Layer formation by 1,7-diphosphono-heptane[*]

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Surface modification of polycrystalline ARMCO iron and an Fe(110) single crystal was performed using a solution of 1,7-diphosphono-heptane (DPH). The changes of the surface properties were studied by subtractively normalised interfacial Fourier transform infrared spectroscopy (SNIFTIRS), scanning tunneling microscopy (STM) and electrochemical impedance spectroscopy (EIS). The immersion of the surfaces into DPH solution resulted in a build up of an ordered thin multimolecular layer after a few hours of continuous adsorption. The orientation of the DPH molecules was influenced by the supporting electrolyte and the electrode potential. The treatment in the absence of oxygen resulted in a lower corrosion protection effect compared to diphosphonate layer formation in an atmospheric environment.

Keywords: adsorption, diphosphonate, EIS, self-assembling molecules, SNIFTRIS, STM.

INTRODUCTION

Over the last decade, research into thin film technology has attracted great interest due to the many technological advantages which are based on the properties exhibited by such films. For example, these films provide an easy way to change surface properties and, as a consequence, to find potential applications in the area of microelectronics, optics, sensors, implants and corrosion protection.[1] One method of producing such films is the self-assembly technique.

Self-assembled monolayers (SAMs) are ordered molecular assemblies formed by the spontaneous adsorption of molecules onto a solid support surface.[2] Molecules that are able to form assembled layers have amphiphilic characters, *i.e.,* these molecules have a small hydrophilic (carboxylic, sulphonic or phosphonic groups *etc*.) and a large hydrophobic (in most cases alkyl, aralkyl) part. Their solubility depends on the number of ionic groups and the length of the alkyl moiety.

Compared to conventional surface modifying techniques, self-assembly is a much easier and more economical way to build 2D structures. Most of the self-asse-

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[*] Dedicated to Professor Dragutin M. Dražić on the occasion of his 70th birthday.

mbly studies were carried out on noble metals or other surfaces,[3] but, due to potential applications in corrosion prevention, investigations of more active metals, like iron, copper, and aluminium, have great importance, too.

Many reports have been published on alkyltiol-based SAMs. The formation of a hydrophobic film as a result of the adsorption of alkylthiols on copper[4–7] and iron [8,9] surfaces have also been shown to hinder the dissolution of the metal. In spite of the good corrosion efficiency, the industrial application of thiol-compounds is limited due to their toxicity. Only few attempts have been made to examine non-toxic or environmental-friendly self-assembling materials for corrosion protection.[10,11] Compounds with a phosphonic functional group are considered to be the most effective chemicals for inhibiting corrosion processes and it is well known that short-chain substituted phosphonic acids are good corrosion inhibitors for iron and low-alloyed steels.[12]

Increasing the alkyl-chain length of the phosphonic acids results in hydrophobic intermolecular interactions and, as a consequence, an ordering effect is expected during the adsorption of the inhibitor on the metal surface. Previous investigations by electrochemical impedance spectroscopy (EIS) of the corrosion inhibition efficiency of α, ω-diphosphonic acids as a function of carbon-chain length revealed an optimal effect of 1,7-diphosphonic acids (DPH).[13,14]

In the present study, subtractively normalised interfacial Fourier transform infrared spectroscopy (SNIFTIRS), scanning tunnelling microscopy (STM), and further electrochemical impedance spectroscopy were used to examine the adsorption of 1,7-diphosphono-heptane on polycrysalline iron (ARMCO iron) and Fe(110) single crystal surfaces.

<div align="center">EXPERIMENTAL</div>

1,7-diphosphono-heptane was prepared from 1,7-dibromo-heptane and triethyl phosphite by the Michaelis-Arbusov reaction.[15] SAMs on pure iron were deposited from a solution of 10^{-3} M DPH in 0.1 M and 0.01 M $NaClO_4$ (Fluka, p.a.) or purified water (Milli-Q). The influence of the electrolyte on the adsorption properties was investigated by EIS and SNIFTIRS in 10^{-3} M DPH solution in the presence and absence of percholorate ions. The pH of the solution was adjusted to 7.0 using a sodium hydroxide solution (Reanal).

