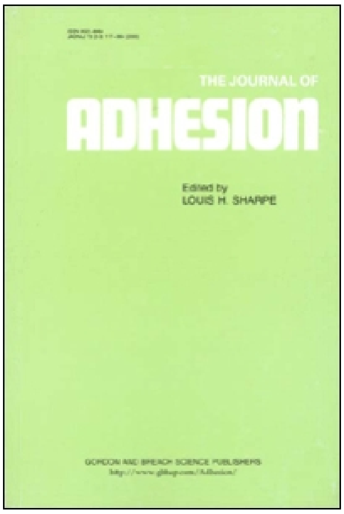

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Investigation of Processes Occurring at the Metal/Polymer Coating/Electrolyte Interface

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Investigation of Processes Occurring at the Metal/Polymer Coating/Electrolyte Interface

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The methodical approach and the cell to study electrochemical processes occurring during cathodic disbondment of a polymer coating are worked out. They permit one to investigate the role of each process separately when supervising the metal substrate potential, electrolyte and polymer coating composition at a metal/polymer/electrolyte interface. The cathodic disbondment of ethylene-vinyl acetate copolymer, polyisoprene and poly(vinyl chloride) coatings are studied. It is found that the cathodic disbondment rate for ethylene-vinyl acetate copolymer coatings depends on double layer parameters at the interface. These parameters are determined by specific volume charge of hydrated cations of the electrolyte, potential of the substrate, the presence of oxygen, surface active substances, *etc*. Based on the data of IR spectroscopy in internal reflection applied to disbonded films, it is established that during the cathodic disbondment an electron transfer to polymer functional groups, as well as an attacking of the adhesion bonds by active intermediates of oxygen reduction, occurs resulting in an electrochemical degradation of the polymer and an adhesion loss. It is shown that the electrochemical transformations at the steel/poly(vinyl chloride) interface can lead to the appearance of new adhesion bonds, increasing adhesion strength and decelerating the cathodic disbondment.

Keywords: Metal/polymer/electrolyte interface; electrochemical processes; cathodic disbondment; double layer; adhesion loss; polymer degradation

1. INTRODUCTION

The application of polymer coatings for metal protection is of increasing importance for many fields of modern technologies. Most

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of the time the coatings fail because of a degradation of the metal/polymer interface, due to the environmental attack of corrosive species [1–6]. The loss of adhesion is a result of electrochemical processes which occur at the metal-polymer interface [7–9]. Usually, the metal substrate is cathodically polarized along the border of a delamination space – the metal/polymer/electrolyte interface (MPEI), due to a charge transport from the anodic zones on the surface where rusting takes place [10, 11]. When the external cathodic potential or current is applied to the metal for the corrosion protection (cathodic protection), the cathodic potential along the MPEI increases accelerating the electrochemical processes which lead to the degradation of the metal/polymer interface. A phenomenon of the adhesion loss under the cathodic control is known as a cathodic disbondment, or a cathodic delamination.

The main appropriateness of cathodic disbondment has been investigated by Mayne [12, 13], Leidheiser and co-workers [14, 15], Schwenk [16], Castle and Watts [17, 18], Hammond, Holubka, de Vries and Dickie [2, 4, 5, 11], Koehler [6, 9] and others. General conclusions of these investigations were summarized by Castle [19, 20] and Nguyen and co-workers [21] in recent reviews. It was concluded that cathodic disbonding is associated with the build-up of hydroxyl ions at the interface through the reduction of the oxygen or the water. This explanation was sufficient to describe the cathodic disbondment for the polybutadiene- and epoxy-based and other coatings on steel, *i.e.*, for the metal/polymer systems, where adhesion strength is mainly associated with acid-base-like chemical bonding at the steel/polymer interface.

However, consideration of cathodic disbondment only within the framework of such a chemical paradigm seems to be simplified and incomplete to judge all the influences at the MPEI which provoke the disbondment. In reality, the bonds are also affected by electric fields of double layers being along the MPEI which, in turn, is always in the zone of the electrochemical reactions (Fig. 1). Consequently, chemical bonds, particularly the adhesion ones, are strongly polarized to, probably, result in a change of their reactivity. Moreover, the aggressive products of cathodic reactions of the components of the medium being at the interface can destroy the adhesion bonds by a chemical process. Besides, gradients, both of the potential and of the electrolyte composition in the neighborhood of the metal substrate surface, along the disbonded film, make the system more complicated. As a result, it is very difficult to evaluate the influence of one concrete process

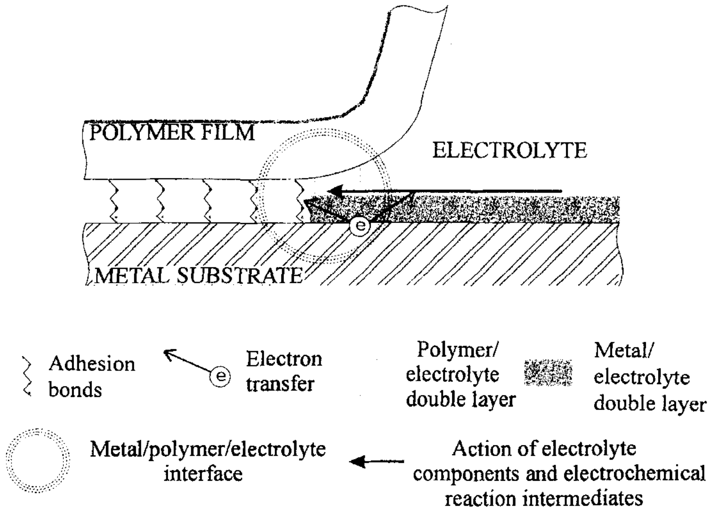


FIGURE 1 The scheme for the metal/polymer/electrolyte interface.

when so many factors change. Therefore, an ability to study cathodic disbondment, as a phenomenon which includes a complex of different factors, depends on experimental approaches and techniques.

Thus, the methods based on ASTM-G8-72, ASTM-G8-85, and their modifications, were usually used for the investigation of cathodic disbondment. In such an experimental condition it is impossible to control the potential and the electrolyte content at the MPEI. Woodruff has stressed back in 1975 [22] the deficiencies of existing experimental approaches for understanding the causes of the delamination process. This problem still remains open.

As cathodic disbondment, and the corrosion reactions under the delaminated coating as well, are electrochemical in nature, application of Electrochemical Impedance Spectroscopy become very popular and useful for the study of the delamination [23–30]. This method permits one to monitor the disbondment itself, to test ion and electron conductivity of a coating, metal corrosion rate, *etc.*, but it provides little information about the processes localized at the MPEI.

