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Critical effect of pH on the formation of organic coatings on mild steel by the aqueous electropolymerization of 2-vinylpyridine

X. LING, J. J. BYERLEY, M. D. PRITZKER*, C. M. BURNS

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada

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Coatings of poly(2-vinylpyridine) have been formed on mild steel substrates in aqueous medium by electrochemical polymerization of the 2-vinylpyridine monomer. The pH of the solution has been found to be critical for this electropolymerization coating process. At low pH (below 3.5), even with an efficient initiation reaction, the propagation process was impeded and no substantial polymer film was formed. At high pH (above 6.0), only a thin and irregular film formed due to the lack of an effective initiation reaction. Only when the solution pH is in the range of 4 to 5.5 can good quality coatings be formed on mild steel substrates. The detailed effects of the pH on the electropolymerization are discussed in terms of a proposed free radical polymerization mechanism. This research has also resolved the issue of some of the non-reproducible experimental results reported in the literature and confirmed the feasibility of forming poly(2-vinylpyridine) coatings on a mild steel substrate by electropolymerization of the monomer.

Keywords: *Organic coatings*, *mild steel*, *pH*

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1. Introduction

The formation of polymer coatings on metal surfaces by electropolymerization has been widely studied [1–7]. Compared with the popular electrophoretic deposition, electropolymerization has distinct advantages [8]. Coatings can be formed *in situ* on metal substrates from low molecular weight and highly soluble monomers. They are uniform and have good adhesion to the metal surfaces, even on irregularly shaped metal substrates. Only mild polymerization conditions and low energy consumption are required and the thermal curing after polymerization can often be avoided. Since chemical initiators are unnecessary, the degradation of the formed polymer coatings, which is often caused by the initiator fragments, is less likely. With appropriate electrochemical techniques, polymer coatings with well controlled molecular weight, molecular weight distribution and predetermined coating thickness could be expected.

According to the characteristics of its electroinitiation process, electropolymerization can be grouped into electrooxidation polymerization (EOP) and electroreduction polymerization (ERP) processes [9]. Sekine *et al.* [10] investigated electropolymerization processes to produce coatings for corrosion protection. Various monomers were investigated in both EOP and ERP processes. It was noticed that film formation by the EOP process was always accompanied by oxidation of the metal substrates. Metal oxide layers which formed on the metal substrates led to discontinuous, porous and thin films. On the other hand, no such oxidation occurred in the ERP process and more compact and thicker films were obtained. This research found that ERP was superior to EOP for coating formation on mild steel substrates. It was also found that poly(2-vinylpyridine) films provided the best properties for corrosion protection. However, de Bruyne *et al.* [11] found that only a scant and irregular poly(2-vinylpyridine) film formed on mild steel substrates under the same reaction conditions used by Sekine because of extensive hydrogen evolution. They could only form the poly(2-vinylpyridine) coating on zinc which has a high hydrogen overpotential.

Due to the superior properties of a poly(2-vinylpyridine) coating for corrosion protection, its application as a polyelectrolyte [12–17] and the important application of its metal complexes as conducting polymers [18, 19], research into the mechanisms of poly(2-vinylpyridine) coating formation using electrolysis has continued. The objective of this study is to examine further the ERP process of formation of poly(2-vinylpyridine) coatings on mild steel from aqueous solution. During the course of our experiments, it was discovered that the solution pH has dramatic effects on the coating formation process. This provides a possible reason for the poor reproducibility reported previously [11] and demonstrates how an effective poly(2-vinylpyridine) coating on mild steel can be obtained by electropolymerization of the 2-vinylpyridine monomer.

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[*] Author to whom correspondence should be addressed.

