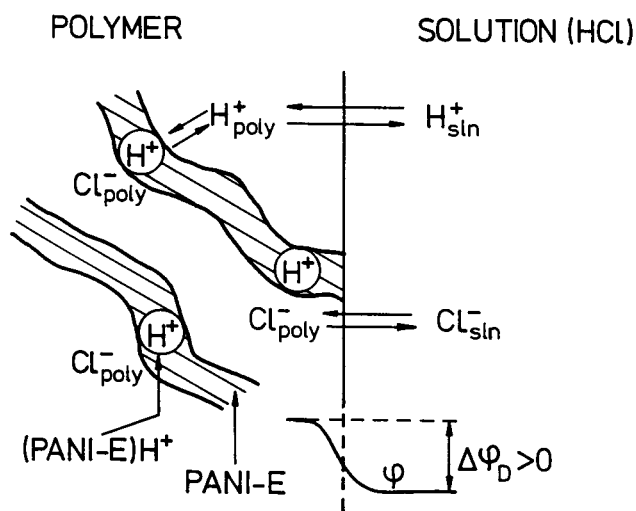


Fig. 2  
Polyaniline in the emeraldine oxidation state (PANI-E) in equilibrium with an HCl solution. The partitioning of the protons into the polymer ( $H_{sin}^+ \rightleftharpoons H_{poly}^+$ ) as well as the protonation reaction (cf. Eq. (1)) are shown.  $\Delta\phi_D$  is the Donnan potential

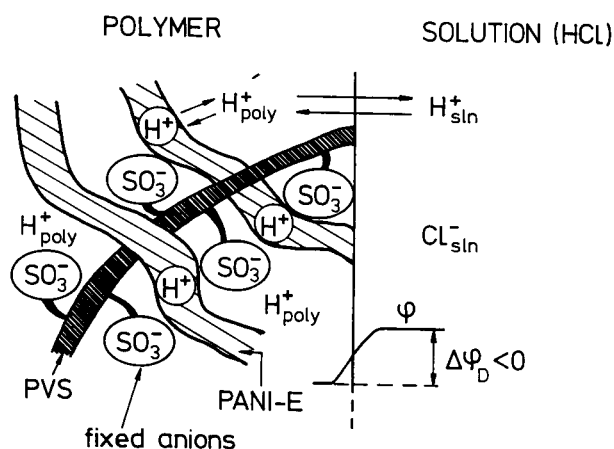


Fig. 3  
The equilibrium state of PANI-E/PVS [a molecular mixture of polyaniline- and poly(vinyl sulfonate) chains] in equilibrium with an HCl solution (cf. Fig. 2 and the text for further explanations)

to depend on the concentration of any additional dissociated species in the electrolyte [9]. Furthermore, if the polymer is transformed into a cation exchanger,  $\Delta\phi_D$  will assume a negative value, so that the protonation reaction should proceed at a much lower value of  $[H_{sin}^+]$  than with the unmodified PANI-E. In Fig. 3 this situation is illustrated for the system PANI-E/PVS, a molecular mixture of polyaniline with poly(vinyl sulfonate).

In this work we present experimental findings which support the above considerations. The analyses are based on estimates of the Donnan potentials, which are supported by the results of Volta-potential measurements. More quantitative work is presently conducted by H. Reiss, P. Chartier and others, see e.g., Ref. [10].

## Experimental

### Preparation of Polyaniline Powder and thin Films

Powder samples of emeraldine base and emeraldine hydrochloride used for conductivity studies were prepared using the conventional chemical synthesis of polyaniline [11]. Thin films of emeraldine hydrochloride used for the Volta-potential measurements were prepared using in-situ chemical deposition [12] on indium-oxide coated (conductive) glass. Powder samples and thin films of emeraldine/poly(vinyl sulfonate), "PANI-E/PVS", were prepared by the same procedure as for the emeraldine hydrochloride, except that 1 M sulfonate in the form of sodium poly(vinyl sulfonate) was added to the reaction mixture [5]. Elemental analysis indicated that the molar ratio between aniline groups (nitrogen) and sulfonate groups (sulfur) was 2:1.

