Electropolymerization of Pyrrole and Electrochemical Study of Polypyrrole. 3. Nature of "Water Effect" in Acetonitrile

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In acetonitrile electropolymerization of pyrrole is considerably facilitated by the addition of a small amount of water. Several mechanisms have been suggested in the past to interpret this dramatic influence of water. However, none of them has explained all the experimental results obtained up to now. On the basis of the mechanism involving the acid-catalyzed formation of a pyrrole trimer, 2,2′-(2,5-pyrrolidinediyl)dipyrrole and its subsequent electropolymerization leading to electrode passivation, it is proposed that water, a fairly strong base in acetonitrile, prevents the acid-catalyzed formation of this trimer by capturing reaction-released protons. This interpretation proved to be consistent with all results. Other substances, such as methanol, ethanol, and tetrahydrofuran, which are more basic than pyrrole, but not basic enough to deprotonate intermediate species, also have a favorable effect on pyrrole electropolymerization in acetonitrile. On the basis of the data so far obtained, other previously proposed mechanisms can be ruled out.

Introduction

The marked effect of water on the electropolymerization of pyrrole in acetonitrile has long been known.[1−5] As has been shown in numerous publications, the addition of 1 wt % (ca. 0.5 mol dm^{-3}) to a solution of pyrrole in acetonitrile increases the polymerization rate, improves the film adherence and morphology, and enhances the conductivity of the resulting polymer. There has been much speculation about the "water effect". Initially, it was suggested that water might reduce the solubility of oligomers[5] and thus lead to a faster deposition on the electrode. Some authors proposed that water, owing to its higher dielectric constant (80 compared to 37 of acetonitrile), reduces the Coulombic repulsion between the radical cations[6−10] and, consequently, facilitates the radical−radical coupling. Obviously, this opinion cannot offer a convincing explanation for other monomer−solvent systems, e.g., thiophene in acetonitrile[11] and pyrrole in propylene carbonate (PC),[12] in which water has even a detrimental effect. Zotti et al.[13] proposed that the reaction-released protons should protonate pyrrole and its oligomers and that such protonated species in front of the electrode should prevent further electrooxidation. Water then scavenges protons because of its stronger basicity compared with pyrrole. However, the role of protons was not thoroughly interpreted. Recently, by showing chemical polymerization[14−18] of pyrrole via protonation[19−22] in HClO$_4$-acidified acetonitrile electrolytic solution, Otero and Rodríguez[23] proposed the coexistence of an electrochemically generated conducting polymer and a chemically produced nonconducting polymer. They further assumed that the addition of water to acetonitrile solution prevented the proton-catalyzed generation of an insulating film, since water has a greater proton-accepting ability than pyrrole. However, their view cannot explain why, in an already acidified acetonitrile solution, the electrode becomes passivated

only when an electrooxidation process take place.[24a] Besides, their evidence does not seem to be strong enough to support their conclusion. One might argue that the use of strongly oxidative perchloric acid could favor a chemically oxidative polymerization, instead of acid-catalyzed polymerization, in their experiments. One might also argue that at the very high potential (3.0 V vs SCE) they applied the polypyrrole (PPy) was overoxidized.

This unsolved issue is one of the focuses of our multipart report of PPy-related electrochemical studies. Taking into account the acid-catalyzed formation of a pyrrole trimer (**1**), which was identified as 2,2′-(2,5-pyrrolidinediyl)dipyrrole,[16−18] the present authors have suggested a side *electrochemical reaction* pathway leading to an ill-defined, partially conjugated variant PPy(III).[24a] Depending on the experimental conditions (applied potential, proton concentration, water amount, etc.), the partially conjugated PPy(III) may be produced mainly from the coupling of trimer (di-)radical (di-)cations (**1**$^{(2)\bullet+}$) or from the copolymerization between **1**$^{(2)\bullet+}$ and monomer radical cations (or conjugated oligomeric cations; both are denoted as Py$^{\bullet+}$). The former is nonconductive and passivates the electrode, whereas the latter shows changeable conductivity and redox potential. The suggestion of an acid-catalyzed electrochemical side reaction is in agreement with all observed phenomena and was further confirmed by a study in which **1** and an ill-defined, structurally unknown byproduct were chemically synthesized and voltammetrically characterized.[24b]

Hence, with regard to the immediate action of water, we share partly the view that water, being a fairly strong base in acetonitrile,[25] captures protons and prevents the formation of **1**. Our opinion differs from Otero's in that the electrochemical oxidative polymerization (or oligomerization) of **1**, instead of the chemical polymerization, plays a crucial role in passivating the electrode.

