

Modified Donnan phenomena in polyaniline with poly(vinyl sulphonate) chains

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We develop a physical model, based on the modified Donnan phenomena ideas introduced previously by the authors, to describe the acid doping of the conducting polymer polyaniline. The theory is motivated by the experimental work of Asturias *et al.* [Ber. Bunsenges. Phys. Chem. **95**, 1381 (1991)]. Good agreement between theory and experiment is found.

INTRODUCTION

This letter aims at developing a physical model, based on the modified Donnan phenomena ideas introduced previously by Chartier and Reiss¹ and by the authors² to describe the phenomena involved in the acid doping of polyaniline. The theory presented here can be considered as an extension of that given in Ref. 2, and was motivated by the experimental work carried out by Asturias, Chang, MacDiarmid, Doblhofer, and Zhong on the equilibrium doping of both the conducting polymer polyaniline in the emeraldine state (PANI-E) and the molecular mixture of polyaniline and poly(vinyl sulphonate) (PANI-E/PVS) (see Ref. 3 and references therein). We hope that the presentation of a simple model for the protonation/deprotonation reaction in the conducting polymer will lead to a better understanding of the abovementioned experimental results,³ and suggest new ideas for future work.

FORMULATION AND SOLUTION OF THE PROBLEM

The problem addressed is illustrated by Fig. 1. Details of the physicochemical assumptions introduced, and of the experimental system are to be found in Refs. 2 and 3, respectively. Here we will proceed directly to give the equations describing the equilibrium situation of a PANI-E/PVS film in an aqueous solution of NaCl and HCl or NH₄OH. The electrochemical equilibrium conditions for the different ions in phases 1 (external solution) and 2 (polymer solution) can be expressed as²

$$\ln(K_n n_1) = \ln n_2 + \varphi_D, \quad (1)$$

$$\ln(K_p p_1) = \ln p_2 + \varphi_D, \quad (2)$$

$$\ln(K_m m_1) = \ln m_2 + \varphi_D, \quad (3)$$

$$\ln(K_r r_1) = \ln r_2 - \varphi_D, \quad (4)$$

$$\ln(K_q q_1) = \ln q_2 - \varphi_D, \quad (5)$$

where n , p , m , r , and q refer to the sodium, hydrogen, ammonium, chloride, and hydroxide ion concentrations, respectively. The K_j 's ($j=n,p,m,r,q$) stand for the partition

coefficients (defined in Refs. 1 and 2), and the subscripts 1 and 2 indicate the aqueous external and polymer phases, respectively. Finally, φ_D is the equilibrium electric potential difference established between the two phases in kT/e units (Donnan potential); k , T , and e have their usual meaning. Electroneutrality in the bulk of phases 1 and 2 requires

$$n_1 + p_1 + m_1 = r_1 + q_1, \quad (6)$$

$$n_2 + p_2 + m_2 + p_3 = r_2 + q_2 + s_3, \quad (7)$$

respectively. Note that the concentrations of hydrogen and hydroxide ion are related in both phases through the equilibrium dissociation constant of water. In Eqs. (6)–(7), p_3 and s_3 refer to the concentration of adsorbed hydrogen ions² and the concentration of $-\text{SO}_3^-$ groups³ in the polymer, respectively. Thus the net charge concentration attached (adsorbed minus fixed) to the polymer is $(p_3 - s_3)$. These concentrations are to be found from the equations describing the adsorption and dissociation equilibria, respectively.

$$\kappa p_2 = \frac{p_3}{N - p_3}, \quad (8)$$

$$\frac{p_2}{K_{\text{dis}}} = \frac{S - s_3}{s_3}. \quad (9)$$

In Eqs. (8–9), N is the concentration of adsorption sites and S , the total concentration of $-\text{SO}_3$ groups in the polymer ionized or not (See Fig. 1). Clearly, κ and K_{dis} are the adsorption and dissociation constants, respectively.