For the electrochemical and SNIFTIRS measurements, the working electrode was polycrystalline ARMCO iron (Fe: 99.8 %, O: 0.03 %, Mn: 0.03 %, N: 0.018 %, S: 0.018 %, C: 0.012 %, P: 0.004 %, Si: 0.002 %). STM experiments were performed on Fe(110) single crystal. The samples were first polished with emery paper (SiC with 600–2000), and then further polished with successively finer grades of alumina powder or diamond paste (down to 0.05 μm). After each polishing step the electrodes were cleaned in an ultrasonic bath. For STM studies, the samples were also polished electrochemically.

Electrochemical measurements were carried out in a three-electrode cell (≈ 500 cm^3) under an argon atmosphere using an IM5d Impedance Spectrum Analyzer (Zahner Elektrik). A half-cylindrical platinum plate (90 cm^2) was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The surface morphology of the sample, which was influenced by the adsorption process, was monitored by *in situ* Scanning Tunneling Microscopy (STM) using a PicoSPM (Molecular Imaging). All the STM measurements were carried out at room temperature inside a glove box filled with argon.
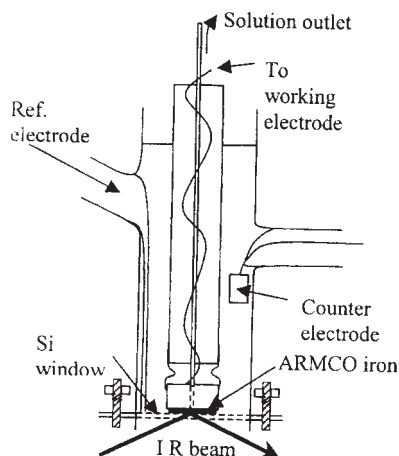
Fig. 1. Schematic view of the cell for SNIFTIRS.

SNIFTIRS was used to examine the adsorption and orientational changes of the SAMs. SNIFTIRS experiments were carried out using a fully evacuated Bruker IFS-113v spectrometer fitted with a *p*-polariser and equipped with a mercury-cadmium-telluride (MCT) detector (cooled to 77 K, using liquid nitrogen). 400 interferograms were collected at each timepoint. The spectral resolution was 4 cm^{-1}. The electrochemical control was accomplished using a Hi-Tek DT-2101 potentiostat.

A schematic diagram of the flow cell used in this work, which has already been described in the literature,[16] is shown in Fig. 1. A small hole (0.5 mm diameter) was drilled in the centre of a flat disc electrode (10 mm diameter) to construct the flow cell. In this case the counter electrode was a platinum plate with an area of $\approx$ 24 mm^2. The reference electrode was a saturated calomel electrode (SCE) and all the potentials are quoted relative to this reference electrode.

The time dependence of DPH layer formation and orientation was investigated. The spectra were calculated as $(R_{t1} - R_{t0}) / R_{t0}$ where R_{t1} and R_{t0} are the reflectance of the electrode at the sampling time and at the reference time (beginning at the measurement), respectively. Taking into account this sign convention, downward (or negative) going bands correspond to increased absorbance with time, whereas upward (or positive) going bands represent decreased absorbance with time. In the case of SAMs, an increase of the absorbance may arise from the reorientation of the monolayer at the surface, enabling different vibrational modes to be excited, with the *p*-polarised radiation.[17]

RESULTS AND DISCUSSION

Vibrational modes of DPH

The frequencies, relative intensities, and shapes of infrared absorption bands may be used for the qualitative characterisation of molecules. The spectrum of 1,7-diphosphono-heptane, which was recorded in the solid phase (KBr disc), is shown in Fig. 2. Table I shows the characteristic vibrational frequencies of DPH and their assignments.

