Notes

Near-Neighbor Interactions in Protonation of Polyaniline

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1. Introduction

Polyaniline (PANi) has generated a special interest in the field of conducting polymers due to its unique chemical structure and properties, such as extended conjugation through a heteroatom, multiple oxidation state, solubility in the conducting state, acid doping, etc.[1−6] Among these, acid doping,[1,2] i.e., creation of charge carriers by protonation, is the best studied but also may be the least understood of all. Protonation of PANi, which is achieved by equilibrating the polymer with an acid, generally in an aqueous medium, raises a question about the correlation between the degree of protonation and the acid concentration of the medium. Like typical polymeric acids and bases, the pK for the protonation of PANi is a function of the degree of protonation.[2,3]

The chemical structure of PANi can be represented as $[(-\mathrm{NHBNHB}-)_{1-y}(-\mathrm{N{=}Q{=}NB}-)_y]_n$, where y ($0 < y < 1$) represents the oxidation state of the polymer and B and Q represent respectively the benzenoid and quinonoid phenyl rings in the polymer backbone.[1] The oxidation state corresponding to $y = 0.5$ is known as the emeraldine form and is the compound of interest for this present work. Studies on the protonation of PANi at different pHs have been interpreted in terms of the protonation of the imine nitrogens, and the change in the pK with the degree of protonation has been explained by theories of polyelectrolytes.[2,3] In a different approach, Ray et al.[4] considered protonation of both amine and imine nitrogens which are coupled by an intramolecular redox reaction. However, the above studies are based on measurement of the degree of protonation by elemental analysis where the equilibrium condition cannot be maintained.

The present work is based on the potentiometric titration of PANi equilibrated in an aqueous medium of a given ionic strength. Though the method used and the nature of the titration curve obtained are similar to those reported by de Surville et al.[5] and later by Menardo et al.[6] in this paper, studies at controlled ionic strengths have been reported and the results analyzed in detail, using the theory of polyelectrolytes with near-neighbor interactions between the ionizable sites on the polymer and taking account of the Donnan equilibrium.[7] The appearance of two inflection points in the titration curves reported earlier and attributed to the protonation of two types of nitrogens present in PANi[5,6] has been rationalized in terms of protonation of only imine nitrogens. Protonation of the amine nitrogens would decrease the extent of conjugation on the chain, decreasing the conductivity of the polymer, contrary to observations.[2] The results obtained in earlier studies[8] using the elemental analysis, which apparently appear quite different from the results of potentiometric titrations, have also been explained.

2. Theoretical Background

The degree of protonation (β) of a polyelectrolyte base is related to the pH of the medium by[9]

$$\mathrm{p}H = \mathrm{p}K_0 + \log\left(\frac{1-\beta}{\beta}\right) - \frac{0.4343}{kT}\left(\frac{\partial F_\mathrm{e}}{\partial \beta}\right) \qquad (1)$$

where K_0 is the intrinsic dissociation constant characteristic of the ionizable group of the polymer and F_e is the electrostatic free energy associated with the polyelectrolyte carrying β charges at a given ionic strength. Numerous studies have been reported in the last 5 decades for the evaluation of the electrostatic free energy term.[7,9−12] They can be categorized into two main approaches; one assumes the charge to be "smeared" uniformly along the polymer backbone,[9] and the other considers the interaction between the neighboring ionizable sites,[10−12] treating the system as a one-dimensional Ising model.[13] The latter approach explains more correctly the properties of polyelectrolyte with closely spaced ionizable groups. For example, the existence of two inflection points in the titration curve of poly(ethylene imine) has been attributed to the strong nearest-neighbor interaction, and also the contribution of the next-nearest-neighbor interaction has been emphasized to explain the shape of the curve.[12]

PANi in the emeraldine form contains an equal number of amine and imine nitrogens. Since it has been reported that, even at pH 0, only a small number of the amine nitrogens get protonated,[14a] it can be assumed that only the imine nitrogens are involved in the titration of PANi above pH 2;[14b] i.e., only half of the total number of nitrogens present are available for protonation. Therefore, if β is defined as the degree of protonation with respect to the total number of nitrogens present in PANi, eq 1 for PANi gives

$$\mathrm{p}H = \mathrm{p}K_0 + \log\left(\frac{0.5-\beta}{\beta}\right) - \frac{0.4343}{kT}\left(\frac{\partial F_\mathrm{e}}{\partial \beta}\right) \qquad (2)$$