In-situ measurement of the local potential distribution has been proposed by Stratmann *et al.*, using a scanning Kelvin-probe [31–33]. By determining the Volta-potential of the polymer-coated metal substrate it is possible to map the potential distribution in the vicinity of a defect. This approach permits one to observe the appearance of the local galvanic elements when the disbonded space appears and to investigate the electrochemical reaction from the anodic zone of the rusting to the cathodic zone near the delamination frontier. It was shown that for technical coatings the mean delamination rate is determined by the potential difference between the defect and the metal/polymer interface [33]. However, applying this modern technique, which demonstrates real advantages for the testing of polymer coatings, the detailed explanation of the effect of the potential, the oxygen reduction and the electrolyte composition has not been given so far, as all these factors, and diffusion processes as well, change during the experiment. It has been shown that the double layer is formed at the metal/polymer interface, inhibiting the incorporation of ions into the polymer [32]. Probably, the effect of the double layer can also be suggested from the side of the disbonded space, along the MPEI.

From our point of view, for judging the causes of the cathodic disbondment it is very important to answer the following questions. What is the role of each process or factor occurring along the MPEI in cathodic disbondment? Which of them are decisive in the adhesion loss for certain metal/polymer systems? Is the framework of the chemical paradigm for coating performance, widely used now [34], worth expanding? Obtaining and analyzing the experimental data, so as to try to find some answers to these questions, is the general idea of the present work.

2. APPROACH AND EXPERIMENTAL PROCEDURE

2.1. Approach and Equipment for the Study of the Cathodic Delamination

The main idea for the methodical approach worked out by us is to study the influence of only one factor on the disbondment process, such as substrate potential, electrolyte content, pH, *etc.*, when the others are fixed.

The express testing of the coating stability under the applied potential, worked out by Bagriy and Shapoval *et al.* [35, 36], is a method of choice. The scheme of the equipment previously developed is presented in Figure 2. Two important principles are laid on this basis: the polarization of the substrate with a constant potential and

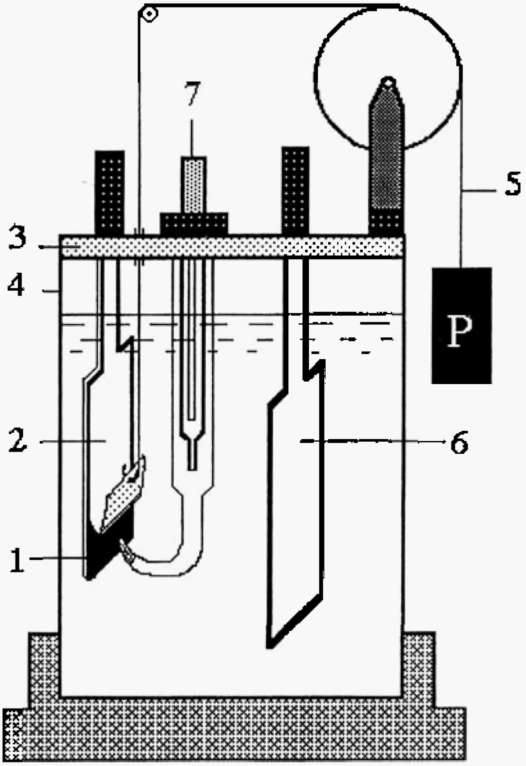


FIGURE 2 The cell used for the estimation of the cathodic disbondment rate. Elements: metal substrate (1); polymer coating (2); Teflon^{TM} lid with fastenings for the electrodes (3); glass cylinder (4); weight (5); carbon anode (6); reference electrode Ag/AgCl (7).

bending back of the lower edge of the delaminated film with a small constant force. Such a technique permits the setting and control of a number of factors which are important for the cathodic disbondment:

1. *The uniform polarization of the metal substrate* It has been shown [36] that the electrode potential near the MPEI is practically the same as applied to the specimen. Based on this, we accept, in the first approximation, that double layer parameters and rates of electrochemical reactions are the same both for a bare metal substrate freely contacted with electrolyte and near the MPEI [37], in spite of a superposition of double layers along the MPEI (Fig. 1).

2. *Practically a free migration of the electrolyte components towards the interface region* It allows one to consider the electrolyte composition at the interface and at the surface of the bare metal substrate as identical. As a consequence, we can accept with some approximation that the surface of the disbonded film withdrawn from the substrate is not affected by the electrochemical reaction products and conserves the transformations of the macromolecule fragments which occurred while adhesive contact was breaking [38].
3. *MPEI is well defined* Using the blocking layers (upper layer of the coating) if the thickness of the coating is not sufficient to avoid the migration of water and electrolyte components to metal/polymer interface through the coating.

In order to reach a more accurate control of experimental conditions a new cell (Fig. 3) was worked out. In this cell the cathodic space, where the specimen is fixed as a cathode, was separated with a porous glass filter from the anodic one to avoid anode reaction products having access to the interface.

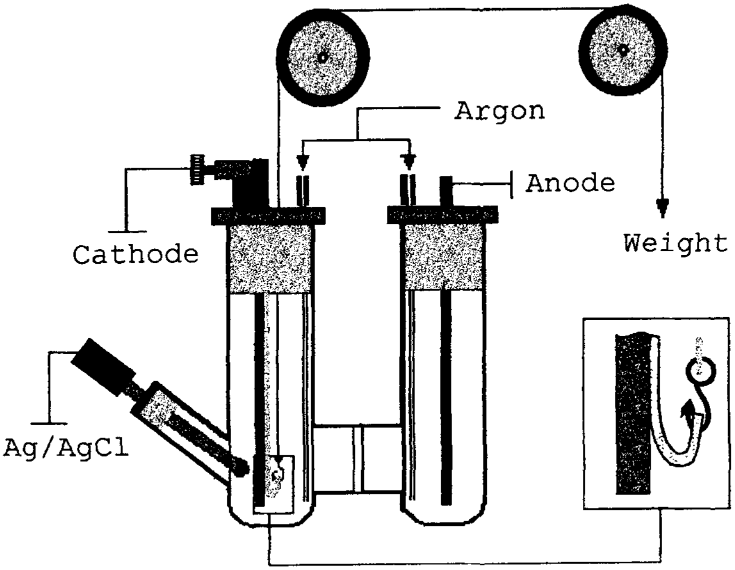


FIGURE 3 The modification of the cell shown in Figure 2.

The metal substrate was a mild steel plate with 5 cm^2 working area (5 × 1 cm). A butt-end sample of the same steel with Ø1.5 mm, pressed into a Teflon™ block, was used as a common electrode in voltammetric and impedance measurements. 0.5 and 0.1 M NaCl aqueous solutions were mainly used as electrolytes.