The method of simultaneous solution of the foregoing equations is straightforward.² First, we substitute for n_2 , p_2 , m_2 , p_3 , r_2 , q_2 , and s_3 in Eq. (7) from Eqs. (1)–(5), and (8)–(9). An equation for $\exp(\varphi_D)$ results immediately. Then, we substitute Eq. (2) into Eq. (8) in order to express $\exp(\varphi_D)$ as a function of p_3 ,

$$\kappa K_p p_1 \exp(-\varphi_D) = \frac{p_3}{N - p_3}. \quad (10)$$

The resulting final equation for p_3 is

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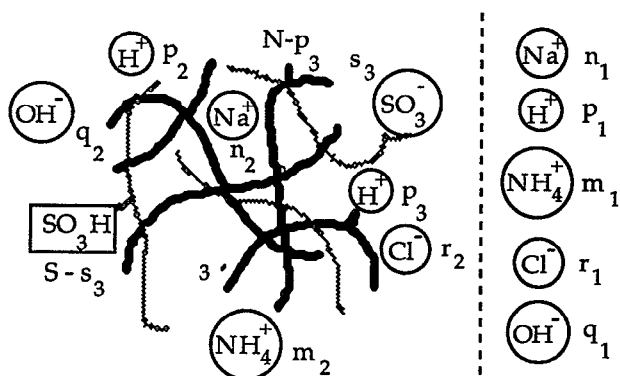


FIG. 1. Schematic view of the equilibrium problem dealt with.

$$\frac{SK_{\text{dis}}K_p\kappa^2p_1(N/p_3-1)^2}{1+K_{\text{dis}}\kappa(N/p_3-1)} + K_p^2\kappa^2p_1^2(K_r r_1 + K_q q_1)(N/p_3-1)^2$$

$$-K_p\kappa p_1(N-p_3) - (K_n n_1 + K_m m_1 + K_p p_1) = 0. \quad (11)$$

Note that N , κ , S , K_{dis} , and the K_j 's are parameters to be determined or estimated by independent means and that the concentrations in phase 1 are known. Once Eq. (11) is solved for p_3 , the Donnan potential, the concentrations in phase 2 and the concentration of $-\text{SO}_3^-$ groups can be found with the aid of Eqs. (10), (1)–(5), and (9), respectively.

RESULTS AND DISCUSSION

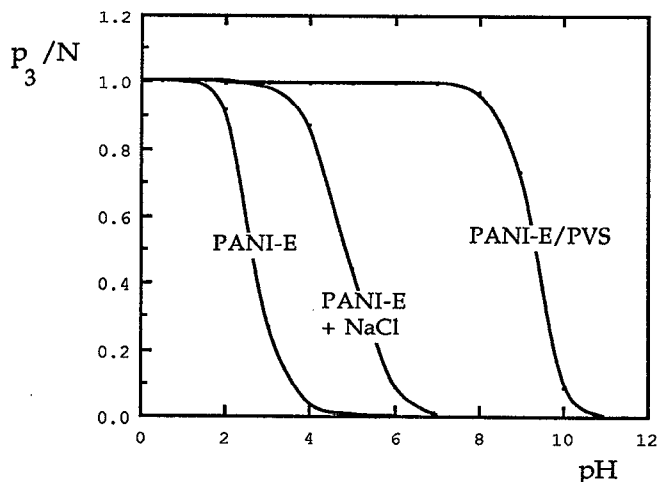
Equations (1)–(11) are rather general and can be applied to very different situations. We estimate³ $N=1$ M, and for the pH ranges considered in Ref. 3, we can consider K_{dis} to be infinitely large, so that $s_3 \approx S=1$ M. In addition, we estimate all the K_j 's in Eqs. (1)–(5) to be unity,^{1,2} and $\kappa=10^5$ M⁻¹ (see Ref. 3).

Estimates for N were arrived at separately, and by slightly different means, in Refs. 1 and 3. Nevertheless they agreed within about a factor of 2. Some of the uncertainties in these estimates relate to the unknown degree of swelling that the polymer experiences when immersed in aqueous electrolyte, and also to the changes in imine site concentration that must occur when PANI-E is blended with PVS. Similar comments can be made concerning S . The best that we can say about accuracy is that N and S are probably known to better than within an order of magnitude and to worse than a factor of 2. Setting the K_j 's=1 is equivalent to assuming that the ions in the membrane solution have the same standard state as those in the bathing electrolyte solution. Finally, the chosen magnitude of K_{dis} amounts to assuming that the pK of the $-\text{SO}_3\text{H}$ groups in the polymer phase is the same as in the bulk aqueous solution.

We will distinguish three cases.³

PANI-E+HCl (0<pH<7)

Here $m_1=n_1=0$. This situation corresponds to the HCl curve in Fig. 4 of Ref. 3.


 FIG. 2. p_3/N vs pH for the three cases considered in the text.

PANI-E+HCl+NaCl (0<pH<7)

In this case, $m_1=0$. This situation is not considered in Ref. 3, but it is presented here in order to predict the effect of the addition of salt ($n_1=1$ M) on the doping process.