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2. Experimental details

A three-electrode system was used for the electrochemical experiments. The working electrode was a mild steel coupon (SAE 1018-1020) with an active surface area of 5.5 cm^2, while the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE, Aldrich Chemical Company), and the potentials reported in this work are all referred to the SCE scale. The working electrode was cleaned ultrasonically first in a soap solution for 30 min and then polished with SiC-type abrasive paper (up to 1200 grade). Polishing to a mirror finish was found to be unfavorable for the formation of good coatings. Degreasing was carried out with trichloroethylene for 2 minutes, followed by a washing with soap solution to remove the grease and trichloroethylene, a rinsing with a large amount of deionized water, and finally a rinsing with ultrapure water (Millipore® ultrapure water system). The prepared metal samples were stored in a desiccator until needed. Since the 2-vinylpyridine (Aldrich Chemical Company) as received contained 0.1 wt % of *p-tert*-butylcatechol to inhibit 2-vinylpyridine homopolymerization, it was necessary to purify it before use by distillation at 70 °C under a vacuum of 97.8 kPa. All other chemicals were analytical grade and used without further purification. The solvent was a water/methanol mixture (volume ratio of 9 : 1). NH_4ClO_4 was used as supporting electrolyte, while $HClO_4$ and NH_4OH were used to adjust the solution pH when required. All solutions were prepared with ultrapure water and a total volume of 60 ml solution was used in each experiment. The composition of the electrolytic solution used in this study is listed in Table 1.

Experiments were performed at 20 °C. A potentiostat (EG & G 273) was used to conduct cyclic voltammetry and chronoamperometry experiments. The output from the experiments was recorded on a data logging computer (JPC 386SX) and was monitored on-line on the computer screen. The cyclic voltammetry experiments were carried out in the potential range of +3 to −2.5 V at a scan rate of 30 $mV\,s^{-1}$. The chronoamperometric experiments were carried out at −1.3 V. Magnetic stirring was maintained during electrolysis. After plating, the metal samples were rinsed with deionized water and dried in vacuum 97.8 kPa at room temperature for one day. Thermal curing was then performed at 120 ~ 130 °C for 30 min [20].

Coating morphology and thickness were examined by confocal scanning beam laser microscopy (CSBLM) [21]. Characteristics of the polymer coating were investigated by ultraviolet–visible spectroscopy (Beckman spectrophotometer DU 600) in a wavelength range of 190 to 1100 nm. The weight increase of the metal samples after electropolymerization was recorded in order to obtain a measure of the rates of the coating formation process. Corrosion resistance of the coated samples was measured by the polarization curve method [22]. Each metal sample was first immersed in a 3 wt % NaCl solution at 20 °C for 3 h and then subjected to a potential scan at a rate of 10 $mV\,s^{-1}$ starting at its open-circuit potential. The scans were carried out in both cathodic and anodic directions, and the current response recorded.

3. Results

Solution pH was found to affect the cyclic voltammetry experiments greatly. Without the addition of $HClO_4$ or NH_4OH for pH control, the solution had an initial pH of 7.5 At this or higher pH values, there was no current peak in the cyclic voltammogram indicating any other cathodic reaction besides hydrogen evolution (which started at about −0.9 V). However, when the solution pH was reduced to about 4.8 using $HClO_4$, a significant cathodic shift of the starting potential for hydrogen evolution to about −1.5 V was observed and a new current peak with an $E_{1/2}$ of −1.2 V appeared. The change in shape of the cyclic voltammograms (cathodic part only) resulting from the change of the solution pH is shown in Fig. 1. The curves have been deliberately shifted horizontally to avoid any overlap. The anodic parts of the cyclic voltammograms which contained only the oxygen evolution current peak are omitted.