The bending mechanical force is specific for a particular polymer coating. Therefore, it was chosen by the test experiments where the following was taken into account:

- the force weight applied to the lower edge of the bent film should not provoke a mechanical disbondment of the coating, but it should be sufficient to provide free exchange of electrolyte components in the volume near the MPEI;
- the delamination rate even under double the weight should not change;

These criteria were used for choosing the bending force for each type of polymer coating. Once defined, this force was applied to the coating in all series of experiments.

The main advantage of the device described above is the possibility to study the influence of one particular factor, such as potential, electrolyte composition and pH, *etc.*, on the disbondment rate, when other conditions are fixed. Applying electrochemical and spectral methods we tried to study their role in cathodic disbondment.

2.2. Coatings

The coatings were prepared of ethylene-vinyl acetate copolymers containing 12 and 45% vinyl acetate groups (EVAC-12 and EVAC-45) of trademarks "Miravithen" and "Levapren", correspondingly, in addition to polyisoprene and poly(vinyl chloride). Selection of these polymers is based on their specific adhesion interaction with the steel substrate. The coatings of EVAC-12 and EVAC-45 were made from their films pressed on the substrate at 150°C at a pressure of 0.03 MPa during 30 min which resulted in a thickness of 0.6 mm. The polyisoprene coatings with the same thickness were made by casting from acetone/ethyl acetate (1 : 1) solution onto the substrate. Drying time was 3 hours (50°C). Poly(vinyl chloride) films were glued to the substrate with poly(vinyl chloride) solution in tetrahydrofuran. Drying out time was 6 hours (50°C) and the coating thicknesses were 0.2 and 0.6 mm. The bending mechanical forces determined for the cathodic disbondment experiments were 100 g/cm for the EVAC coatings, 20 g/cm for polyisoprene and 10 g/cm for poly(vinyl chloride).

2.3. Equipment and Methods

An investigation of the cathodic disbondment rate was carried out using the described equipment (Figs. 2 and 3). Potentiostat PI-50-1.1 (USSR) was employed to apply a potential. The time of the costing delamination from the tested space (5 × 1 cm) was used for determination of the delamination rate. The values of the cathodic disbondment time, used in the present work, mean the time of the delamination of the coating from the lower edge of the specimen along its testing space (5 cm). Averaged values from 5 tests for EVAC and polyisoprene coatings and from 5–7 tests for poly(vinyl chloride) coatings were obtained for the analysis.

For voltammetric and impedance measurements the electrochemical machine ECM-700 (DDR) was used with the standard electrochemical cell in 3-electrode mode. Impedance measurements were carried out at a working frequency of 1 KHz when potential scanning. The double layer capacitance has been estimated from impedance measurements taking into account the electrolyte resistance (in series) and the Faraday component (resistance in parallel). The values of electrode potentials for the data presented in this work are taken *vs.* Ag/AgCl reference electrode.

Surfaces of the delaminated polymer films were investigated by Infrared Spectroscopy in internal reflection using the spectrometer SPECORD M80 (DDR). The crystal KRS-5 (TlCl and TlBr) was used as an element for internal reflection. Four films delaminated in identical conditions were fixed at both sides of the crystal to get the spectrum. For every set of the polymer film, six spectra were obtained to be integrated. The integrated intensity of the bands was taken to be analyzed. The band at 1464 cm^{-1} corresponding to vibrations of the $—CH_2—$ group was used as the internal standard in the case of EVAC films and the band of the $CH_3—$ group (1376 cm^{-1}) was used for the polyisoprene films. The surface spectrum of poly(vinyl chloride) has no bands which can be chosen as an internal standard in our case.

For this reason the spectrum was recorded in the signal accumulation mode and the six separately obtained spectra were averaged for analysis. Therefore, absolute values of integrated band intensities were used.

3. RESULTS AND DISCUSSION

3.1. Effect of the Electric Double Layer

The effect of the double layer on cathodic disbondment was first suggested by Bagriy and Shapoval [39]. They used EVAC-12 as the coatings. Its adhesion interaction with the steel substrate is realized through acetate ester groups. Such a bond has a more donor-acceptor nature than an ionic bond. That makes it less sensitive to the pH change [40]. For these coatings, the cathodic disbondment rate strongly depends on the potential; but, at the same potential, tests in strongly alkaline and neutral electrolytes showed practically the same disbondment rate [39].

The data, obtained by us for the EVAC-45 (Tabs. I and II) testify that neither the presence of oxygen, nor high pH of the electrolyte, change the delamination time considerably. In which case, the strong effect of the potential remains a question. It is hardly possible to give a definitive answer based only on chemical concepts. There are three

TABLE I The effect of oxygen in the cathodic disbondment of the EVAC-45 coatings

Potential, V	*Cathodic disbondment time, min*	*Presence of O_2 (+)*
− 1.0	18 ± 1	+
	21 ± 1	−
− 1.2	2.6 ± 0.2	+
	2.7 ± 0.2	−

TABLE II The effects of pH and potential on the delamination time of the EVAC-45 coatings

pH ($c_{Na^+} = 0.1$ mole/L)	*Delamination time without substrate polarization, min.*	*Delamination time at $E = -1.2$ V, min*
6.8	190 ± 20	2.6 ± 0.2
14	150 ± 20	2.2 ± 0.2

previously-proposed suggestions which can be taken into account. The first is the double layer concept proposed by Bagriy and Shapoval [36, 39]. The second one is the attacking of the adhesion bonds by the intermediates of oxygen reduction such as H_2O_2, $OH^{\bullet}$, *etc.*, as was supposed by Stratmann *et al.* [31–33]. The possibility of the participation of the polymer fragments in the electrochemical reactions at the MPEI is also worth taking into account as one of the courses of the degradation of the metal/polymer interface [41, 42].

In order to verify the concept of the double layer, we find it reasonable to compare the dependencies of the disbondment rate of the EVAC coating and the double layer capacitance of the metal substrate on the main parameters defined by the disbondment process. We have obtained these dependencies for the EVAC-12 coatings with respect to the substrate potential (Fig. 4), electrolyte concentration (Fig. 5) and pH of the solution (Fig. 6). These data show that an increase of the double layer capacitance of the steel substrate correlates with a decrease of the disbondment time.