TABLE I. Vibration frequencies of DPH

Functional groups	Measured band/cm^{-1}	Regions in the literature/cm^{-1}	Type of vibration
> POOH	1127	1335–1080	P=O stretching
	(941), 960, (979), (1010)	1040–910	P–O stretching
	533	540–450	P–O stretching

TABLE I. Cont.

Functional groups	Measured band/cm^{-1}	Regions in the literature/cm^{-1}	Type of vibration
P–CH$_2$–	1410	1440–1405	CH$_2$ deformation
	786	780–760	P–C stretching
–CH$_2$–	2932, 2907	2940–2915	Asymmetric vibr.
	2845	2870–2840	Symmetric vibr.
	1466	1480–1440	Scissor vibr.
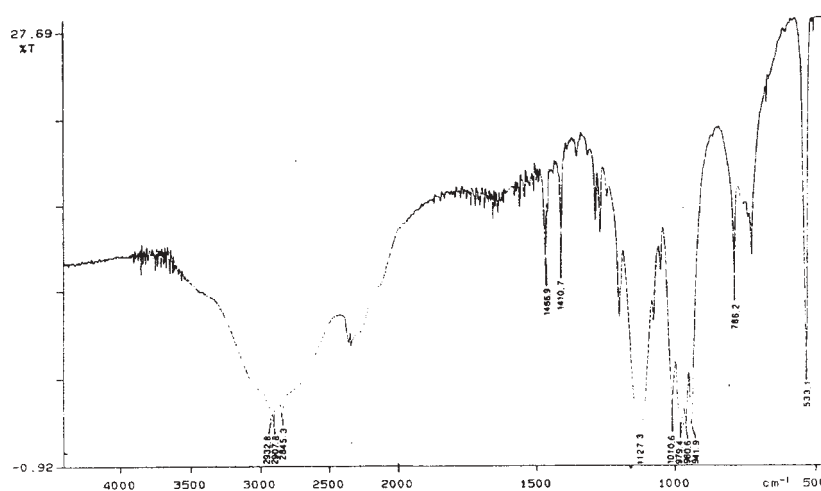
Fig. 2. Spectrum of 1.7-diphosphono-heptane in the solid phase (KBr disc).

Table I clearly shows that the vibrational frequencies reported here are very similar to those qiven in the literature.[18]

The effect of supporting electrolyte

Adsorption measurements were carried out in 1,7-diphosphono-heptane solution both with and without NaClO$_4$ in order to detect the effect of the electrolyte. Perchlorate ions also adsorb onto the surface and, even though it is quite weak, this adsorption could influence the formation and ordering of the DPH film.

The SNIFTIRS spectra recorded in 10^{-3} M DPH/0.1 M NaClO$_4$ solution exhibit changes in two main spectral regions, where characteristic bands of the phosphonate compound can be observed (Fig. 3).

In the region 1350 cm^{-1} – 910 cm^{-1}, the stretching modes of P–O and P=O are detected at 987 cm^{-1} and 1084 cm^{-1}, respectively. The band intensities increase continuously and uniformly with time, which points to a continuous, monotone adsorption (Fig. 4a). The concurrent growth of the bands may indicate an already oriented adsorbed layer after an hour. The two P–O and one P=O bond per molecule could give a constant difference between the intesities, if:
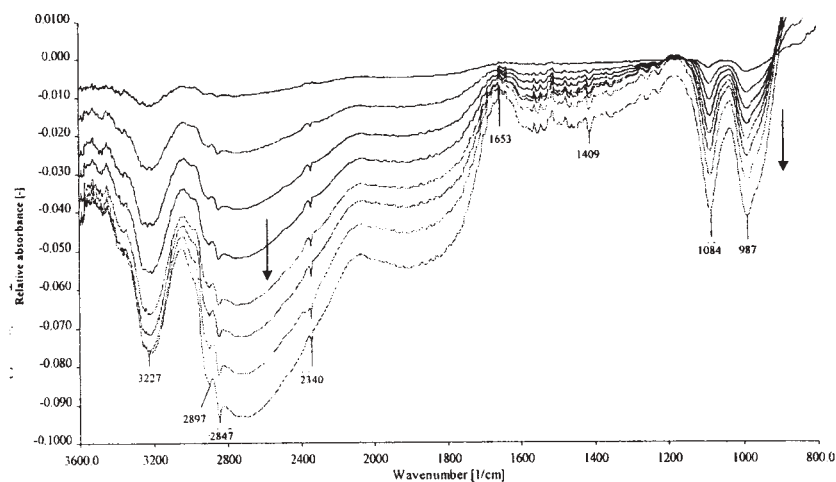
Fig. 3. Normalised spectra of 1.7-diphosphono-heptane in 0.1 M NaClO$_4$ (time increase: 20 min – marked by arrow, the first curve: 10 min).