### Conductivity Measurements

The powder samples were equilibrated in the solutions of desired composition, filtered, dried under vacuum and compressed into pellets for 4-probe conductivity measurements as described earlier [13]. The instrument allowed reliable measurements down to conductivities of  $10^{-5}$  S/cm.

### Volta-Potential Measurements

The Volta-potential measurements were conducted in principle as described previously [14,15]. The polymer-coated electrodes were mounted in a holder which permitted them to be moved down into the electrolyte solution where they were polarized to the potential of 0.386 V/SCE. After stabilisation they were withdrawn ("emersed") into an atmosphere of nitrogen saturated with water, and positioned in front of the Kelvin vibrator ready for measurements.

It turned out that the polymer films were more hydrophilic than, for example, the polypyrrole films investigated earlier [3]. Hence it was necessary to create a more hydrophobic polymer surface (for the emersion process) by covering with several adsorbed monolayers of polystyrene. This was achieved by dipping the polymer coated electrodes into a solution of 0.5 g polystyrene / 100 ml methylene chloride. In some cases not even this procedure lead to completely hydrophobic films. Another problem is the fact that the state of the film (even the equilibrium potential) is also a function of the concentration of inert electrolytes, such as the KCl used here. All these factors rendered the results less reproducible and thus less reliable than previous experiments. The results are therefore analyzed only in a semi-quantitative way.

## Results

A collection of conductivity results for PANI-E and PANI-E/PVS is given in Fig. 4. Before the conductivity measurements the powder samples were equilibrated with the following electrolytes:

**PANI-E + HCl:** pure aqueous solutions of HCl.  
**PANI-E + buffer:** aqueous solutions of 0.05 M 2-(HOOC)-C<sub>6</sub>H<sub>4</sub>(COOK) plus appropriate amounts of HCl or NaOH.  
**PANI-E/PVS + buffer:** 0.05 M phosphoric or boric acid plus appropriate amounts of NaOH.  
**PANI-E/PVS + NH<sub>4</sub>OH:** the polymer was originally in the protonated form; it was equilibrated with NH<sub>4</sub>OH solutions of increasing concentration.

The conductivity was measured in a dry box. In the ambient atmosphere the conductivity values were typically higher by an order of magnitude. The reproducibility of the conductivity results was within an order of magnitude.

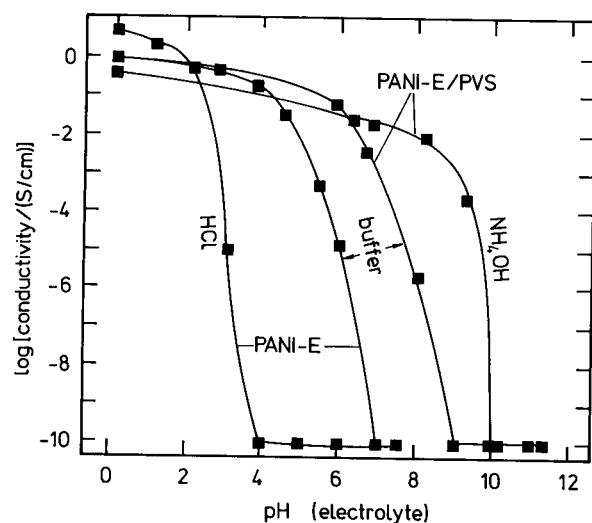


Fig. 4 The conductivity of polyaniline in the emeraldine state (PANI-E) with and without poly (vinyl sulfonate) (PVS) incorporated into the polymer matrix, as a function of the composition of the electrolyte with which the polymer was equilibrated

Typical results of the Volta-potential measurements are reported in Fig. 5. The electrolyte consisted of KCl of concentration  $C^S$  plus KOH or HCl to obtain the indicated pH values. The repeated calibration of the Kelvin vibrator indicated that its surface state (to be precise, its electronic work function,  $\phi^{Me}$ ) was sufficiently stable that it was assumed to be constant during the reported experiments [16].