The role of the double layer parameters can also be demonstrated considering the influence of different cations. For the EVAC-12 coatings in the series of alkali metal cations from Li^+ to Cs^+ the

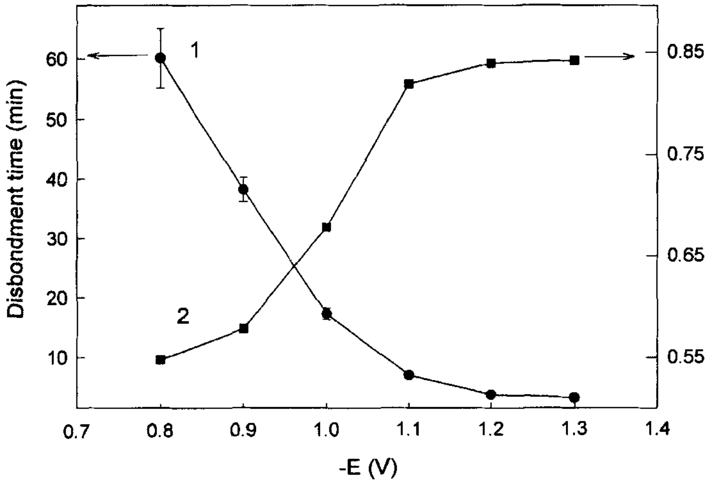


FIGURE 4 Dependence of cathodic disbondment time of the EVAC-12 films (1) and differential capacitance of the steel electrode (2) on potential in 0.1 mole/L NaCl.

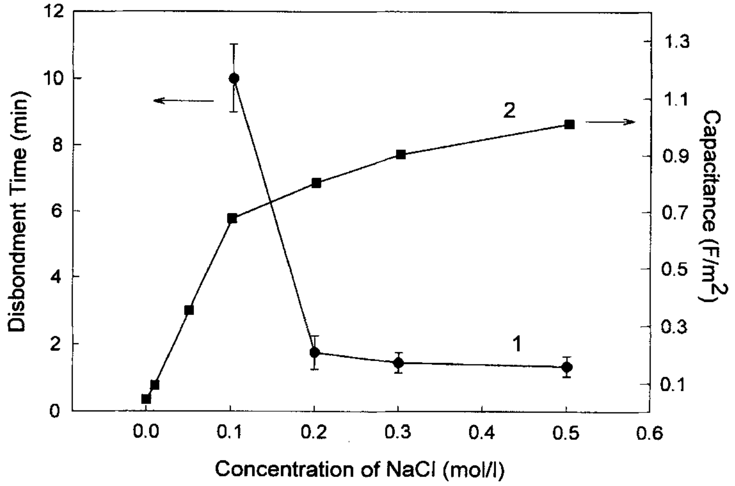


FIGURE 5 Dependence of cathodic disbondment time of the EVAC-12 films and differential capacitance of the steel electrode on the NaCl concentration at $E = -1.0$ V *vs.* Ag/AgCl.

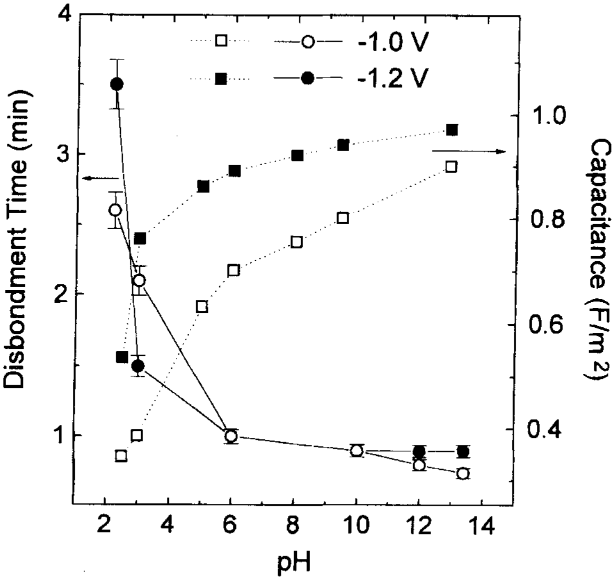


FIGURE 6 Dependence of the cathodic disbondment time of the EVAC-12 films and differential capacitance of the steel electrode on pH of electrolyte at $c_{Na^+} = 0.1$ mole/L.

delamination accelerates [37]. This fact was observed before [43], but it was explained in terms of the difference in the migration speed of the hydrated cations through the coating and the formation of the alkali medium with different alkali concentration under the coating [44–46]. The technique used by us permits exclusion of the migration and the concentration effects and makes this explanation deficient, at least for the conditions under our investigation. As the most appropriate parameter characterizing the cation influence we used a specific volume charge of the hydrated cation ($Q_{V(h)}$). The volume of the hydrated cation $V(h) = 4/3\pi R(h)^3$, where $R(h)$ is the hydrated cation radius and $Q_{V(h)} = ne/V(h)$, n is the cation charge and e is the elementary electron charge. As one can see from Figure 7 the $Q_{V(h)}$-delamination time dependence obtained by us is practically a straight

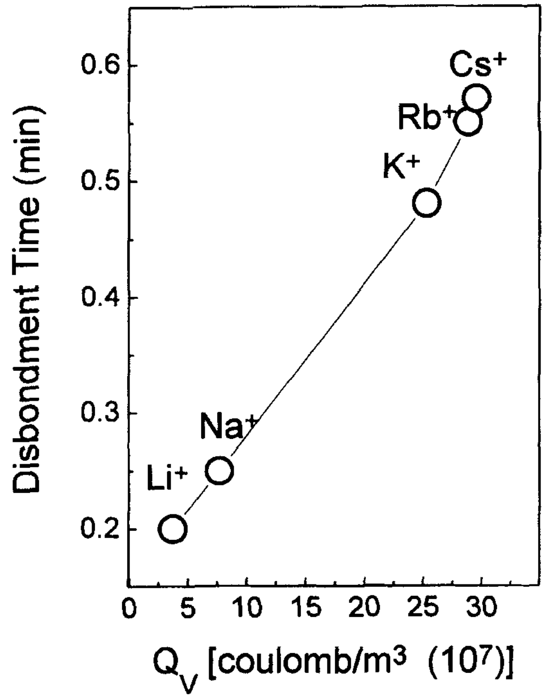


FIGURE 7 Dependence of the cathodic disbondment time of the EVAC-12 films on the specific volume charge density of the hydrated cation at the electrolyte concentration of 0.1 mole/L and substrate potential of – 1.0 V *vs.* Ag/AgCl. The values of the hydrated cation radii were taken from Ref. [47].

line. A similar dependence was observed for the sequence of cations Ca^{++}, Sr^{++} and Ba^{++} [37]. These dependencies suggest that the increase of $Q_{V(h)}$ of the cations and, correspondingly, a rise of electric intensity in the dense part of the double layer, lead to the augmentation of the cathodic disbondment rate, *i.e.*, the change in cations makes the effect close to that of the potential [39].