Solution pH also influenced the coating formation process significantly. After a one-hour chronoamperometric electrolysis at constant cathodic potential of −1.3 V, the images of the coated sample morphology obtained by CSBLM showed very scattered deposits formed on the electrode surface from a solution of pH 7.5 (Fig. 2(b)). At higher values of pH, even less film was formed and it was still quite irregular (Fig. 2(c)). Only when the solution pH reduced to lower than 5.5 did a uniform coating form on the electrode surface (Fig. 2(a)). The average thickness of the coating as measured by CSBLM using a previously reported technique [21] was found to be 15.5 μm. However, when more $HClO_4$ was added to the solution to lower the pH below 4, hydrogen evolution was observed at more positive potentials and very little deposit formed on the substrates. When the pH was lower than 2, no film

Table 1. The composition of the electrolytic solution used in this study

Solute	*Solvent*	*Supporting electrolyte*	*Other additives*
0.25 M 2-vinylpyridine	Water : methanol mixture of 9 : 1 (volume ratio)	0.05 M ammonium perchlorate	Various amounts of perchloric acid or ammonium hydroxide to adjust solution pH

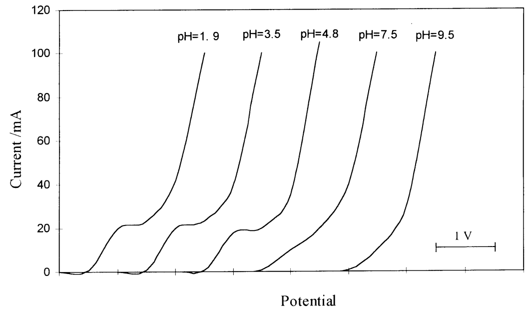


Fig. 1. The effect of solution pH on the shape of the cyclic voltammograms. Potential scan range is between −0.7 to −2 V and scan rate is 30 mV s^{-1}. The curves have been shifted along the potential axis deliberately to avoid any overlap.

formation could be observed. During the chronoamperometric electrolysis, the bulk solution pH maintained constant. The results from these experiments are summarized in Table 2.

During the chronoamperometric electrolysis at −1.3 V and at various values of pH, the current was found to decrease rapidly after the onset of the electrolysis (Fig. 3). Interestingly, even when very little or no film had formed on the substrate surface at low pH (e.g. below 3.5), the current still decreased very rapid with time. At high pH, on the other hand, a good coating also did not form, but the current dropped off less sharply. The reasons for this behavior are not clear yet. A possible explanation may be that some extremely thin but very compact films had been formed on the substrate surfaces.

Hydrogen evolution was observed to occur simultaneously with film formation during the chronoamperometric electrolysis at −1.3 V. Hydrogen bubbles were clearly visible on the cathode surface. As a consequence, the formed films contained some small pits, with dimensions from a few micrometres to one millimetre (Fig. 2(a)). These pits did not extend down to the surface of the original mild steel substrates, however, because thin film layers were still visible at the base of the pits. In order to minimize the effect of hydrogen evolution, the standard chronoamperometric plating procedure was modified by first applying a constant cathodic potential of −1.3 V for 1 h and then gradually decreasing the potential from −1.3 to −0.7 V over 0.5 h. The potential waveform and the resulting current response are shown in Fig. 4. During the stage when the potential was being diminished, the evolution of hydrogen gas bubbles was observed to subside significantly and the coating formation process, although reduced as well, appeared to occur primarily on the thinner recesses within the pits. Consequently, the pits were filled to a certain degree, thereby making the coating more uniform (Fig. 5), although the overall coating thickness did not appear to increase.

The formed coating had a golden-brown colour which became darker after thermal curing. The coatings were insoluble in water, but slightly soluble in methanol. Coatings were electrically insulating even before thermal curing and had excellent adhesion to the metal substrates. Although not included in this paper, the measured ultraviolet-visible spectra of the coating were identical to those in the literature [10, 11, 23–25], confirming that poly(2-vinylpyridine) coatings have been formed on the mild steel substrates. Evaluation of the corrosion resistance using the polarization curve method described previously shows a significant improvement for a coated sample compared to a bare mild steel sample (Fig. 6).