Our earlier investigation of the effect of acid on polymer led us to produce a diagram of the varied voltammetrical properties

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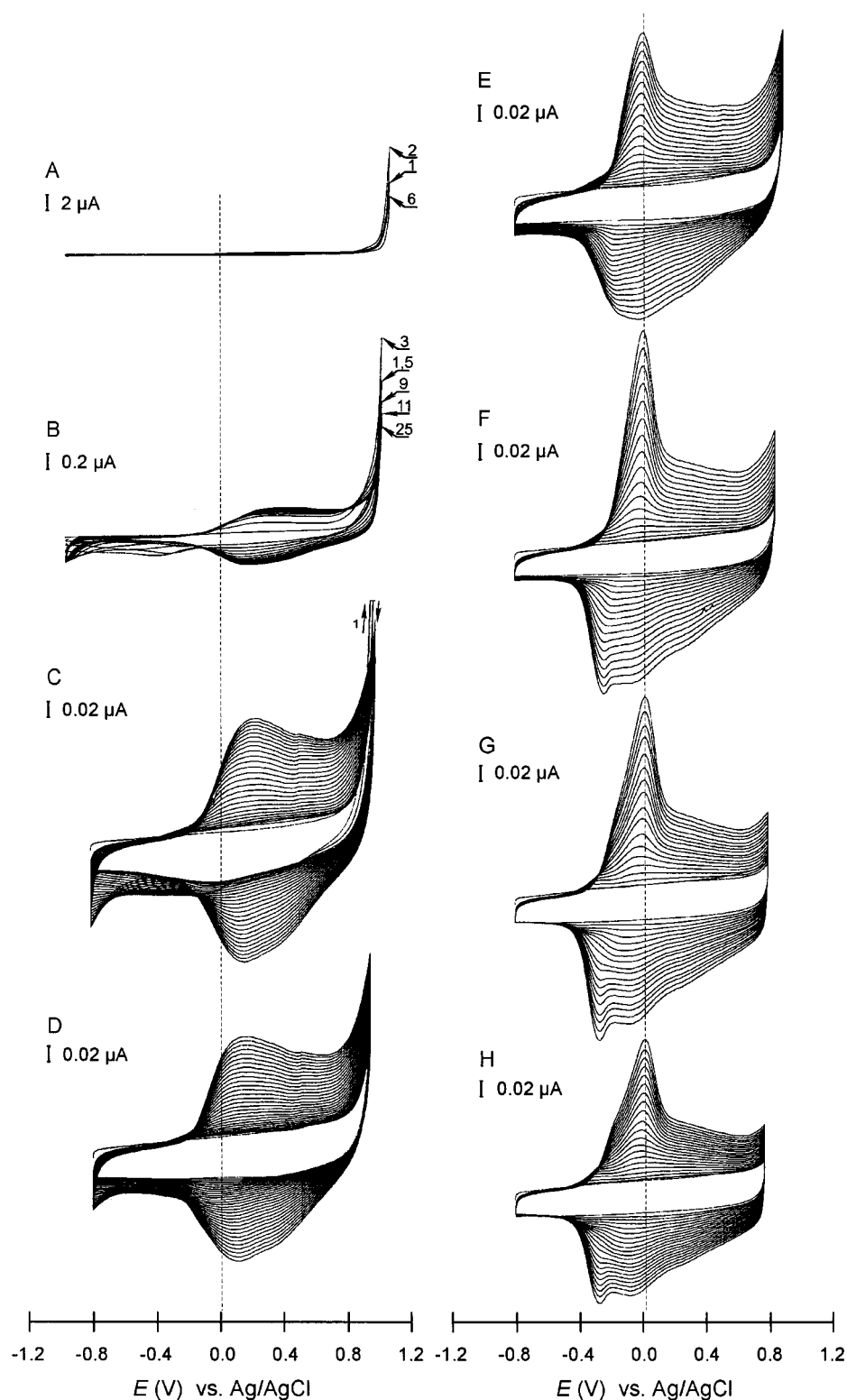
Figure 1. Electrode passivation at higher potential and potential dependence of the potentiodynamic growth of PPy films in water-free acetonitrile solution (0.1 M pyrrole, 0.1 M TBAPF$_6$, −20 °C, 100 mV s^{-1}): (A) −0.97 to 1.08 V, 6 scans; (B) −0.97 to 1.03 V, 25 scans; (C) −0.82 to 0.98 V, 27 scans; (D) −0.82 to 0.93 V, 30 scans; (E) −0.82 to 0.88 V, 40 scans, every second scan recorded; (F) −0.82 to 0.83 V, 85 scans, every fifth scan recorded; (G) −0.82 to 0.78 V, 170 scans, every tenth scan recorded; (H) −0.82 to 0.755 V, 200 scans, every tenth scan recorded. The scan number is indicated in the figure.

of PPy at different potentials in acetonitrile with different content of hydrochloric acid. The amount of water used in these experiments was 1 wt %. In this paper we put forward more arguments for our assumption and against other opinions.