The manifestation of the double layer effect can also be expected in the following experiment. The steel substrate surface was modified with $[(C_{16}H_{33})(CH_3)N(C_2H_4OH)_2]I$ solution before the EVAC film pressing. This cationic surfactant, adsorbing at the cathodic potential region, displayed a desorption-adsorption effect which appeared in the double layer capacitance–potential curves [48]. We have found that this effect occurs in the case of the cathodic disbondment time dependence on the substrate potential as well (Fig. 8). In the potential regions, where the surface active compound is in the adsorbed state, the disbondment

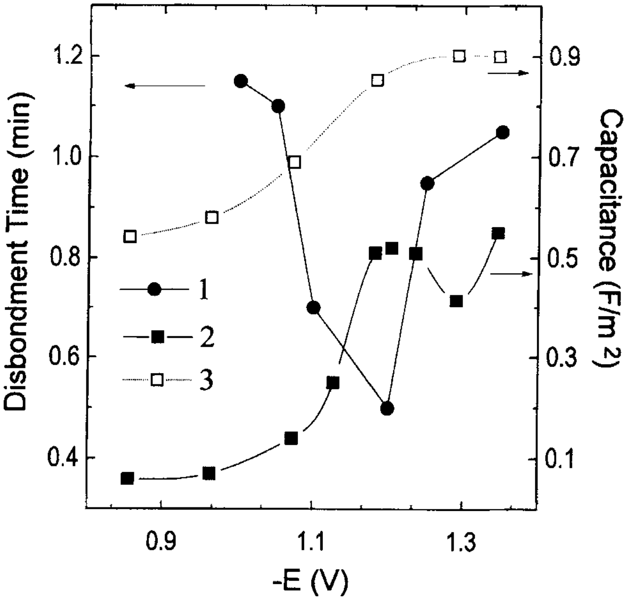


FIGURE 8 Dependence of the cathodic disbondment time of the EVAC-12 films from the steel substrate modified with $[(C_{16}H_{33})(CH_3)N(C_2H_4OH)_2]I$ solution (5×10^{-5} mole/L) on potential (1); the dependence of differential capacitance of the steel electrode on the potential in the presence of $[(C_{16}H_{33})(CH_3)N(C_2H_4OH)_2]I$ (5×10^{-5} mole/L NaCl) (2) and 0.1 mole/L NaCl (3).

process is decelerated; the increase of the double layer capacitance, because of the desorption process, corresponds to the decrease of the disbondment time. Such an influence of the surface active compounds is similar to the effect of potential and cations on the cathodic disbondment of the EVAC coating, described above. It is increasing or decreasing the charge density in the double layer. In the last case, this parameter is regulated by the presence of adsorbed organic compound.

It should be noticed that our observations have an approximate character; yet, because they do not take into account the possible difference in the double layer structure in the presence of different cations and surface active compounds, can also be reflected in the difference in the electrochemical reactions at the MPEI and in some distance from it. We are planning to study this in our next work. At the same time, the obtained experimental results gave us the grounds to support the existence of the double layer effect.

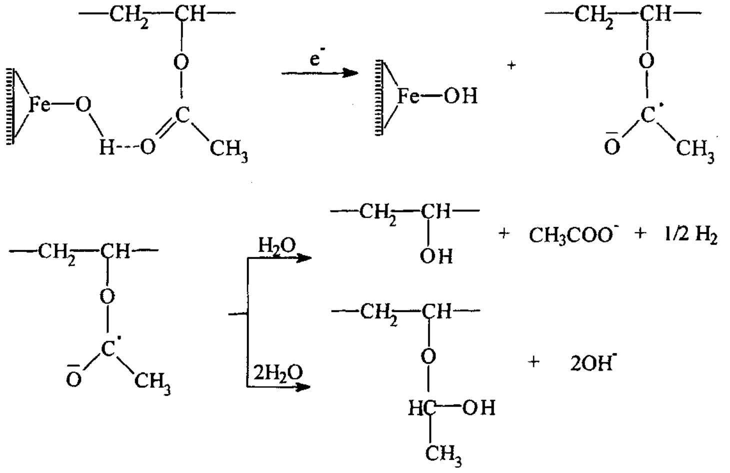
3.2. Effect of Electrochemical Reactions at the Interface

The cathodic disbondment is accompanied by metal corrosion and polymer coating degradation, as a rule. However, from our point of view, in the presence of both a conductive medium and a metal substrate cathodic polarization makes possible electrochemical reactions with participation of the adhesion bonds to be broken. This follows from the fact that solid phase polymers can accept electrons to be electrochemically degraded [41, 42]. In particular, the EVAC-45 film mechanically contacted with the grid cathode was transformed at the high cathodic potential (– 2.2 V *vs.* Ag/AgCl) during 5-hour electrolysis in both aprotic and water electrolytes, but EVAC-12 film was stable in these conditions [49]. Nevertheless, during the cathodic disbondment of the EVAC-12 films at the more positive potential (– 1.0 V *vs.* Ag/AgCl) perceptible change of the surface functional composition appeared to be detected by IR spectroscopy [50]. The participation of the EVAC acetate groups in electrochemical processes at rather low cathodic potential (– 1.0 V) along the interface was confirmed both for EVAC-12 and EVAC-45 films [51]. The IR data for the disbonded EVAC-45 films (Tab. III) illustrate an increase in the intensity of the absorption bands of O—H groups C—O groups and a decrease in bands of C=O and CH_3 groups. On the basis of detailed

TABLE III Infrared data for the EVAC-45 films disbonded from the steel substrate

Exposure of the films	*Band integrated intensities (normalized to —CH_2— band intensity at* 1464 *cm*$^{-1}$)			
	O—H (3600–3150 *cm*$^{-1}$)	*C=O* (1739 *cm*$^{-1}$)	—*CH_3* (1371 *cm*$^{-1}$)	*C—O* (1237 *cm*$^{-1}$)
Cathodic disbondment at − 1.0 V in 0.5 mole/L NaCl	0.84 ± 0.15	3.11 ± 0.05	1.72 ± 0.02	8.1 ± 0.2
Cathodic disbondment at − 1.2 V in 0.5 mole/L NaCl	0.63 ± 0.1	2.33 ± 0.05	1.36 ± 0.02	5.4 ± 0.2
Control (30 min exposure in 0.5 mole/L NaCl)	0.097 ± 0.02	3.60 ± 0.05	1.72 ± 0.01	5.9 ± 0.2
30-min exposure in alkali (pH = 14)	0.1 ± 0.02	3.60 ± 0.05	1.72 ± 0.01	5.9 ± 0.2
5-day exposure in alkali (pH = 14)	0.44 ± 0.2	2.80 ± 0.05	1.35 ± 0.02	5.6 ± 0.2

analysis made in Ref. [51] it was found that electron transfer to the acetate ester groups occurred and resulted in the formation of hydroxyl and hemiacetal groups instead of acetate ester ones. The mechanism of such transformations can probably be illustrated with the scheme:



The formation of conjugated C=C bonds in the macromolecular chain due to EVAC electrolysis [49] is absent here. However, for the conditions under investigation the potential rise and a higher vinyl acetate group content in EVAC make the transformations easier and probably can lead to an appearance of such bonds. From our viewpoint, the fact that the transformations proceed during the cathodic disbondment of the coating having adhesion bonds with the steel substrate testifies that these bonds and the action of the double layer field facilitate the electron transfer to the functional polymer groups.

There is an important question about the influence of the nature of the adhesion bonds on the electrochemical transformations of the polymer along the interface. For this reason the polyisoprene coatings also were investigated. IR data for the disbonded films testify that their surface functional composition is changeable, depending on the substrate potential and pH of the electrolyte (Tab. IV). Thus, the increase of the absorption bands of O—H and C=O groups, as well as the decrease of the bands of C=C bonds and the appearance of ionized carboxylic groups, are observed even at −0.85 V. For this potential, the direct electron transfer on the macromolecule would be last thing to expect, but the changes observed were absent for the polyisoprene coatings after their mechanical delaminating (Tab. IV).

Similar results were obtained by Kendig *et al.* [52] for the cathodic disbondment of polyimide films from an Al substrate. This cannot, also, be explained only by the chemical action of electrochemically-generated alkali. In order to understand such data we took into account the effect of the oxygen electrochemical reduction intermediates, particularly O_2^-, $OH^\bullet$, H_2O_2, as suggested by Stratmann [31–33]. Their presence on the cathodically-polarized metal can be fixed by differential pulse polarography [53, 54]. The action of the intermediates at the interface may explain the degradation of the polyisoprene C=C bonds and its other transformations at the low cathodic potential in accordance with such a scheme:

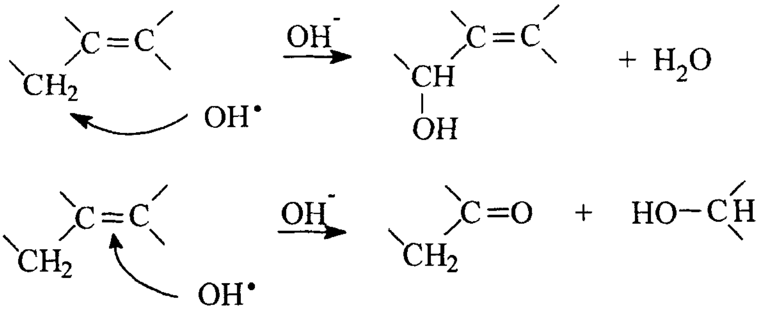
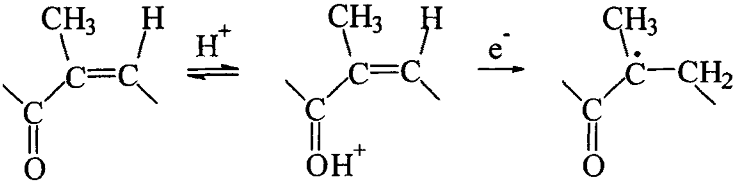


TABLE IV Infrared data for the polyisoprene films disbonded from the steel substrate (normalized to —CH_3 band inten

Disbonding mode	$3600-3100\ cm^{-1}$ $(O—H)$	$1700-1600\ cm^{-1}$ $(C{=}C)$	$1732\ cm^{-1}$ $(C{=}O)$	$1576\ cm^{-1}$ $(—COO)^{-}$ Fe^{2+}
Control	2.00 ± 0.1	0.97 ± 0.01	0.30 ± 0.02	–
Mechanical tearing off in 0.5 mole/L NaCl	2.25 ± 0.2	0.95 ± 0.02	0.32 ± 0.03	0.32 ± 0.
Cathodic disbondment at – 0.85 V (pH = 7)	2.40 ± 0.2	0.73 ± 0.03	0.86 ± 0.03	0.34 ± 0.01
Cathodic disbondment at –1.0 V (pH = 7)	2.77 ± 0.2	0.71 ± 0.03	0.96 ± 0.03	0.26 ± 0.01
Cathodic disbondment at –1.2 V (pH = 7)	3.15 ± 0.2	0.62 ± 0.02	0.95 ± 0.03	0.18 ± 0.01
Cathodic disbondment at –1.2 V (pH = 2.2)	2.16 ± 0.2	0.55 ± 0.2	0.90 ± 0.03	–

The high cathodic potential provokes more substantial transformations. In this case, direct electron transfer can be supposed. The adhesion bonds of polyisoprene with the steel substrate are mainly realized with C=O and —COO groups of the real polyisoprene macrochain [55, 56] and, therefore, electron transfer through C=O, as was the case for EVAC, can be suspected. Since the form $C=O^{\delta-}H^+$ is stable, the electron transferred localizes on the C=C bond [57, 58]. This process is easier in solution [57]. It agrees with the fact that the decrease in the intensity of the C=C IR bands after the disbondment is more considerable at pH = 2.2 than in neutral medium (Tab. IV). Moreover, the double band of the ionized carboxyl group disappears from the IR spectra (Fig. 9) when intensity of the C=C absorption becomes lower (Tab. IV). At the same time, the intensity of the C=O band for the films delaminated at – 1.2 V (*vs.* Ag/AgCl) decreases on going from neutral to acid media (Tab. IV). Taking into account these data it can be supposed that the direct electron transfer on polyisoprene occurs during the cathodic disbondment. This process proceeds more easily with the low value of pH that results in protonation of oxygen-containing groups, C=O, for example:



Further transformations of the radical lead to a break of the polymer chain as well as to C—C bond formation [58].