4. Discussion

To form poly(2-vinylpyridine) coatings successfully on metal substrates, it is important to have a good understanding of the characteristics of 2-vinylpyridine monomer. Abundant background information is available in the literature [23, 26–29]. We propose the following reaction mechanism as a possible explanation for the process of formation of poly(2-vinylpyridine) coatings by electrolysis.

Due to the presence of an electronegative nitrogen atom in the pyridine ring, 2-vinylpyridine is weakly basic with an *e* value of −0.42 in the *Q*-*e* scheme [30]. The nitrogen atom can attract cations in solution, for example, hydrogen ion in an acidic aqueous medium,

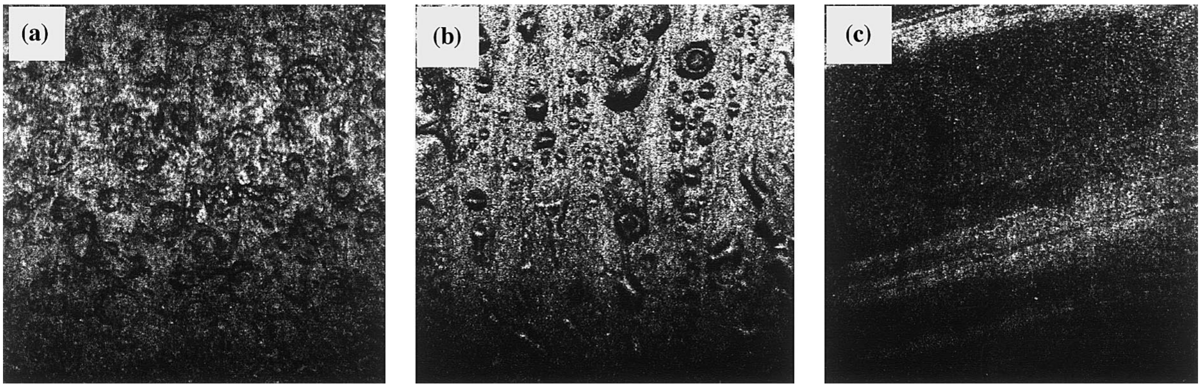


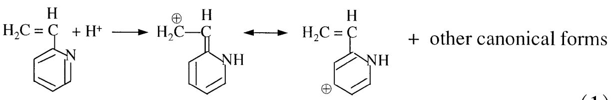
Fig. 2. The effect of solution pH on coating morphologies (in 4 mm × 4 mm scanning areas), after a 1 h chronoamperometric electrolysis at a constant potential of −1.3 V. (a) pH 4.8: coating is uniform although small pits can be seen; (b) pH 7.5: coating is scattered and irregular; (c) pH 9.5: very thin and irregular coating.

Table 2. Summary of the experimental results of the effects of solution pH on coating formation

Solution pH	$E_{1/2}$/V*	*Weight increase/μg*	*Current change in chronoamperometric electrolysis*†	*Coating morphology*
1.9	−1.15	0	Current decreases quickly; reaches a final value of 1.35 mA cm^{-2}	No visible film
3.5	−1.15	0.5	Current decreases quickly; reaches a final value of 0.82 mA cm^{-2}	Very little visible film
4.8	−1.20	3.5	Current decreases quickly; reaches a final value of 0.45 mA cm^{-2}	Smooth and compact film
7.5	–	1.8	Current decreases quickly; reaches a final value of 0.91 mA cm^{-2}	Scattered and irregular film
9.5	–	1.1	Current decreases quickly; reaches a final value of 1.64 mA cm^{-2}	Very thin and irregular film

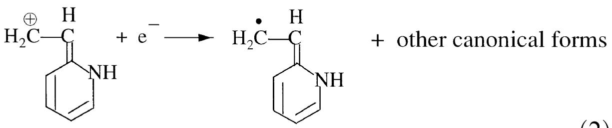
* The $E_{1/2}$ corresponds to the half wave potential for the electroinitiation reaction (Equation 2).
† Duration of experiments 1 h.