Experimental Section

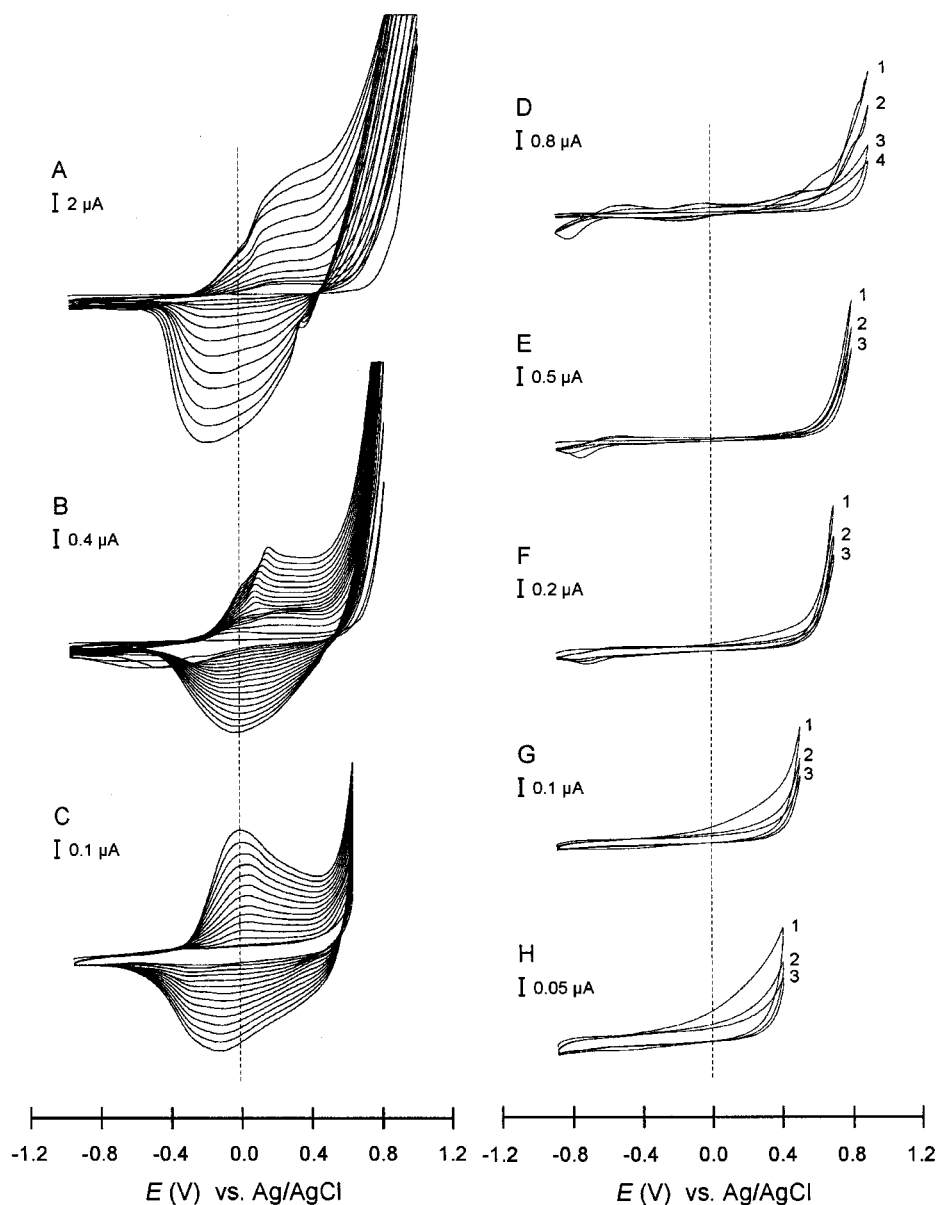See companion paper.[24a] Protocol 2 was employed to prepare solutions.

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Figure 2. Potentiodynamic growth of PPy films in 0.1 M TBAPF$_6$ pyrrole solutions (20 °C, 100 mV s^{-1}) with (A−C) pyrrole distilled once from CaH$_2$ and (D−H) pyrrole distilled twice from CaH$_2$: (A) −0.99 to 1.01 V; (B) −0.99 to 0.81 V; (C) −0.99 to 0.61 V; (D) −0.90 to 0.90 V; (E) −0.90 to 0.80 V; (F) −0.90 to 0.70 V; (G) −0.90 to 0.50 V; (H) −0.90 to 0.40 V. The scan number is indicated in the figure.

Results and Discussion

In Water-Free Solution. According to our assumption,[24a] the CVs showing broad waves with an anodic current maximum at potentials higher than 0.0 V result from the charging and discharging of the partially conjugated PPy(III), which can be formed either in an initially acidified acetonitrile solution over a wide potential range or in a neutral acetonitrile solution by applying high oxidation potentials. For the electropolymerization of pyrrole the optimal content of water in acetonitrile has proved to be about 1 wt %. In such solutions, the broad and symmetrical redox waves of PPy(III) only appear at oxidation potentials higher than 1.1 V vs Ag/AgCl (see Figure 1 in ref 24a). If our assumption about the "water effect" is correct, a decrease in water content would lead the PPy(III) to form at less positive potentials because the reaction-released protons cannot be removed as effectively as in a solution containing 1 wt % of water.