– the molecules are well ordered in the film with a constant orientation angle or

– the molecules are ordered well in domains, in which the direction of orientation is constant.

In the latter case, the spectrum would shows an average of the orientation. However, the presence of methylenic symmetric and asymmetric vibrations points towards an ordered structure.

In the region of 2940 – 2840 cm^{-1}, the C–H symmetric and asymmetric stretching vibrations at 2847 cm^{-1} and 2897 cm^{-1}, respectively, can be observed. The intensity changes of these bands are the consequences of a continuously increasing and ordered adsorption (Fig. 4b). The appearance of these vibrations indicates that the methylenic groups possess dipole moments which have a vector perpendicular to the surface, implying that the chains are either perpendicular to the surface or slightly tilted.
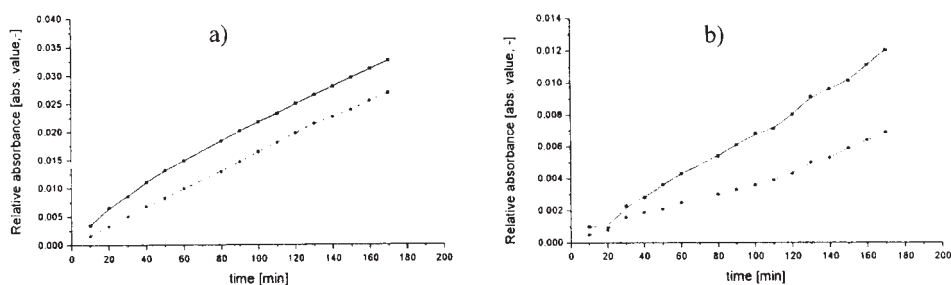

Fig. 4. Changes of band intensities as a function of time in 10^{-3} M DPH solution with 0.1 M NaClO$_4$: a) in the (–) PO$_3$H$_2$ group: (■) at 987 cm^{-1} (P–O stretching) and (●) at 1084 cm^{-1} (P=O stretching); b) in the carbon chain: (■) at 2923 cm^{-1} (–CH$_2$–asymmetric vibr.) and (●) at 2848 cm^{-1} (–CH$_2$– symmetric vibr.).
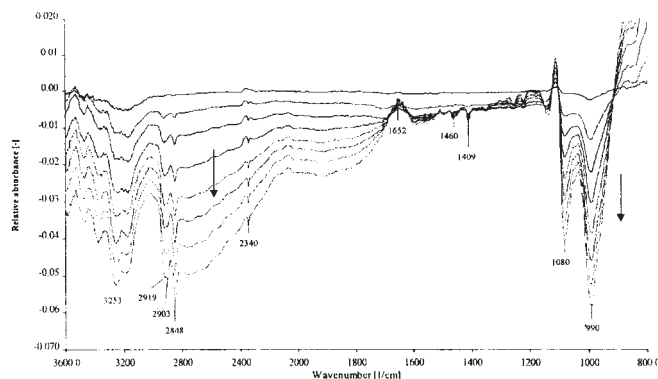
Fig. 5. Normalised spectra of 1.7-diphosphono-heptane without NaClO$_4$ (time increase: 20 min – marked by arrow, the first curve: 10 min).