Thus, the surface electrochemical transformations of the polyisoprene film are quite considerable in affecting the adhesion loss. This agrees with the results of the cathodic disbondment test for the polyisoprene coatings at different potentials (Tab. V). Indeed, the deceleration of the cathodic disbondment in acidic media in comparison with the EVAC case (Fig. 6) is much less, especially for a potential of –1.2 V (Tab. V). However, it should be noted that, for high cathodic potentials, alkali media have a rather small effect both for polyisoprene and EVAC (Tab. V, Fig. 6). When the potential is not high, but sufficient for oxygen reduction the influence of the products of oxygen

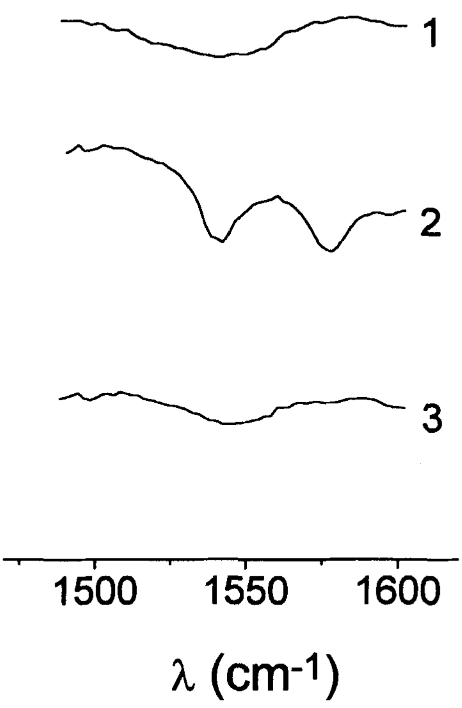


FIGURE 9 A fragment of the IR spectrum of polyisoprene: delaminated without cathodic polarization (1); after cathodic disbondment in 0.5 mole/L NaCl (pH = 6.8, $E = -1.0$ V *vs.* Ag/AgCl) (2); after cathodic disbondment in 0.5 mole/L NaCl with HCl (pH = 2.2, $E = -1.0$ V) (3).

TABLE V The dependence of the cathodic disbondment time of the polyisoprene films (min) on the substrate potential and pH of the electrolyte ($c_{Na^+} = 0.1$ mole/L)

	pH = 2.2	*pH* = 6.8	*pH* = 12	*Accuracy*
$E = -0.85$ V	49.0	30.0	28.0	±0.5
$E = -1.00$ V	15.5	6.2	5.5	±0.2
$E = -1.20$ V	3.2	3.0	2.3	±0.1

reduction can be considered as essentially zero and the cathodic disbondment of the polyisoprene coatings from steel can be analyzed in the framework of the widely-used concept [1–20], for example, in the work of Castle and Watts [17] for a steel/polybutadiene system, taking into account interpretations of Stratmann [31–33] concerning the influence of the active intermediates of the oxygen reduction.

In contrast to the above mentioned polymers, poly(vinyl chloride), having another type of adhesion bond with the metal substrate, shows unusual cathodic disbondment behavior. Thus, under cathodic polarization both the poly(vinyl chloride) coating adhesion and the cathodic disbondment time increase [59]. A similar effect of the increasing of adhesion strength was observed by Feliu *et al.* [60] for poly(vinyl chloride) paint exposed to humidity and UV radiation.

In order to understand the unusual PVC behavior we studied the effect of cathodic polarization on the adhesion strength of the PVC coatings. The latter was measured by a pull-off test after a certain time of cathodic polarization. The initial value of the adhesion strength considerably increases with polarization time (Fig. 10). For the thinner coating this effect is more pronounced. It is known that poly(vinyl chloride) film is permeable, especially in a potential gradient, to both water and electrolytes [61]. Therefore, for thin coatings the electrolyte coming through the coating can provoke the electrochemical modification of the polymer chains at the metal surface, which reinforces the adhesion effect occurring along MPEI.

Measuring the cathodic disbondment rate, we have found that the influence of the thickness is also considerable (Tab. VI). This also testifies to the occurrence of electrochemical processes at the metal/polymer interface resulting in an inhibition of the cathodic disbondment. Besides, the dependence of the delamination time on the substrate potential goes through a maximum around −1.1 and −1.2 V. During the exposure of the sample under the cathodic potential we can notice two processes: formation of the adhesion bonds and their degradation. The magnitude of the potential defines an equilibrium between them and, consequently the kinetics of the disbondment.

The following changes in IR spectra for the delaminated poly(vinyl chloride) films can be noticed (Fig. 11 and Tab. VII): the decrease of band intensities for the C—Cl bands ($644\,\mathrm{cm}^{-1}$) and —CH_2— groups ($1426\,\mathrm{cm}^{-1}$); the appearance of a band corresponding to C=C bonds ($1648\,\mathrm{cm}^{-1}$); the integrated intensity rising in the wide range of $3700-3100\,\mathrm{cm}^{-1}$ assigned to the —OH group absorption.

The transformation observed by us is very similar to the results obtained by Feliu *et al.* [60]. They showed by X-ray photoelectron spectroscopic study the increase of C—O, C=O and O—C=O functionalities and the decrease of hydrocarbon content at the steel/

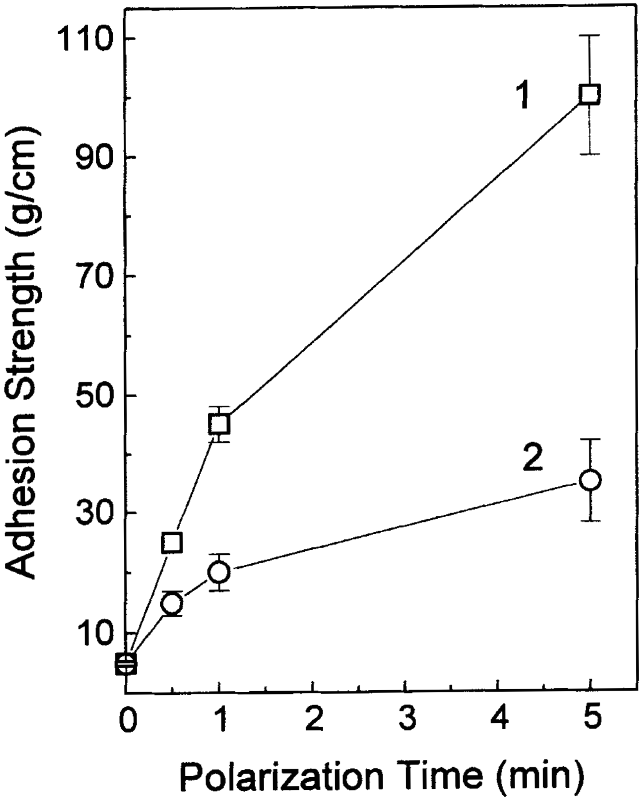


FIGURE 10 Dependence of the adhesion strength of the poly(vinyl chloride) coatings as a function of time of substrate polarization ($E = -1.2\,\mathrm{V}$ *vs.* Ag/AgCl) when the lower edge of the coating is bent back. Coating thickness is 0.2 mm (1) and 0.6 mm (2).