## Discussion

### 1. The Membrane States of the Polymers

It is now well accepted that conducting polymers have membrane properties, i.e., they may act as anion- or cation-exchangers. The Volta-potential measurements of Fig. 5 substantiate this view for the PANI-E and PANI-E/PVS films considered. If the surface dipole potential of an emersed polymer film is independent of the electrolyte concentration, from which the film was emersed, then, under the given experimental conditions, Eq. (4) should be valid [15,17]:

$$\Delta\psi^{Me-M} = \text{const.} - \Delta\phi_D \quad (4)$$

It follows from the results of Fig. 5 that PANI-E is indeed an anion exchanger at pH = 2 and 3, i.e., in the conductive state (the Donnan potential becomes more positive as the ionic strength decreases, see Fig. 2). On the other hand, with

the PVS incorporated into the polymer matrix, the Donnan potential is in all cases negative. This means, the concentrations of  $-\text{SO}_3^-$  groups in the matrix must exceed the effective concentration of positive sites. These films act as cation exchangers.

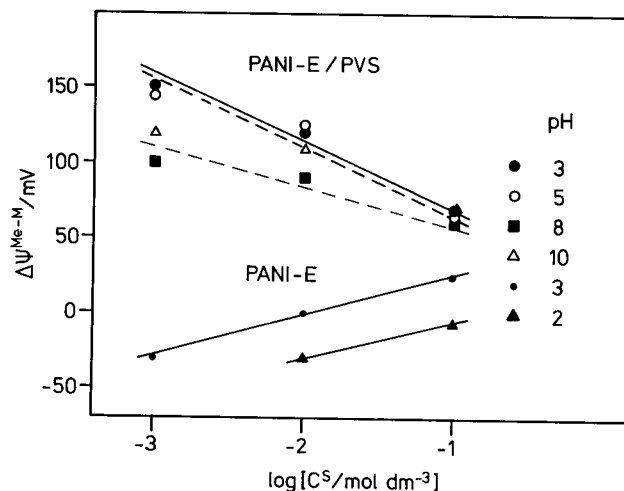


Fig. 5 Volta-potential differences,  $\Delta\psi^{Me-M}$ , between the surface of a calibrated Kelvin vibrator (Me) and the surface of a polymer (M) emersed from an electrolyte consisting of KCl (concentration indicated as  $C^S$ ) with the pH adjusted by the addition of HCl or KOH. Before emersion the polymer (present as a thin film on an inert electrode) was stabilized in the electrolyte at 0.386 V/SCE. The abbreviations for the polymers are the same as in Figs. 3 and 4

### 2. Analysis of the Conductivity - pH Results

For a semi-quantitative analysis of the results of Fig. 4 we first make the assumption that the conductivity value of  $10^{-5}$  S/cm (= 10  $\mu$ S/cm) corresponds to the same doping percentage of 10% in all systems considered [18]. Secondly, we assume (based on order-of-magnitude stoichiometric considerations) that the concentration of cationic sites in PANI-E at this doping level is 1 M (= 1 mol/dm<sup>3</sup>), and also that the concentration of mobile counter ions, e.g.,  $[\text{Cl}_{\text{poly}}^-]$ , has the same value. For PANI-E/PVS at this conductivity value we assume that the concentration of excess  $-\text{SO}_3$  groups, and thus of mobile cations, is 1 M. The Donnan potentials used for the analyses of the data are obtained [9] from the ratio of the counter ion concentrations in the polymer and the solution, i.e., for the case of anions,  $X^{z-}$ , and cations,  $K^{z+}$ :

$$\Delta\phi_D = \frac{RT}{zF} \ln \frac{[\text{X}_{\text{poly}}^{z-}]}{[\text{X}_{\text{sln}}^{z-}]} \quad (5a)$$

$$\Delta\phi_D = - \frac{RT}{zF} \ln \frac{[\text{K}_{\text{poly}}^{z+}]}{[\text{K}_{\text{sln}}^{z+}]} \quad (5b)$$