The baseline shift above 1200 cm^{-1} may be due to a change in reflectance of the surface brought about by the adsorption of the DPH. This may indicate that the adsorption changes the electronic structure at the surface.

Figure 5 shows the normalised spectra of 1,7-diphosphono-heptane adsorption in the absence of perchlorate.

The growth of the symmetrical peaks at 987 and 1084 cm^{-1} measured in perchlorate solution became asymmetrical. The peak position and the peak ratio change compared to the perchlorate containing solution. The P=O stretching band is shifted towards lower wavenumbers (1080 cm^{-1}), whereas the P–O stretching band is shifted towards higher wavenumbers (990 cm^{-1}). However, the continuous increase in the intensity of the absorption bands is similar to the previous case (Fig. 6).
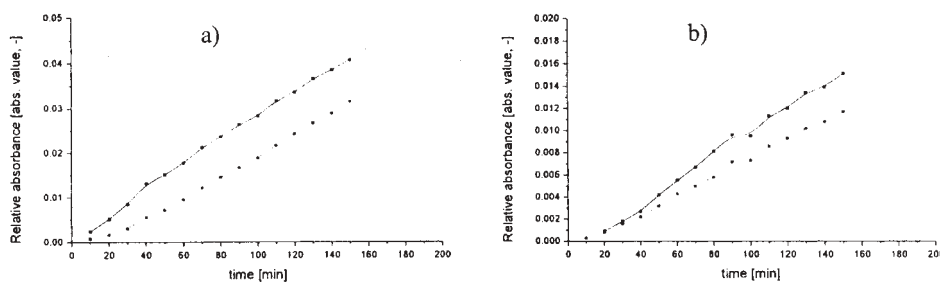

Fig. 6. Changes of band intensities as a function of time in 10^{-3} M DPH solution without perchlorate: a) in the (–) PO$_3$H$_2$ group: (■) at 990 cm^{-1} (P–O streching) and (●) at 1080 cm^{-1} (P=O stretching); b) in the carbon chain: (■) at 2919 cm^{-1} (–CH$_2$– asymmetric vibr.) and (●) at 2848 cm^{-1} (–CH$_2$– symmetric vibr.).

The most important change is that the difference of the band intensities has increases in the P–O (P=O) region (Fig. 7). The intensity changes could be taken to imply that the molecules are bonded more "asymmetrically", mainly across the P–O groups (and less across the P=O groups). The relatively higher intensity of the 990 cm^{-1} absorption indicates a smaller angle between the bond-direction-vector (Fe–O–P axis) and the normal to the surface. This kind of bonding is due to the tilting of the DPH molecules.

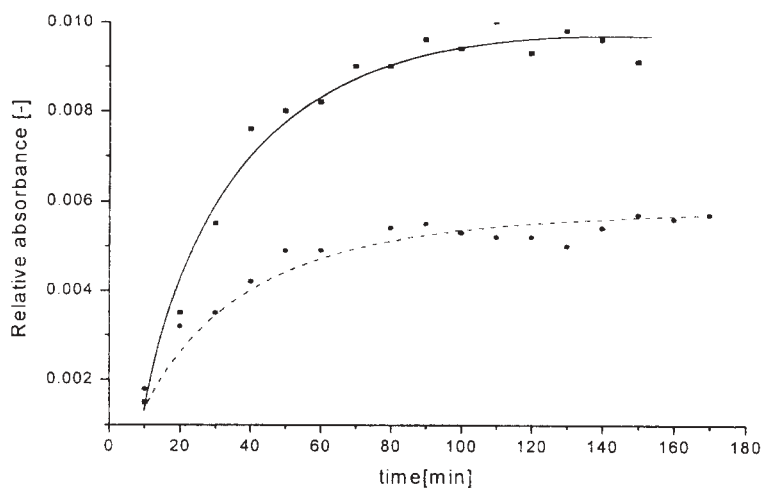Fig. 7. Intensity difference between the P–O stretching and the P=O stretching band (($\blacksquare$) without NaClO$_4$ and ($\bullet$) with NaClO$_4$) as a function of time.