Figure 1 shows the results obtained in a water-free acetonitrile solution. As discussed in the companion paper,[24a] PPy(II) with

an oxidation potential at −0.23 V was hardly produced owing to the application of alumina. When switching potential increases, a clear change from PPy(I) to PPy(III) begins to occur at 0.88 V (Figure 1E). Compared to Figure 1F−H, CV obtained at 0.88 V exhibits a higher plateau following the anodic peak of PPy(I) and a broad cathodic wave. When switching potentials were set at 0.98 and 0.93 V, pronounced symmetrical redox waves appeared (Figure 1C,D). Moreover, the current maximum shifts positively with increasing potential. By a conservative estimate, the potential required for the formation of polymer with the characteristics of PPy(III) is 0.93 V in this case. This is, as expected, markedly lower than 1.1 V for the solutions containing 1 wt % water. It must be pointed out that the so-called water-free solution used here may still contain a trace amount of water (less than 10^{-5} M). In an absolutely water-free solution, the formation potential for PPy(III) is supposed to be even lower.

Of particular interest is the electrode passivation in Figure 1A−C. In Figure 1C, the first potential scan generated a current

response (beyond the recording range) much higher than the second and following scans. At even higher switching potentials (Figure 1A,B), the currents from monomer oxidation at switching potentials decrease successively after the first several scans, leading to almost no (Figure 1A) or only limited (Figure 1B) polymer redox waves.

Since our discussion is associated with the broad and symmetrical CV waves, which we assign to the partially conjugated PPy(III), one might argue from another point of view that higher potential invokes a high reaction rate and consequently causes not only cross-linked chains and a wide distribution of chain length but also an ill-stacked tertiary structure; such an irregular chain structure and tertiary structure constitute the reason for the broad and symmetrical waves.

In this regard, we draw attention to the following facts. First, the similarly wide and symmetrical redox waves emerge readily in an acid-added solution even at very low potential (see Figure 4 in ref 24a), and second, in Figure 1, both the monomer oxidation current and the polymer growth rate are much lower than the cases in which water is added to the solutions. Note that the current scale for Figure 1C−H is 0.02 μA compared with 0.1−4 μA per unit bar in Figure 1 of ref 24a. This is clearly not the condition required for the formation of the less-ordered structure stated in the above argument. Therefore, this argument cannot refute our opinion of the formation of PPy(III). On the contrary, results in Figure 1 further support the suggestion that the wide redox waves result from the partially conjugated PPy-(III).

The passivation behavior in acid-added solutions has been thoroughly discussed in the companion paper.[24a] An interesting difference is that the electrode becomes passivated at lower potentials in acetonitrile solutions containing added acid, whereas in a neutral and water-free solution the electrode turns passivated only when higher potentials are applied (Figure 1A−C). The proton-catalyzed formation of **1** followed by electrochemical poly- or oligomerization provides a rational explanation for both cases.

Because it is impossible to prepare absolutely water-free acetonitrile, we are not able to experimentally confirm that electrode passivation occurs once the pyrrole is electrochemically oxidized. We have, however, corroborated this point by using solventless electrolytic solutions composed only of pyrrole and TBAPF$_6$. Figure 2 shows the results obtained with pyrrole dehydrated by two procedures. Pyrrole used for Figure 2A−C was distilled only once under argon from CaH$_2$, whereas pyrrole used for Figure 2D−H was refluxed and distilled twice under argon from CaH$_2$. From the comparison, it is clear that the electrode becomes passivated upon electrochemical oxidation of pyrrole in the extremely dried pyrrole solution in a wide
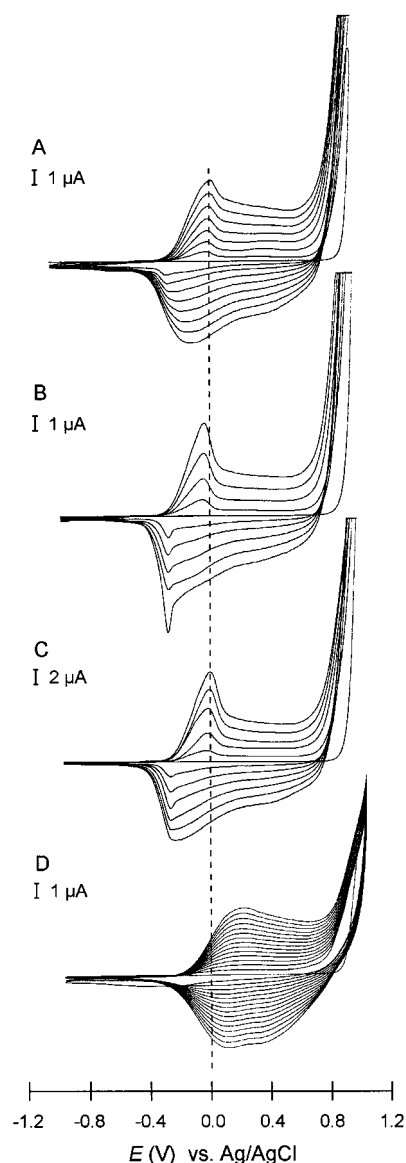
TABLE 1: pK_a Values and Dielectric Constants of Different Solvents