PANi can be considered as a mixed-valent compound where the oxidation state of the sites interchange by an intramolecular redox reaction.[15] Hence, every nitrogen has an equal probability of being charged, and the evaluation of the electrostatic free energy requires counting all the nitrogens, both amine and imine, present in the polymer. Therefore, the polymer can be considered as a special case of systems with more than one type of site, distributed randomly.[16] Reiss, in a recent work,[3] assumed the number of sites as the total number of nitrogens for both the free energy term and the "trivial" entropy term for mixing of the charged and uncharged sites in the equation of titration; the saturation of PANi at $\beta = 0.5$ was obtained due to a large nearest-neighbor interaction. Hence, he assumed incor-

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rectly that the pK_0s for amine and imine are equal. However, this assumption does not affect the final result much because the strong nearest-neighbor interaction makes PANi behave somewhat like a diacidic base.

It has been shown[10] that the problem of near-neighbor interactions can conveniently be solved by treating the polymer as a separate phase in equilibrium with its immediate surrounding and separately accounting for long-range interactions. The PANi aqueous system is actually a two-phase system, and β can be related to the pH inside the polymer phase (pH$_{\text{int}}$) using the expression derived by Lifson et al.[11] for titration of polyelectrolytes which considers the nearest- and next-nearest-neighbor interactions. From the expression, the free energy term can be written as

$$\left(\frac{\partial F_{\text{e}}}{\partial \beta}\right) = \frac{kT}{0.4343}\left[\log\left(\frac{1-\beta}{\beta}\right) - \log(auv)\right] \qquad (3)$$

where $u = \exp(-E_1/kT)$ and $v = \exp(-E_2/kT)$, E_1 and E_2 being the nearest- and next-nearest-neighbor interaction energies, respectively, and a is proportional to the ratio of the activities of the charged and uncharged sites. It may be noted that $\log a$ in the last term of the above equation includes both the electrostatic free energy and the trivial entropy contribution for a system where all the sites are available for protonation. The expression for the electrostatic free energy is obtained by taking out the entropy term. As mentioned earlier, for PANi the evaluation of the former term requires counting of all nitrogens present. It has been shown[11] that

$$\log a = 0.4343 \times 2 \times \cosh^{-1}[G\{uV(1-\tau^2)\}^{-1/2}] \qquad (4)$$

and

$$\beta = \frac{1}{2} - \frac{G}{2G_1}\frac{a-1}{a+1} \qquad (5)$$

where

$$G = \left(\frac{1+u}{2}\right)\tau + \left(\frac{1-u}{2}\right) - \left(\frac{1-u}{4}\right)(1+V)(1-\tau^2)$$

$$G_1 = \left(\frac{1+u}{2}\right) + \left(\frac{1-u}{2}\right)\tau + \left(\frac{1-u}{4}\right)(1+V)\tau(1-\tau^2)$$

with $V = v/1 - v$ and $\tanh^{-1}(\tau)$ is linearly related to the logarithm of the grand canonical partition function. Putting eq 3 in eq 2, the pH in the polymer phase, pH$_{\text{int}}$, can be expressed as

$$\text{p}H_{\text{int}} = \text{p}K_0 + \log\left(\frac{0.5-\beta}{1-\beta}\right) + \log(auv) \qquad (6)$$

where a and β can be obtained for a particular value of u and v from eqs 4 and 5, respectively. The pH of the bulk solution (pH$_{\text{ext}}$) can be related to pH$_{\text{int}}$ by considering the Donnan equilibrium between the polymer and the aqueous phase which has already been estimated for PANi.[17] The pH$_{\text{ext}}$ has been related to the pH$_{\text{int}}$ by a cubic equation

$$[\text{H}^+]_{\text{ext}}{}^3 + [\text{M}^+][\text{H}^+]_{\text{ext}}{}^2 - ([\text{NH}^+] + [\text{H}^+]_{\text{int}})[\text{H}^+]_{\text{int}}A[\text{H}^+]_{\text{ext}} - [\text{H}^+]_{\text{int}}{}^2[\text{M}^+]A = 0 \qquad (7)$$

where [H$^+$], [M$^+$], and [NH$^+$] are the concentrations of the hydrogen ions, metal ions in the bulk solution, and protonated sites on the polymer, respectively, the subscripts "int" and "ext" refer to the polymer and the bulk solution phases, and A is the ratio of the products of the activity coefficient of each species in the polymer phase and the bulk phase, respectively. It has been assumed to be a constant and estimated[17] at 0.5. For the calculation of [NH$^+$], it is assumed[17] that concentration of nitrogen atoms in the PANi phase is 4.1×10^{21} cm^{-3}. Since the above equation has only one variation of sign, according to Descrates rule it can have only one real root, which is of physical significance. Hence, the pH$_{\text{ext}}$ can be directly related to β by using pK_0, E_1, and E_2 as parameters and compared with the experimental results.