Previous electrochemical investigations revealed that DPH – above a critical concentration – can be regarded as an anodic inhibitor.[19] The polarisation resistance of DPH layer was medium high in the presence of 0.1 M NaClO$_4$ (7–9 kΩ cm^2).

EIS measurements revealed a change of the polarisation resistance and corrosion potential in the presence of 10^{-3} M 1,7-diphosphono-heptane with and without 0.01 M NaClO$_4$ (Fig. 8).
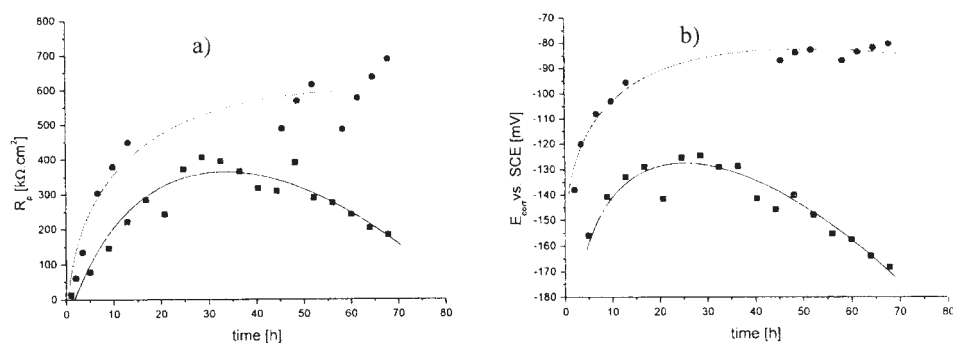

Fig. 8. a) Polarisation resistance and b) corrosion potential of ARMCO iron as a function of immersion time in a solution of 10^{-3} M DPH in the presence of oxygen. (($\blacksquare$) in 0.01 M NaClO$_4$, ($\bullet$) in blank solution).

A spontaneous formation of a protective layer took place both in the perchlorate-free and 0.01 M perchlorate containing solution. After the first hour, the R_p values in both cases exceed the values obtained in solutions containing higher concentrations of perchlorate ions. The polarization resistance values increase in time reaching their maximal values of 600 kΩ cm^2 in perchlorate-free solution and 400 kΩ cm^2 in the pres-

ence of 0.01 M NaClO$_4$. These values are two order of magnitude higher than those obtained in a 0.1 M NaClO$_4$ solution. The increase of polarization resistance with increasing adsorption time is probably related to the organisation process of the organic film. A long-term protection was obtained in perchlorate-free solution, whereas the maximal protection was observed between 20 – 40 h in the presence of 0.01 M NaClO$_4$. It is also obvious that the presence of perchlorate salt results in a deterioration of the protective layer after longer immersion times. After 2 days of immersion, corrosion spots appear on the iron surface, which are due to the perchlorate ions present in the solution.

The high polarisation resistance values, and slow layer formation observed by EIS measurements are in agreement with the results obtained for other self-assembling processes. The different growth tendency of R_p value in the presence of perchlorate compared to the distilled water indicate that perchlorate ions could hinder the layer formation of DPH. The decrease of R_p after 30 h refers that perchlorate ions build into the layer. Perchlorate ions change the structure of the DPH layer.