Of course, the Eqs. (5a) and (5b) are valid also for co-ions, and Eq. (5b) will be used in the following to calculate the values of  $[\text{H}_{\text{poly}}^+]$ . We now consider the four conductivity-pH curves of Fig. 4:

**PANI-E + HCl:** The reference value of conductivity (10  $\mu\text{S}/\text{cm}$ ) corresponds to a pH value of about 3. The polymer constitutes an anion exchanger with  $\text{Cl}^-$  as the counter ions. Since only HCl is present in the electrolyte,  $[\text{Cl}_{\text{sin}}^-] \approx 10^{-3}$  M. According to Eq. (5a) we expect a value of  $\Delta\phi_{\text{D}} = +180$  mV. Thus, the concentration of protons in the polymer phase at this point is  $[\text{H}_{\text{poly}}^+] \approx 10^{-6}$  M.

Since at this point  $[\text{PANI-E}]/[(\text{PANI-E})\text{H}^+] \approx 10$ , we derive a value of the dissociation constant of  $(\text{PANI-E})\text{H}^+$  (according to Eq. 2) of  $K_a \approx 10^{-5}$ , i.e.,  $\text{p}K_a \approx 5$ .

**PANI-E + buffer:** The 10  $\mu\text{S}/\text{cm}$  point of the conductivity-pH curve is at pH = 6. The exchanging anionic species is mainly  $\text{C}_6\text{H}_4(\text{COO}^-)_2$ , which is present in the electrolyte at a concentration of 0.04 M and in the film at 0.5 M. Neglecting the effect of  $(\text{HOOC})\text{C}_6\text{H}_4(\text{COO}^-)$ , the Donnan potential is 32 mV, and the concentration of protons in the film is  $[\text{H}_{\text{poly}}^+] \approx 3 \cdot 10^{-7}$  M, corresponding to a value of  $\text{p}K_a \approx 5.5$  for  $(\text{PANI-E})\text{H}^+$ .

**PANI-E/PVS + buffer:** The 10  $\mu\text{S}/\text{cm}$  point of the conductivity-pH curve is at pH = 7.8. We make the reasonable assumption [9] that the ion-exchange equilibrium constant for the two counter ions  $\text{H}^+$  and  $\text{Na}^+$  is 1, i.e., the ratio  $[\text{H}^+]/[\text{Na}^+]$  is the same in the solution and in the polymer phases. The Donnan potential is then determined essentially by the ratio  $[\text{Na}_{\text{poly}}^+]/[\text{Na}_{\text{sin}}^+]$ . Since the buffer solution at this pH is 0.09 M in  $\text{Na}^+$ ,  $\Delta\phi_{\text{D}} \approx -62$  mV. Thus, the concentration of protons in the polymer will be  $[\text{H}_{\text{poly}}^+] \approx 2 \cdot 10^{-7}$  M, corresponding to a value of  $\text{p}K_a \approx 5.7$  for  $(\text{PANI-E})\text{H}^+$ .

**PANI-E/PVS +  $\text{NH}_4\text{OH}$ :** The 10  $\mu\text{S}/\text{cm}$  point of the conductivity-pH curve is at pH = 9.7. The Donnan potential is determined by the concentration of  $\text{NH}_4^+$  in the solution (which practically equals the concentration of  $\text{OH}^-$ ). The Donnan potential calculated on this basis is  $\Delta\phi_{\text{D}} \approx -254$  mV, which leads to  $[\text{H}_{\text{poly}}^+] \approx 4 \cdot 10^{-6}$  M and a value of  $\text{p}K_a \approx 4.4$  for  $(\text{PANI-E})\text{H}^+$ .

## Conclusions

The above analysis of the conductivity-pH curves (Fig. 4) is based in the Brønsted acid dissociation equilibrium of  $\text{PANI-E}/(\text{PANI-E})\text{H}^+$  as formulated in Eq. (2). Note that thereby the concentration of (free)  $\text{H}^+$  in the polymer phase,  $[\text{H}_{\text{poly}}^+]$  is used. It is shown that one value of  $\text{p}K_a \approx 5$  characterizes this protonation equilibrium for all experimental circumstances considered.