3. Experimental Methods

PANi in the emeraldine form was prepared using the standard chemical oxidation method,[1] and the deprotonated PANi was washed with chloroform to remove the low molecular weight fractions. A measured amount of powdered PANi was equilibrated with an aqueous KCl solution of known ionic strength at pH ~ 1.5, under a nitrogen atmosphere in a closed cell immersed in a constant temperature bath at 27 °C, and was titrated with an aqueous KOH solution of the same ionic strength as the equilibrating medium. Since the system is a heterogeneous mixture of PANi powder distributed in an aqueous solution, the mixture in the cell was stirred for at least 8 h for equilibration after each addition of the titrant. At the end of the titration, the UV–visible spectra of the deprotonated PANi was compared with the spectra of the same recorded before the titration, to confirm the stability of the compound. The effect of ionic strength on the pH measured using glass electrodes, though small for KCl solutions, was corrected for ref 18.

4. Results and Discussion

The results of the potentiometric titration of PANi at different ionic strengths are shown in Figure 1. A large change in the pH with β in the whole range is observed which is typical of the titration curve of polyelectrolytes.[9] The experimental results are fitted with the theoretical curves obtained from eqs 6 and 7 using pK_0 = 5.8, $E_1/kT = 7$, and $E_2/kT = 5$. All three titration curves for different ionic strengths are fitted with the *same* set of parameters and a reasonably good fit is obtained, especially in the range $0.05 < \beta < 0.32$ (within ±3%). The pK_0 of 5.8 is close to the average value of pK of 5.5, reported earlier.[6] The values for the interaction energies E_1/kT and E_2/kT are found to be very high and, to the best of our knowledge, the highest reported so far for any polyelectrolyte (e.g., for poly(ethylene imine), the values are only 2.08 and 0.46, respectively[12]). The reason for large interaction energies is that the interaction between the charges on PANi occurs through the conjugated double bonds by a resonance effect, in contrast to the through-space interaction in the case of conventional polyelectrolytes. Strong interaction through the conjugated double bonds is common in aromatic diacidic bases such as 4-aminopyridine, where the pK_1 and pK_2 differ by 16 units though aniline and pyridine have almost equal basic strengths.[19] The large value for E_2 is also justified due to the existence of degenerate structures formed by an exchange of charge between the next-nearest neighbors which is found to occur at a fast rate.[20] Such an exchange of charge between sites separated by more than one nitrogen is not possible in the polymer. Hence, contribution of interactions from sites farther than the second neighbor is expected to be small compared to E_2 and has been assumed to be negligible. This is further