Influence of potential on DPH adsorption

The layer formation of DPH is influenced by the chemical quality of the surface - *e.g.* oxidation state, oxide layer thickness and structure, *etc.* DPH molecules prefer the oxidised sites during adsorption. Otherwise phosphono compounds form insoluble complexes at the anodic sites of a metal surface.[20] The properties of the iron surface change during polarisation of the sample. The surface is rich in oxygen at anodic potentials (Fig. 9a–b) and oxygen depleted at cathodic potentials (Fig. 9c–d).
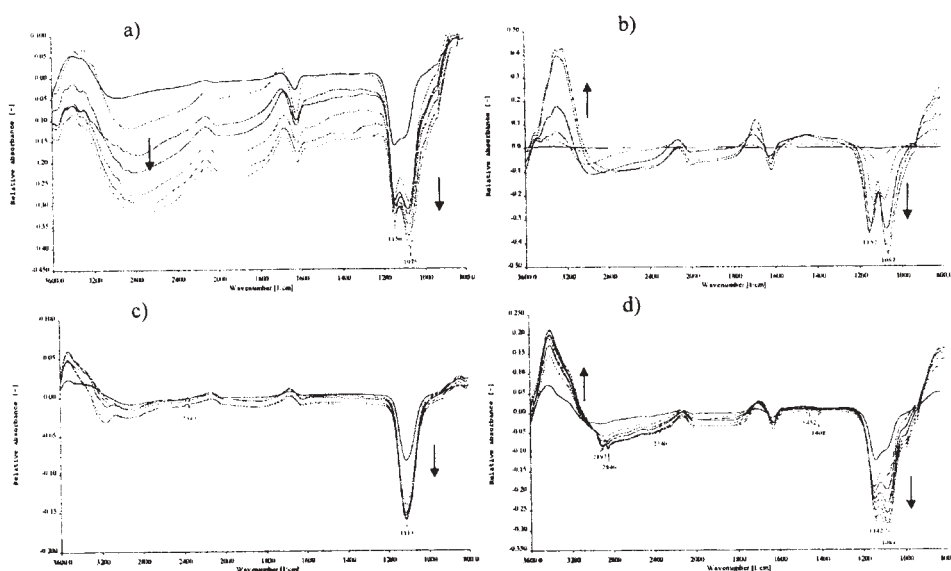

Fig. 9. Normalised spectra of 1.7-diphosphono-heptane in 0.1 M NaClO$_4$ (time increase: 20 min – marked by arrow, the first curve: 10 min); a) +500 mV, b) 0 mV, c) –500 mV, –1000 mV, *vs.* SCE.

SNIFTIRS measurements show that the band intensities in the polarisation experiments exceed the obtained OCP intensities, which is an indication of strong multimolecular adsorption. A thick disordered layer was formed on the iron surface. During the first period of the adsorption, the P=O stretching signal was dominant, later the P–O stretching became more important, but the transition between these two "states" was not supported by a significantly increasing character. The absence of –CH$_2$– vibration bands supports the theory of "disordering" and "thick layer formation". The only exception was observed at –1000 mV (Fig. 9d), when a longer distance ordering in the vertical direction is presumed.

Investigation of the DPH surface pattern in the absence of oxygen

For practical applications, experiments in an aerate solutions are important but these measurements gave no information about the structure of the SAM. This was the consequence of iron oxide formation in the presence of the highly reactive iron surface. *In situ* high-resolution STM – demand conducting surfaces, so oxide formation should be avoided by applying inert conditions (*e.g.,* purification of the solution with argon). Therefore the behaviour of DPH in the absence of oxygen was studied by EIS and STM.

The polarisation resistance of the ARMCO iron was monitored by EIS. The experiments were performed in a neutral solution of 10^{-3} M 1,7-diphosphono-heptane in the presence of 0.1 M NaClO$_4$. The solution was purged with argon (for 30 min) before each measurement. Figures 10 and 11 show a moderate influence of DPH on the corrosion. The compound inhibits the dissolution only for a few hours, when the inhibition effect is about 50 %. This fact confirms the hypothesis, which supposes the formation of an oxide-phosphonate complex as the preventing layer.