It is shown that the different solution-pH values required to produce the same conductivity of the polymer (cf. Fig. 4, our reference value was 10  $\mu\text{S}/\text{cm}$ ) produce, in fact, about the same value of  $[\text{H}_{\text{poly}}^+]$ , i.e., they all bring the polymer into the same state of protonation.

It follows further that the buffer solutions lead to different results not because of their pH-buffer capacity. The reason for the different behaviour is the difference in salt concentration which results in a different value of the Donnan

potential and thus in a different partitioning equilibrium of  $\text{H}^+$ . This conclusion was substantiated by repeating some of the experiments with KCl solutions of the same pH and about the same ionic strength as the buffer solutions of Fig. 4. The obtained conductivities were indeed the same.

Finally, it should be noted that the described phenomena are of considerable practical interest. For applications as a "synthetic metal" it will be necessary to keep the polymer in the electronically conducting  $(\text{PANI-E})\text{H}^+$  state. It follows from the results of Fig. 4 that, for example, in equilibrium with pure water the unmodified polymer is present in the insulating PANI-E form, while the modified polymer is present in the conducting  $(\text{PANI-E}/\text{PVS})\text{H}^+$  form.

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## References

- [1] P. Burgmayer and R. W. Murray, in: "Handbook of Conducting Polymers", Vol. 1, p. 507, ed. T. A. Skotheim, M. Dekker, New York 1986.
- [2] C. Zhong and K. Doblhofer, *Electrochim. Acta* 35, 1971 (1990).
- [3] C. Zhong, W. Storck, and K. Doblhofer, *Ber. Bunsenges. Phys. Chem.* 94, 1149 (1990).
- [4] J. R. Reynolds, N. S. Sundaresan, M. Pomerantz, S. Basak, and C. K. Baker, *J. Electroanal. Chem.* 250, 355 (1988).
- [5] A. G. MacDiarmid and A. J. Epstein, in: "Proceedings of EIWG: Science and Application of Conducting Polymers", p. 117, eds. W. R. Salaneck, D. T. Clark, and E. J. Samuelsen, IOP Publishing, Bristol 1990.
- [6] G. Bidan, *J. Chim. Phys.* 86, 45 (1989).
- [7] E. M. Genies, A. Boyle, M. Lapkowsky, and C. Tsintavis, *Synth. Met.* 36, 139 (1990).
- [8] A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc.* 88, 317 (1989).
- [9] F. Helfferich "Ionenaustauscher", Vol. 1 (Grundlagen), in particular p. 77, Verlag Chemie Weinheim 1959; english translation: "Ion Exchange", McGraw-Hill, New York 1962.
- [10] H. Reiss et al., *Bull. Am. Phys. Soc.* 36, 426 and 781 (1991).
- [11] A. G. MacDiarmid, J.-C. Chiang, A. F. Richter, N. L. D. Somasiri, and A. J. Epstein, in: "Conducting Polymers", p. 105, ed. L. Alcacer, Reidel Publications, Dordrecht 1987.
- [12] S. K. Manohar, A. G. MacDiarmid, and A. J. Epstein, *Bull. Am. Phys. Soc.* 34, 582 (1989).
- [13] J.-C. Chiang and A. G. MacDiarmid, *Synth. Met.* 13, 193 (1986).
- [14] M. Cappadonia, K. Doblhofer, and M. Jauch, *Ber. Bunsenges. Phys. Chem.* 92, 903 (1988).
- [15] K. Doblhofer and M. Cappadonia, *Colloids Surf.* 41, 211 (1989).
- [16] K. Doblhofer and M. Cappadonia, *J. Electroanal. Chem.* 243, 337 (1988).
- [17] M. Cappadonia, K. Doblhofer, and D. Woermann, *J. Coll. Interf. Sci.* 143, 222 (1991).
- [18] A. G. MacDiarmid, J.-C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Met.* 18, 285 (1987).

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