substance	pK_a	dielectric constant (temp)
acetonitrile	−4.2[a]	36.64 (293.2)
pyrrole	−3.8[b]	8 (293)
water	−2.35[a], 2.35[c]	80.1 (293.2)
	−3.43[d]	
methanol	−2.17[e]	33.0 (293.2)
ethanol	−1.93[e]	25.3 (293.2)
tetrahydrofuran	−2.08	7.52 (295.2)
PC		66.14 (293)

[a] In glacial acetic acid, ref 29. [b] In aqueous sulfuric acid, ref 21. [c] In acetonitrile. Water acts as a fairly strong base, ref 28. [d] Reference 26. [e] From HCl solubility data, using water pK_a of −3.43 as standard, refs 30 and 31.

Figure 3. Potentiodynamic growth of PPy films in acetonitrile solutions containing different additives (0.1 M pyrrole, 0.1 M TBAPF$_6$, 20 °C, 100 mV s^{-1}): (A) THF, 1 wt %, −1.05 to 0.95 V; (B) methanol, 1 wt %, −0.98 to 0.97 V; (C) ethanol, 1 wt %, −0.97 to 0.98 V; (D) PC, 20 wt %, −0.96 to 1.04 V.

potential range (Figure 2D−H), whereas a trace amount of water can result in a continuous growth of PPy (Figure 2A−C).

Addition of Other Substance to Acetonitrile. Further evidence for the proton-capturing effect of water comes from studies of electropolymerization in acetonitrile containing other additives more basic than pyrrole. Table 1 lists the proton affinities (expressed by the pK_a of the conjugate acids) and dielectric constants of selected substances.

It was found that the addition of methanol, ethanol, or tetrahydrofuran (all at 1 wt %) to dried pyrrole−acetonitrile solutions also increases the reaction rate of pyrrole as dramatically as water does. In all these events, the resulting PPy films show well-shaped voltammograms (Figure 3A−C) quite similar to those generally observed in water-containing solutions, and no passivation behavior is exhibited. These findings certainly have dual implications. First, they provide further support to the assumption associated with the proton-accepting ability of water, and second, these results contradict and unequivocally rule out speculation from the viewpoint of polarity factor, since

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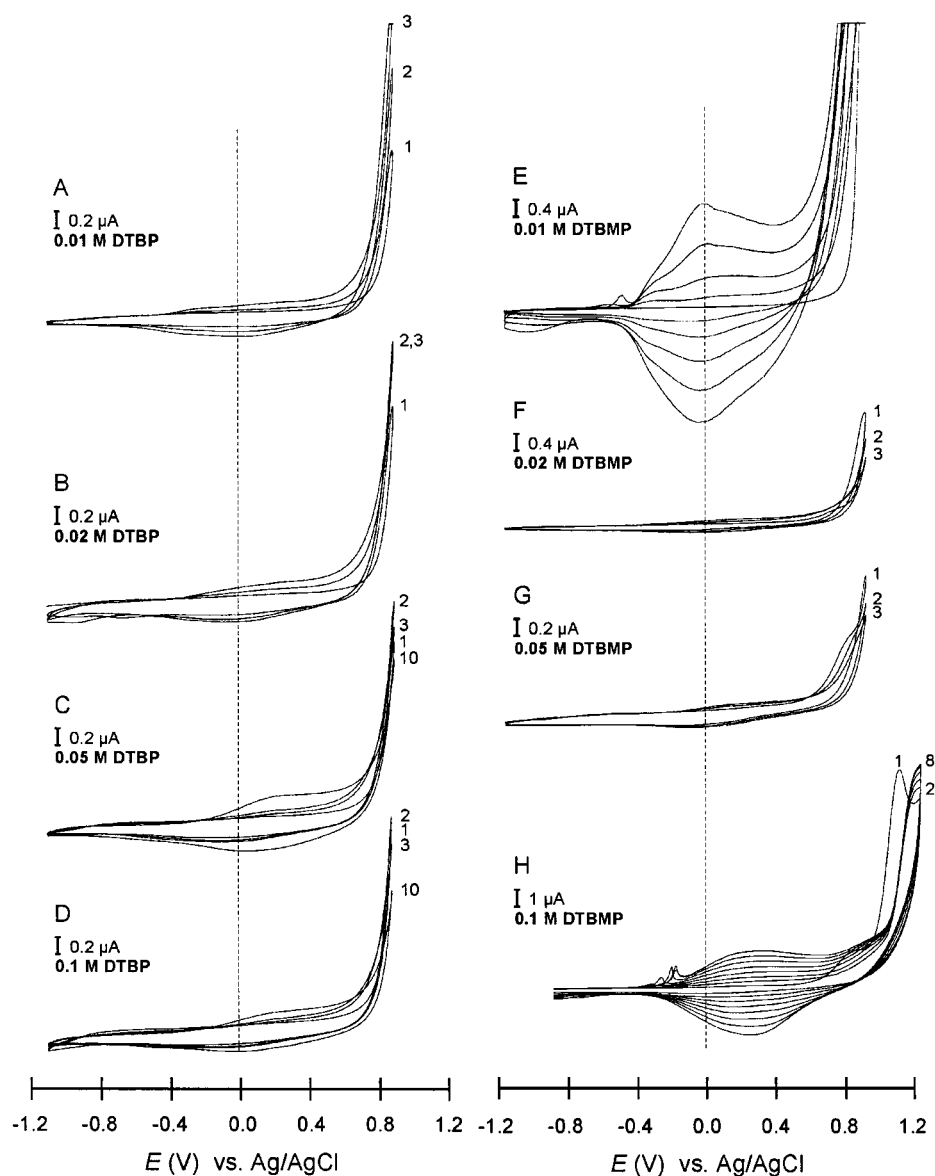*J. Phys. Chem. B, Vol. 103, No. 40, 1999* **8455**