and make the 2-vinylpyridine molecule positively charged so that it migrates to the cathode in an electric field:



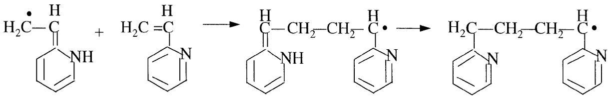
(1)

The protonated 2-vinylpyridine molecule, which is more easily reduced than a neutral molecule, is then reduced to an unstable free radical at the cathode:



(2)

The unstable free radical can react with a neutral monomer molecule which is also present in the solution to form a more energetically favoured secondary radical. This radical can then undergo head-to-tail propagation (energetically favoured) with other neutral monomer molecules to form a growing polymeric radical with an eneamine structure which would likely tautomerize back to the aromatic pyridine:



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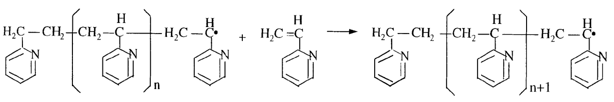
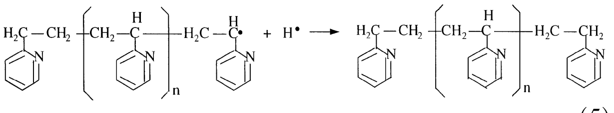


(4)

The propagation process is eventually terminated when the propagating radical reacts with another radical, such as with the hydrogen radical generated at the cathode surface by H^+ reduction:



(5)

or with another propagating radical by either combination or disproportionation.

The distribution of the neutral and protonated forms of 2-vinylpyridine molecules in an aqueous solution is pH dependent and can be determined by considering the following equilibrium:

$$\mathrm{M{-}H^+} \overset{K_a}{\rightleftharpoons} \mathrm{M} + \mathrm{H^+} \tag{6}$$

where M and $M{-}H^+$ present the neutral and protonated forms of 2-vinylpyridine molecules, respectively, and $K_a = 10^{-4.92}$ [28]. Therefore, we have

$$pK_a = \mathrm{pH} - \log\frac{[\mathrm{M}]}{[\mathrm{M{-}H^+}]} \tag{7}$$

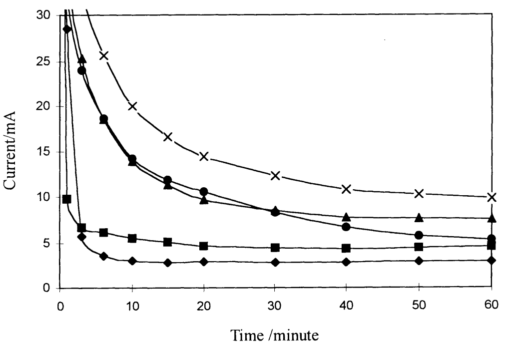


Fig. 3. The effect of solution pH on cathodic current during chronoamperometric electrolysis at a constant potential of −1.3 V. pH: (●) 1.9, (■) 3.3, (◆) 4.8, (▲) 7.5, (×) 9.5.

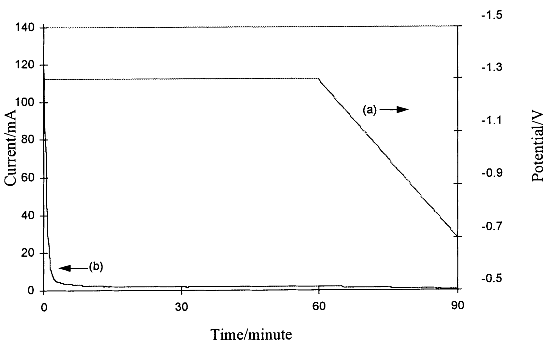


Fig. 4. Modified electrolytic process to minimize formation of pits, due to hydrogen evolution. Waveform of the applied potential (a) and the resulting current response (b).