TABLE VI Dependence of the cathodic disbondment time of poly(vinyl chloride) coatings on potential in 0.1 mole/L NaCl (pH = 7)

Substrate potential, V	*Delamination time, min*	
	Coating thickness 0.2 *mm* (*averaging of* 5 *tests*)	*Coating thickness* 0.6 *mm* (*averaging of* 7 *tests*)
−0.9	50 ± 5	1.3 ± 0.1
−1.0	60 ± 5	1.5 ± 0.1
−1.1	80 ± 5	2.2 ± 0.1
−1.2	80 ± 5	2.7 ± 0.1
−1.3	70 ± 5	2.0 ± 0.1

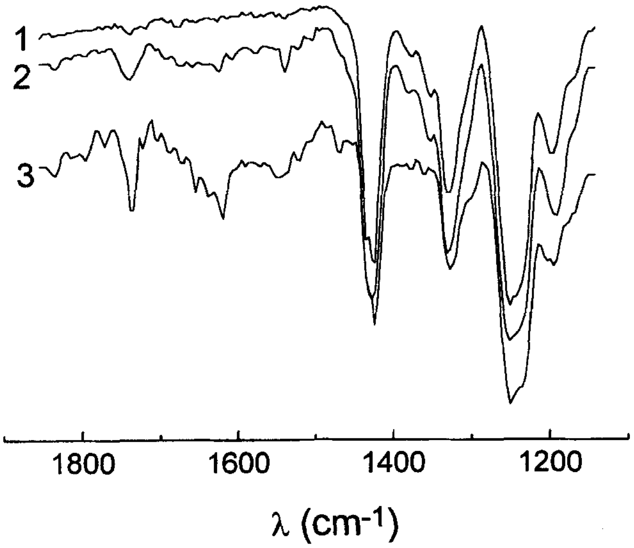


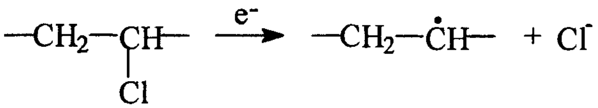
FIGURE 11 A fragment of the IR spectrum of poly(vinyl chloride) delaminated without cathodic polarization (1) and after cathodic disbondment at − 1.0 V (2) and − 1.2 V (*vs.* Ag/AgCl).

TABLE VII Infrared data for the poly(vinyl chloride) films disbonded from the steel substrate

Applied potential, V	*Integral intensity*			
	3700–3100 cm^{-1} (—OH)	1426 cm^{-1} (CH_2)	1330 cm^{-1} (CH_2)	684 cm^{-1} (C—Cl)
Mechanical tearing off in 0.5 mole/L NaCl	1.6 ± 0.05	5.0 ± 0.01	15.1 ± 0.05	16.4 ± 0.1
− 1.0	3.1 ± 0.1	4.9 ± 0.02	14.9 ± 0.1	16.2 ± 0.1
− 1.2	3.0 ± 0.1	4.0 ± 0.02	14.3 ± 0.1	15.6 ± 0.1
− 1.3	2.3 ± 0.1	3.5 ± 0.03	7.6 ± 0.1	14.1 ± 0.1

poly(vinyl chloride) interface after the influence of humidity and UV radiation.

Such changes in the poly(vinyl chloride) composition testify to the splitting off of the chlorine atoms as occurs in the electrochemical dehalogenation of poly(vinyl chloride) in aprotic media [62, 63]:



$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}- \xrightarrow{e^-} -CH_2-\overset{\bullet}{C}H- + Cl^-$$

This process is also catalyzed in the presence of iron [64]. Further transformations and reaction of short-lived radicals in the polymer chain with the water and oxygen results in the formation of C—O and C=O and COOH groups. It leads, obviously, to the formation of new adhesion bonds.

However complete loss of the adhesion is observed after long-time polarization at – 1.2 V (about 1 and 3 hours for the coatings of thickness 0.2 and 0.6 mm, respectively). Obviously, this is a result of more deep degradation of the interface layer because of degradation in the coating structure [4], interfacial failure [9] and oxide dissolution [8]. All these three mechanisms can be applied to the steel/PVC system under a strong cathodic potential, but it is difficult to say which one is the most important.

4. CONCLUSIONS

The investigation of the three different polymer coatings presented in this work shows the great importance of the nature of the adhesion bonds for the mechanism of the disbondment process. There are many possible factors of the cathodic disbondment and processes responsible for the degradation of the metal/polymer interface and the contribution of each of them to the adhesion loss can be very specific for a particular metal/polymer system. We realize that the presented experimental material is not sufficient either to stand up for a new concept or for the possibility to describe completely the processes at the MPEI. Nevertheless, some conclusions from this work would be very helpful for further investigation.

The proposed experimental technique permits one to investigate cathodic disbondment with control of the properties of a metal surface, polymer coatings and the electrolyte composition. This method can also be successfully applied for an estimation of the adhesion strength under the electrochemical conditions, as is testified to by preliminary experiments provided by us.

The role of the double layer in the cathodic disbondment of polymer coatings from a metal substrate can be very valuable, as in the case of the steel/EVAC system. Both the cathodic disbondment rate and double layer capacitance at the metal/electrolyte interface have similar dependencies on the substrate potential, electrolyte concentration, pH of the medium, *etc*. The increase of the charge density in the double layer can lead to an acceleration of the cathodic disbondment. We can expect great importance of the effect of the double layer for systems where the adhesion interaction has a mainly electrostatic and donor-acceptor nature. In order to estimate the influence of the double layer effect at the MPEI, we have to consider the superposition of the metal/polymer, the metal/electrolyte and the polymer/electrolyte double layers. Unfortunately, we have neither theoretical nor experimental backgrounds for this analysis.

The obtained data suggested that functional groups of the polymer coatings take part in electron transfer reactions at the metal/polymer/electrolyte interface at the potentials of cathodic protection (−0.85 to −1.3 V, *vs*. Ag/AgCl) in aqueous media. The adhesion bonds and the action of the electric field of the double layer can probably facilitate electron transfer to the functional polymer groups. This process, as well as the attack of the MPEI by the reactive intermediates of oxygen reduction, is obviously one of causes of the breaking of the adhesion bonds. In contrast to this, the exposure of the poly(vinyl chloride) coatings under the polarization resulted in formation of new oxygen-containing groups in the polymer chain leading to the appearance of adhesion bonds reinforcing the adhesion strength.

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