Figure 4. Passivating effect of nonnucleophilic bases on the electrode during electropolymerization of pyrrole (0.1 M pyrrole, 0.1 M TBAPF$_6$, 20 °C, 100 mV s^{-1}): (A−D) DTBP added, −1.1 to 0.9 V; (E−G) DTBMP added, −1.16 to 0.94 V; (H) DTBMP added, −1.16 to 1.24 V. The scan number is indicated in the figure.

these additives, except water, all have smaller dielectric constants than acetonitrile (Table 1).

Since water is believed to be unnecessary for electropolymerization of pyrrole in PC, the proton-accepting ability of PC is supposed to be better than pyrrole and acetonitrile. Our results show that the addition of PC to acetonitrile solution has only a limited proton-capturing effect, and changing the amount of PC from 1 to 20 wt % did not modify the CV significantly. Although no passivation was observed, the CV in Figure 3D, which was obtained in solution with 20 wt % PC, is typical of PPy(III). Unfortunately, we failed to find quantitative data concerning the protophilicity of PC in the literature. Hence, discussion of this point makes no sense. However, the relatively lower conductivity of PPy prepared in PC[12] is consistent with our observation of poor protophilicity of PC.

Since the effect in question is not caused by water alone, the concept of "water effect" should be abandoned now.

Effect of Strong Bases. The discussion of the influence of protons and proton-capturing effect of water raises a question as to the effect of strong bases.

No film formation was observed when pyridine was introduced into an acetonitrile solution containing Bu$_4$NBF$_4$.[32−34] Apart from the proton-capturing effect, the strong nucleophilicity of pyridine was believed to block the cationic intermediates produced by electrooxidation. However, the nonnucleophilic 2,6-di-*tert*-butylpyridine (DTBP) also suppress electropolymerization of pyrrole in both acetonitrile and water solutions.[35] Owing to steric hindrance, DTBP is not believed to act as a nucleophile blocking reactive radical cations. This result from DTBP has been an argument against the explanation of the "water effect" based on its proton-accepting ability. This result also led Qian et al.[35] to propose a preprotonation scheme of pyrrole electropolymerization.

On the other hand, Andrieux et al.[36] did not observe any noticeable effect of DTBP on the voltammograms in a cyclic voltammetric experiment in acetonitrile containing DTBP up to 100 mM.