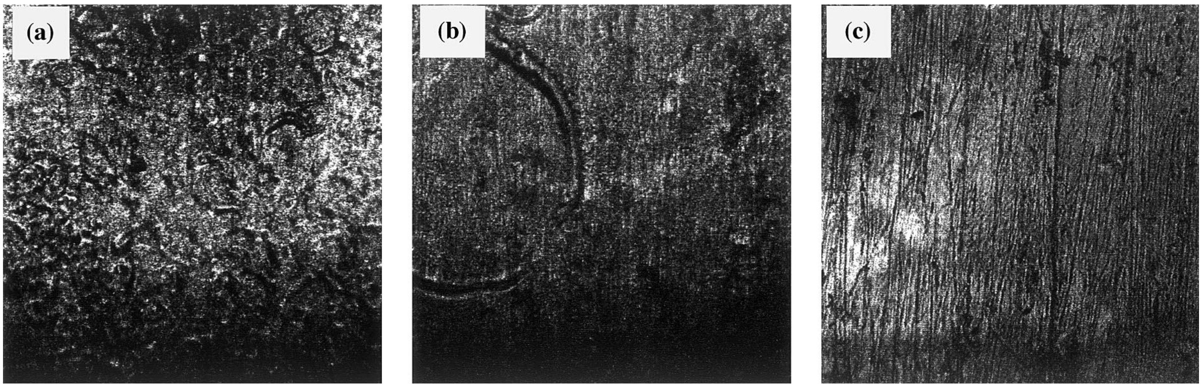


Fig. 5. Morphologies of coatings produced by electrolytic process described in Fig. 4. CSBLM images of partially filled pits at different magnification: (a) 4 mm × 4 mm area, (b) 1 mm × 1 mm area and (c) 200 μm × 200 μm area.

Solving Equation 7, we obtain the concentration distribution curves for M and M—H$^+$ as a function of solution pH (Fig. 7). It is clear that at the natural solution pH of 7.5, most 2-vinylpyridine molecules in solution exist in their neutral form, while the protonated 2-vinylpyridine represents only 0.2% of the total 2-vinylpyridine mass. Furthermore, since the pH of the electrolyte adjacent to the cathode is higher than that in the bulk solution during the electrolysis, an even lower concentration of the reducible protonated 2-vinylpyridine is likely present at the cathode. As a result, the initiation reactions of the electropolymerization process (Equations 2 and 3) are impeded and hydrogen evolution becomes dominant. This explains why the cyclic voltammograms (curve at pH 7.5 in Fig. 1) showed no reduction current peak other than that for hydrogen evolution and why only some very scattered polymer deposits were observed on the electrode surface (Fig. 2(b)). It is not surprising, then, that the quality of the deposits became even poorer when the solution pH was raised (Fig. 2(c)).

When the solution pH is reduced to lower than 5.5, there is an abundance (at least 20% of the total mass) of 2-vinylpyridine molecules existing in their protonated form. Therefore, part of the initiation reaction, the radical generation reaction (Equations 2), occurs and the corresponding reduction current peak appears in the voltammograms (curves at pH 1.9, 3.5 and 4.8 in Fig. 1). The half wave potentials of these reduction current peaks are very close to the standard 2-vinylpyridine reduction half wave potential reported in literature [26]. On the other hand, when the solution pH is too low (below 3.5), most 2-vinylpyridine molecules exist in solution in the protonated form, with the neutral form being less than 3.7% of the total mass of 2-vinylpyridine. Although the protonated 2-vinylpyridine is necessary for the reduction reaction and hence the initiation reaction, it is unlikely to participate in the free radical propagation reaction because of repulsion due to the high positive polarity of the C═C double bonds [31]. The neutral form of 2-vinylpyridine would be needed for the propagation reaction. Thus, even when the cathodic current plateau corresponding to radical formation appears in the cyclic voltammograms (curves at pH 1.9 and 3.5 in Fig. 1), very little or no polymer deposit was formed on the electrode surface. Only when the solution pH is in an intermediate range (i.e. between 4 to 5.5) is there an abundance of both neutral and protonated forms of 2-vinylpyridine in solution so that uniform polymer coatings can form on the electrode surface. Although de Bruyne *et al.* [11] did not report the pH in their experiments, we can speculate from these results that their electrolytic solutions were not in the appropriate