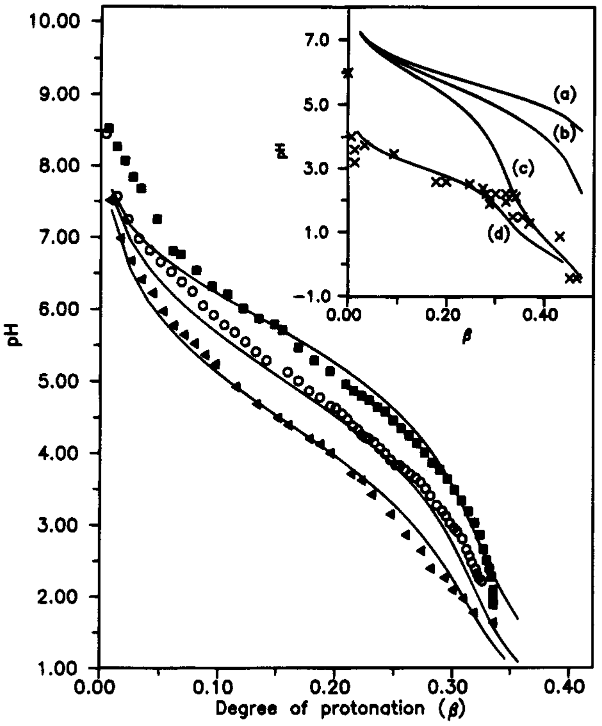

Figure 1. Titration curves for the emeraldine form of polyaniline in (■) 1 M, (○) 0.1 M, and (▲) 0.03 M aqueous KCl solutions. Solid lines are the corresponding theoretical curves obtained from eqs 6 and 7 using $pK_0 = 5.8$, $E_1/kT = 7$, and $E_2/kT = 5$. Inset: Theoretical curves for titrations with $pK_0 = 5.8$ and (a) $E_1/kT = 0$, $E_2/kT = 0$, (b) $E_1/kT = 7$, $E_2/kT = 0$, (c) $E_1/kT = 7$, $E_2/kT = 5$ in 1 M KCl. (d) Parameters the same as in c but with no added salt. (×) Experimental points taken from ref 8.

confirmed by the fit of the theoretical curve with the experimental data.

The experimental points (Figure 1) are found to deviate from the theoretical curves at $\beta < 0.05$ and, particularly for high ionic strength, at $\beta > 0.32$. Deviation is expected at low values of β because of the sensitivity of the pH at small values of β. For $\beta > 0.32$, the magnitude of the slope of the curves does not show any inflection point as expected from the theoretical model, even at a pH as low as 1.5. The accuracy of the results for titration at any practicable ratio of the polymer to aqueous phase deteriorates below pH 2 and, hence, the measurements were not made at lower pH. However, it is well-known that, at lower pH, PANi is protonated to a higher degree.[8,14] The unexpected behavior above $\beta \sim 0.3$, in the present system, can be due to a large change in the intrinsic properties of the polymer with the appearance of the metallic state. Based on measurements of the Pauli magnetic susceptibility[21] as a function of β, the transition to the metallic state has been ascribed to the formation of the polaronic metal phase. Interestingly, though not noted by the authors,[21] the Pauli susceptibility can be observed to change sharply at $\beta \sim 0.3$, as expected from the present studies. Optical spectra have also been found to[22] change similarly at the same value of β. Thus, inclusion of other factors in the theoretical model, such as the change in the dielectric constant of the polymer, is necessary to explain the protonation property of PANi better. The sharp increase in the magnitude of the slope of the pH vs β curve, with or without the inflection point, however, may be the actual reason for the appearance of the inflection point on the pH vs *volume-of-titrant* curve, which had been assigned to the protonation of amine nitrogens in earlier interpretations.[5,6] Further, the inflection point corresponds to $\beta = 0.32$, which matches the value expected from the present work. The appearance of an inflection point at $\beta = 0.5$ due to the strong nearest-neighbor interaction is already known for some polyelectrolytes.[12] In the present paper, a sharp change in the titration curve (or an inflection point as observed earlier[5,6]) at $\beta = 0.33$ has been proposed to be due to strong next-nearest-neighbor interaction for the first time.

The simulated titration curves for the systems with different extents of intersite interactions and an external salt concentration of 1 M are compared in Figure 1 (inset). Curve b, obtained by considering only the nearest-neighbor interactions ($E_1/kT = 7$, $E_2 = 0$), though has a steeper slope than curve a, for which $E_1 = E_2 = 0$ cannot fit the experimental points which are fitted with curve c ($E_1/kT = 7, E_2 = 5$). At the high value of $E_1/kT = 7$, the effect of the nearest-neighbor interactions tends to saturate, and increasing the value of E_1 further has little effect on curve b. Actually, the expression derived considering only the nearest-neighbor interactions ($E_2 = 0$) for the limit $E_1 \to \infty$ and fitted[3] by taking $pK_0 = 1.5$, with the experimental data of the earlier work[8] (reproduced in the inset of Figure 1), does not fit the result obtained in the present study even with $pK_0 = 5.8$ (pK_0 is just an additive constant which translates the curve along the y-axis). Therefore, the protonation characteristics of PANi cannot be explained considering only the nearest-neighbor interactions, and the contribution of the next-nearest-neighbor interactions must also be included.