PANI-E/PVS+HCl (0<pH<7) and PANI-E/PVS+NH₄OH (7<pH<11)

Here $n_1=0$. This situation corresponds to the NH_4OH curve in Fig. 4 of Ref. 3.

Figure 2 shows the fractional occupation of adsorption sites (i.e., the ratio of the concentration of adsorbed protons to that of the adsorption sites) as a function of the pH of the external solution. Since the conductivity of the polymer (the measured quantity in Fig. 4 of Ref. 3) is related to this fraction (see Ref. 4), our theory can be used to understand the measured results reported in Ref. 3. Indeed, we have estimated the PANI-E conductivity from our Fig. 2 with the aid of Fig. 2 in Ref. 4. This figure gives the conductivity vs the doping percentage. The estimated values for the conductivity have been compared to those reported in Ref. 3 (Fig. 4). They all agree within an order of magnitude. In particular, our model does fairly well in predicting the pH values at which PANI-E and PANI-E/PVS exhibit conductor to insulator transitions (see Fig. 4 of Ref. 3 and our Fig. 2). Also, we have been able to confirm the order of magnitude of the estimations for p_2 and φ_D presented in the Discussion section of Ref. 3. Finally, the theoretical curve PANI-E+NaCl clearly shows that addition of NaCl electrolyte ($n_1=1$ M) shifts this transition to higher pH values (see Refs. 1–3 in this context).

Figure 3 considers the Donnan potential values corresponding to Fig. 2. As anticipated previously,^{3,5,6} this magnitude proves to be central for an understanding of the doping process. Indeed, we see in Fig. 3 that the deprotonation of PANI-E at high pH values is caused by an increase in the (positive) Donnan potential that excludes hydrogen ions from the polymer solution. Addition of elec-

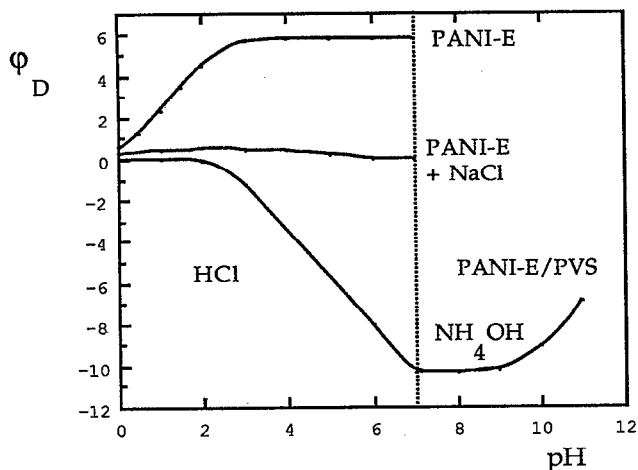


FIG. 3. φ_D vs pH for the three cases considered in the text.

trolyte decreases the φ_D values, so that in this case deprotonation requires higher pH values (see the PANI-E + NaCl curves). Finally, blending of poly(vinyl sulphonate) chains into the polymer phase causes φ_D to be negative, and thus the deprotonation is clearly inhibited (see the PANI-E/PVS curves in the $0 < \text{pH} < 7$ range). Now, only very high pH values will cause deprotonation, since φ_D becomes less negative for these values (see the PANI-E/PVS curves in the $7 < \text{pH} < 11$ range).

The use of the PANI-E/PVS polymer rather than the unmodified PANI-E has considerable practical importance:³ in equilibrium with pure water the PANI-E is present in the insulating PANI-E form, while the modified polymer is present in the conducting (PANI-E/PVS) H^+ form. According to our model the pH range within which this last form is stable can be extended even further if an

electrolyte with a cation not able to enter the polymer is used, because it is the incorporation of the cation in the solution phase of the polymer that causes deprotonation. Indeed, in this case, the concentration of the hydrogen ion in the polymer solution will remain high even as the pH increases, since the cation will be absent in the polymer. (Note that the concentration of positive ions in the solution phase of the polymer must be high enough to compensate for the negative charge bound to the polymer.) This "size" effect can be accounted for in our model by taking values smaller than unity in the partition coefficient K_m .

Finally it should be noted that the interesting studies of Ref. 3 together with the analysis of the present paper provide much needed experimental confirmation of the basic equations developed in Refs. 1 and 2. Indeed, in Ref. 1 the available experimental data necessary to test the theory was minimal.

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