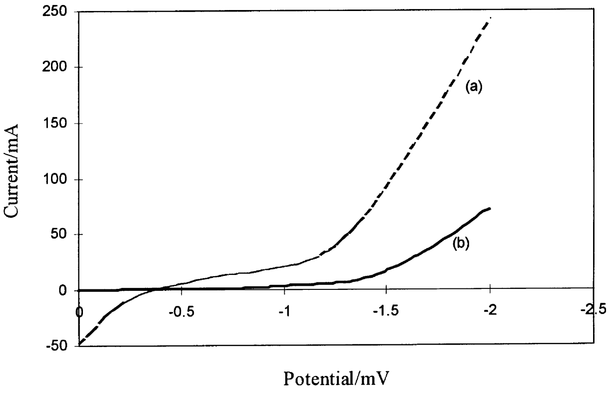


Fig. 6. The polarization curves of mild steel after immersion in 3 wt% NaCl solution at 20 °C for 3 h: (a) bare metal sample and (b) metal coated with poly(2-vinylpyridine). Potential scan rate was 10 mV s^{-1}.

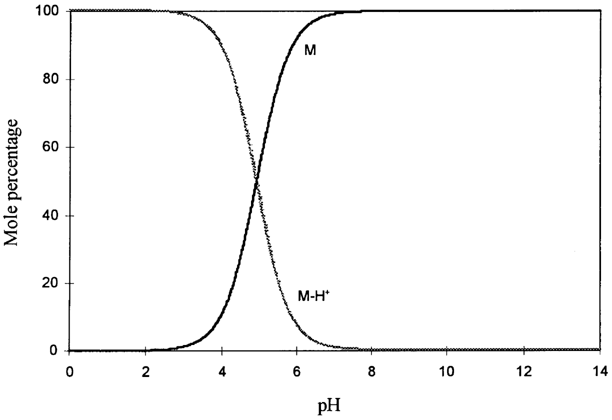


Fig. 7. The concentration distribution curves of neutral (M) and protonated (M—H$^+$) 2-vinylpyridines in aqueous solution at different pH.

pH range for good film formation. When propagation cannot occur readily, the generated 2-vinylpyridine radicals may combine with each other to form dimers or they may disproportionate.

The foregoing explanation proposes that the electropolymerization of 2-vinylpyridine follows a free radical mechanism. Although anionic and combined anionic and free radical mechanisms have been suggested for the polymerization of 2-vinylpyridine [23, 32], an anionic mechanism is not likely to occur in an acidic aqueous system with a monomer of such a low *e* value, especially when methanol is one of the principal solvents. Strong proton donors in the solution (e.g. hydrogen ions, water and methanol) can very easily scavenge any generated anion. As a result, we would expect no anionic polymerization in such an environment. Experiments are currently underway in our laboratory to obtain more information on this mechanism using such techniques as NMR.

5. Conclusions

The pH of the solution has been found to be critical to the formation of poly(2-vinylpyridine) coatings on mild steel by electropolymerization. At low solution pH (below 3.5), no significant polymer film was found to form on the mild steel surface. At high solution pH (above 6), only thin and irregular films formed. Only when the solution pH is in a range between 4 to 5.5 did good quality coatings form on the mild steel surface. Once a good quality coating is formed, it has been found to show good corrosion resistance. The pH effect can be explained in terms of a free radical mechanism in which the protonated form of 2-vinylpyridine is needed for electroinitiation and the neutral form of 2-vinylpyridine is needed for propagation. Thus, only at intermediate values of pH when both forms are abundant do good coatings form.

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