The theoretical model proposed in the present work also matches closely with the results of the earlier studies[8] on protonation of PANi in a salt-free aqueous HCl solution, using elemental analysis. The theoretical fit with the experimental data of the earlier work, obtained using the same set of parameters that fits with the results of the present study and taking the concentration of the external salt as zero, is shown in Figure 1 (inset, curve d). Hence, the large difference in the degree of protonation of PANi observed in the earlier[8] and the present work can be attributed to the Donnan effect. At low pH, however, the experimental values of β are found to be higher than expected. This may be due to the perturbation to the system during the process of drying which, among other factors, is dependent on the phase transition properties of the system; the concentration of HCl in aqueous media increases with drying, and it forms an azeotropic mixture at around 5.5 M HCl.[23] The UV–visible spectrum of a PANi film equilibrated with aqueous HCl of pH 2.35 was found to show a large change after drying, indicating an increase in protonation of the polymer. Previous attempts to explain the above data using theory[3] similar to that developed by Rice et al.[7] resulted in an unrealistic pK_0 of ~1.5 due to the neglect of the next-nearest-neighbor interactions and the Donnan effect.

5. Conclusion

The potentiometric titration of PANi at different ionic strengths has been interpreted in terms of protonation of the imine nitrogens by considering the nearest- and next-nearest-neighbor interactions between the ionizable sites on the polymer and including the Donnan equilibrium in the theoretical model. The inflection point at $\beta = 0.32$ on the titration curve reported earlier could be explained by involving only the imine nitrogens in the protonation of PANi, which is supported by the experimental evidence. It would be interesting to apply the concept of nearest-neighbor interactions to the process of doping of other conducting polymers where strong nearest-neighbor interaction may lead to the appearance of two redox potentials for the same redox process.

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References and Notes

(1) (a) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317. (b) Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139. (c) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Adv. Polym. Sci.* **1993**, *106*, 135.

(2) Chiang, J.-C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.

(3) Reiss, H. *J. Phys. Chem.* **1988**, *92*, 3657.

(4) Ray, A.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E151.

(5) de Surville, R.; Jozefowicz, M.; Yu, L. T.; Perichon, J.; Buvet, R. *Electrochim. Acta* **1968**, *13*, 1451.

(6) Menardo, C.; Nechtschein, M.; Rousseau, A.; Travers, J. P.; Hany, P. *Synth. Met.* **1988**, *25*, 311.

(7) Rice, S. A.; Nagasawa, M.; Morawetz, H. *Polyelectrolyte Solutions: A Theoretical Introduction*; Academic Press: New York, 1961; and references therein.

(8) MacDiarmid, A. G.; Chiang, J.-C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285.

(9) Katchalsky, A.; Shavit, N.; Eisenberg, H. *J. Polym. Sci.* **1954**, *13*, 69.

(10) Marcus, R. A. *J. Phys. Chem.* **1954**, *58*, 621.

(11) Lifson, S.; Kaufman, B.; Lifson, H. *J. Chem. Phys.* **1957**, *27*, 1356.

(12) Smits, R. G.; Koper, G. J. M.; Mandel, M. *J. Phys. Chem.* **1993**, *97*, 5745.

(13) Ising, E. *Z. Phys.* **1925**, *31*, 253.

(14) (a) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Macromolecules* **1990**, *23*, 2918. (b) According to ref 4, the protonation of amine nitrogen may be high at an intermediate pH of around 3. However, in the absence of any direct evidence for such a behavior of PANi, we proceed with this assumption.

(15) Wnek, G. E. *Functional Polymers [Proceedings of the 6th Annual IUCCP Symposium]* Bergbreiter, D. E., Martin, C. R., Eds.; Plenum: New York, 1988; p 107.

(16) Hill, T. L. *J. Am. Chem. Soc.* **1956**, *78*, 5527.

(17) Chartier, P.; Mattes, B., Reiss, H. *J. Phys. Chem.* **1992**, *96*, 3556.

(18) Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal Ion Control*; Chapman and Hall: London, 1974.

(19) Liler, M. *Adv. Phys. Org. Chem.* **1975**, *11*, 267.

(20) Engert, C.; Umapathy, S.; Kiefer, W.; Hamaguchi, H. *Chem. Phys. Lett.* **1994**, *218*, 87.

(21) (a) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; Woo, H. S.; Tanner, D. B.; Richter, A. F.; Huang, W. S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303. (b) Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Solid State Commun.* **1987**, *63*, 97.

(22) Ghosh, S. Doctoral thesis to be submitted at Indian Institute of Science, Bangalore, India.

(23) Elvers, B., Hawkins, S., Ravenscroft, M., Schulz, G., Eds. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH: Weinheim, Germany, 1989; Vol. A13, p 283.

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