Since the effect of a strong base is closely connected with our explanation of the "water effect", we carried out similar experiments by adding DTBP and 2,6-di-*tert*-butyl-4-methylpy-
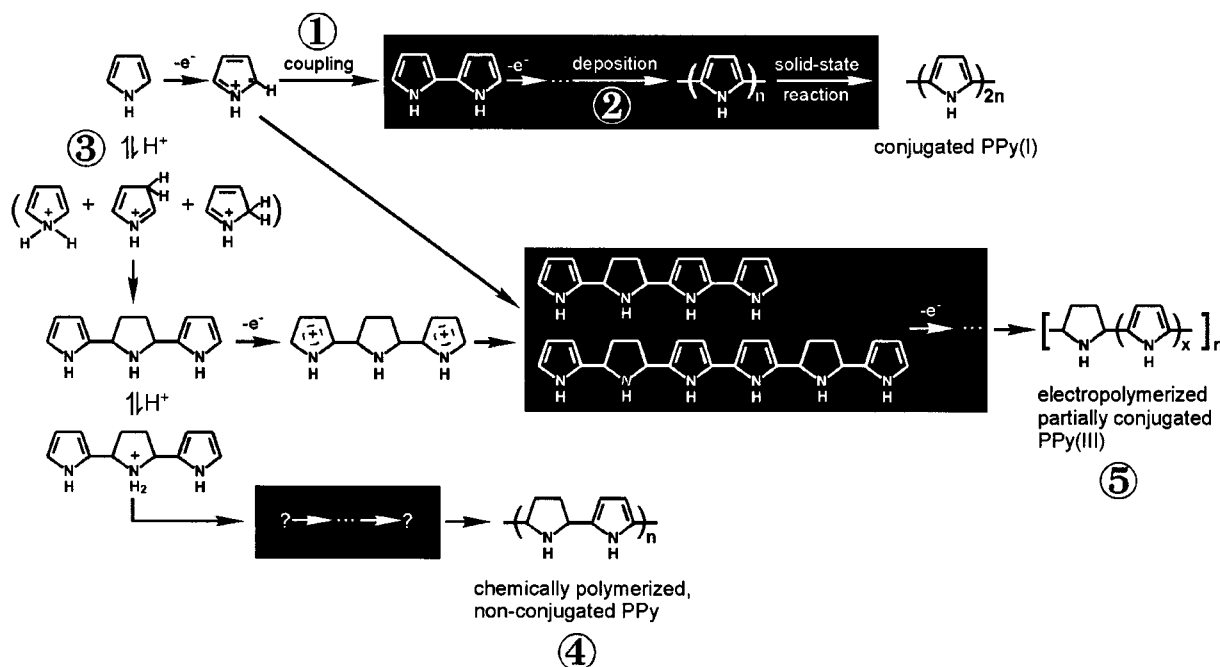
Figure 5. Reaction pathways and the viewpoints from which the "water effect" is explained.

ridine (DTBMP) to water-free electrolytic solutions. The results shown in Figure 4 demonstrate that the addition (greater than ca. 0.02 M) of both DTBP and DTBMP has an adverse effect on the electropolymerization of pyrrole in acetonitrile. The greater the amount of DTBP and DTBMP, the quicker the electrode becomes passivated. A similar adverse effect of DTBP is also found in the acetonitrile solution containing 1 wt % water. This is in agreement with the observation of Qian et al. However, if the results are compared with that obtained in water-free solutions, a conclusion similar to Andrieux's might be drawn because the polymer growth in both cases (with DTBP and without any additive at all) is too slow to be voltammetrically characterized.

It is clear that strong nonnucleophilic bases, unlike water, do not show a favorable effect on the pyrrole electropolymerization. This seems to be puzzling. In their studies of *pyridin*[37] intervention, Morse et al.[33] have reasonably drawn a well-founded mechanism of *pyridin* intervention. Namely, the *pyridin* acts to remove the proton from the nitrogen atom of the first-formed pyrrole radical cation before dimerization occurs. Because of the lower reaction selectivity of neutral radicals, the coupling reaction of neutral radicals results in a polymer that probably has $\alpha-\beta$ and $\beta-\beta$ links along the chains, in addition to the $\alpha-\alpha$ link. The polymer with a highly mislinked chain structure is of course less, or even not, conductive and passivates the electrode. This provides a good explanation of the adverse effect of strong nonnucleophilic bases on pyrrole electropolymerization. In studying thiophene electropolymerization in the presence of strong nonnucleophilic bases, Visy et al.[38] proposed a similar mechanism in which deprotonation (here, from C atoms) takes place before the radical−radical coupling and generates more reactive, but less selective, neutral radicals.

Review of Other Proposed Mechanisms. Although results discussed above provide strong support for our interpretation of the "water effect", one can still argue that this might be yet another speculation. To rule out other possibilities, we now review all the different viewpoints, which, for an easier overview, are numbered and integrated into the reaction scheme shown in Figure 5.

Viewpoint 1 is associated with ϵ of water. As we mentioned in the Introduction, the higher dielectric constant of water does not have a favorable effect on the electropolymerization of thiophene and *N*-methypyrrole in acetonitrile. Moreover, the results displayed in Figure 3 and Table 1 show the same effect of other additives with ϵ lower than that of acetonitrile and exclude unequivocally the possibility of using the dielectric constant of water for the explanation.

Viewpoint 2 is based on the mechanism in which the formation of a polymer film is due to the deposition of an insoluble long oligomer (or polymer) from solution at the electrode. The addition of water might greatly decrease the solubility of oligomer with a certain length. This explanation is mere conjecture because, to our knowledge, no quantitative study of the solubility of pyrrole oligomers in acetonitrile−water electrolytic systems has been performed so far. If this conjecture were true, we could expect a quick formation of film with good quality under the conditions of higher currents or potentials. This is, however, not in agreement with the results shown in Figure 1. Another argument against this explanation is the fact that electropolymerization of a pyrrole oligomer (ter-, quarter-, penta-, and heptapyrrole) in acetonitrile does not need the assistance of water.[39,40]

Unlike viewpoints 1 and 2, protonation of pyrrole and the proton-capturing ability of water are realized in viewpoints 3−5. However, without considering further reactions of protonated pyrrole molecules, viewpoint 3 fails to explain electrode passivation after electrochemical oxidation of pyrrole in a dried acetonitrile solution. This is also the most unconquerable obstacle encountered by viewpoints 1−3.

We hold electrode passivation to be the key to the issue. The acid-catalyzed chemical polymerization of pyrrole is undoubtedly present in an acidic acetonitrile solution, but a newly polished electrode can never be passivated quickly in a deliberately acidified acetonitrile solution if no electrochemical oxidation of pyrrole occurs on the electrode. So viewpoint 4 seems unlikely. Furthermore, the fact that the rather stable intermediate **1** can be isolated from the acid-catalyzed polymerization course indicates a relatively slower follow-up chemical polymerization from **1**. In the case of electropolymer-

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ization of pyrrole in a dried acetonitrile solution, **1** must be generated in the acidified reaction zone. Compared to the further chemical polymerization, on which viewpoint 4 is based, the electrochemical oxidation of **1** and the follow-up coupling reaction involving **1**[•+] must be much faster. Thus, the formation of chemically polymerized, nonconjugated PPy on the electrode is unlikely. Instead, the electropolymerized, partially conjugated PPy, on which viewpoint 5 is based, is the most likely reason for electrode passivation.

However, this is not to say that chemical polymerization is not possible. When the reaction rate or potential is higher and the acidified zone extends from the electrochemical reaction zone to the bulk solution, chemically acid-catalyzed polymerization may take place. This could be the reason for the orange-yellow cloud mentioned by some authors[5,23] and observed by ourselves.

Conclusions

The dramatic "water effect" on pyrrole electropolymerization in acetonitrile solutions has long been debated. The fact that such a favorable effect is only found in pyrrole−acetonitrile system leads us to consider the specific chemistry of pyrrole. The key to this issue is the passivation of the electrode. The voltammograms obtained under systematically varied conditions provide direct experimental evidence for the explanation of the "water effect".

In dried acetonitrile, parallel to the anodic oxidation and electropolymerization of pyrrole, side electrochemical reactions involving pyrrole trimer **1** take place and result in partially conjugated PPy(III). If reaction-released protons cannot be removed, the electropolymerization will be frustrated by electrode passivation because of deposition of the poorly conductive PPy(III). Water, having a stronger basicity than pyrrole, captures the reaction-released protons and prevents pyrrole from being protonated. Consequently, the acid-catalyzed formation of **1** and of the subsequent electrochemically synthesized PPy(III) is depressed.

According to this mechanism, not only water but also other substances that are more basic than pyrrole, but not basic enough to deprotonate intermediate radical cations, have a favorable effect on pyrrole electropolymerization in acetonitrile. Some examples, like methanol, ethanol, and tetrahydrofuran (all at a concentration of 1 wt %), proved to be as effective as water. In this context, the "water effect" is not the right concept for pyrrole electropolymerization in acetonitrile.

We hope that the results reported here bring the "water effect" issue to an end.

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(25) In the strict sense, the proton affinities of water, acetonitrile, and pyrrole should be compared with each other in the real electrolytic system, i.e., acetonitrile solution containing 0.1 M pyrrole, 0.1 M TBAPF$_6$, and 1 wt % water. Unfortunately, no quantitative data based on a uniform methodology can be found. The basicity measured by pK_a of the conjugate acids of water and pyrrole in aqueous sulfuric solutions indicates that water is a stronger base than pyrrole, reported values for H$_3$O$^+$ being -3.43[26] and for α-protonated pyrrole being -3.8,[21] or -4.4[22] when converted to the H$_R$′ scale. The values for β-protonated and *N*-protonated pyrrole were estimated at -5.9[21] and ca. -10.[27] No direct comparison between water and pyrrole in acetonitrile is available. However, water proves to be a fairly strong base in acetonitrile (pK_a for H$_3$O$^+$ is 2.35[28]). Since the acid-catalyzed trimerization starts from the β-protonated pyrrole,[16−18] the pK_a values cited in ref 23 are questionable, although the order of basicity is right. As regards the comparison between pyrrole and acetonitrile, the pK_a values of β-protonated pyrrole (-5.9) and acetonitrile (-4.2, listed in Table 1) are not convincing. It is, however, well-known that the oligomer, polymer, and salts of pyrrole dimer are readily formed in dilute aqueous acid, whereas nitriles can be only protonated by sufficiently strong acids under anhydrous conditions in aprotic media and do not form salts with mineral acids in aqueous media. These facts substantiate the view that pyrrole is a relatively stronger base than acetonitrile.

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