In situ STM measurements on SAMs of DPH grown in an argon atmosphere at room temperature were also carried out. The DPH was adsorbed onto the iron-oxi-
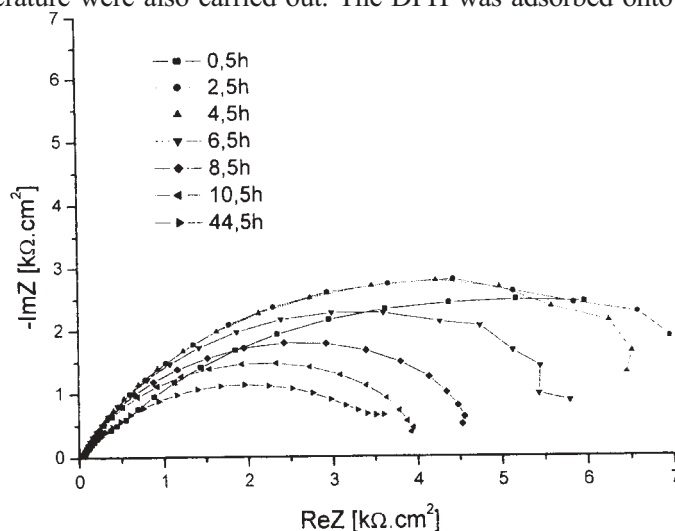

Fig. 10. EIS spectrum of ARMCO iron in a neutral solution of 10^{-3} M DPH and 0.1 M NaClO$_4$ (purged with Ar(3.5)).
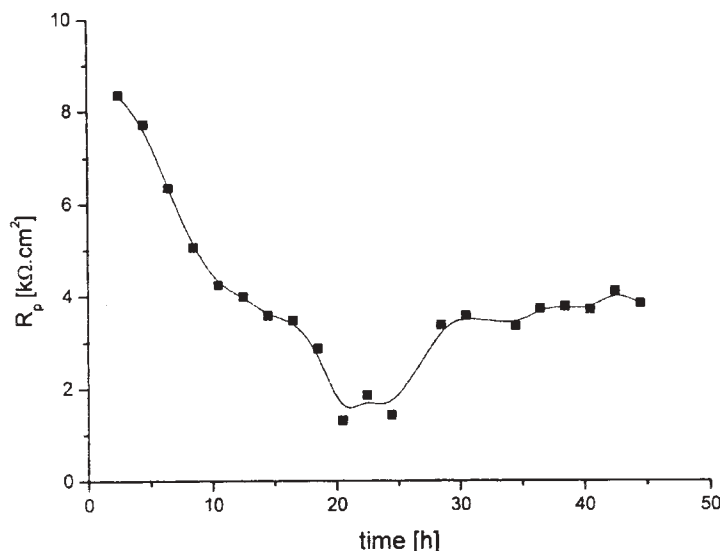
Fig. 11. Polarisation resistance of ARMCO iron as a function of immersion time in a solution of 10^{-3} M DPH in the presence of 0.1 M NaClO$_4$ (purged with Ar(3.5)).

de/hydroxide surface in multimolecular layers. The upper layer, visualised by STM, showed a disordered structure. In an argon atmosphere, the oxidation of iron is slow (Fig. 12a), therefore the formation of the first layer was recorded without any problem. After 45–50 minutes, the surface showed characteristic patterns with two dominant perpendicular orientations that were about several thousands Å in length, several hyndred Å in width and 10–20 Å in average height (Fig. 12b – d). The structure of the films was not stable in time. The surface pattern started to disrupt after 60 min. The orientations were lost and the surface formations showed a more globular, oxide like structure (Fig. 12e).

CONCLUSION

It was shown that thin multimolecular layers of 1,7-diphosphono-heptane are formed on an iron surface. The SNIFTIRS measurements showed continuous adsorption on the iron surface, without saturation even after 2–3 hours. The bond orientation of the phosphonate group depends on the media. The characteristics of adsorption and the properties of the layers strongly depend on the electrode potential. At open circuit potential, a less thick and more ordered layer forms. It is supposed that a stronger adsorption process takes place at other potentials, which results in a thicker layer.

The features revealed by STM measurements show well observable orientations of 1,7-diphosphono-heptane on the iron surface after less then one-hour. The observable ordering is decreasng with time probably due to slow oxidation of iron surface. On the other hand electrochemical measurements have shown the increased protecting effect of 1,7-diphosphono-heptane in the presence of oxygen, which can be explained by the phosphono-oxo-complex formation.
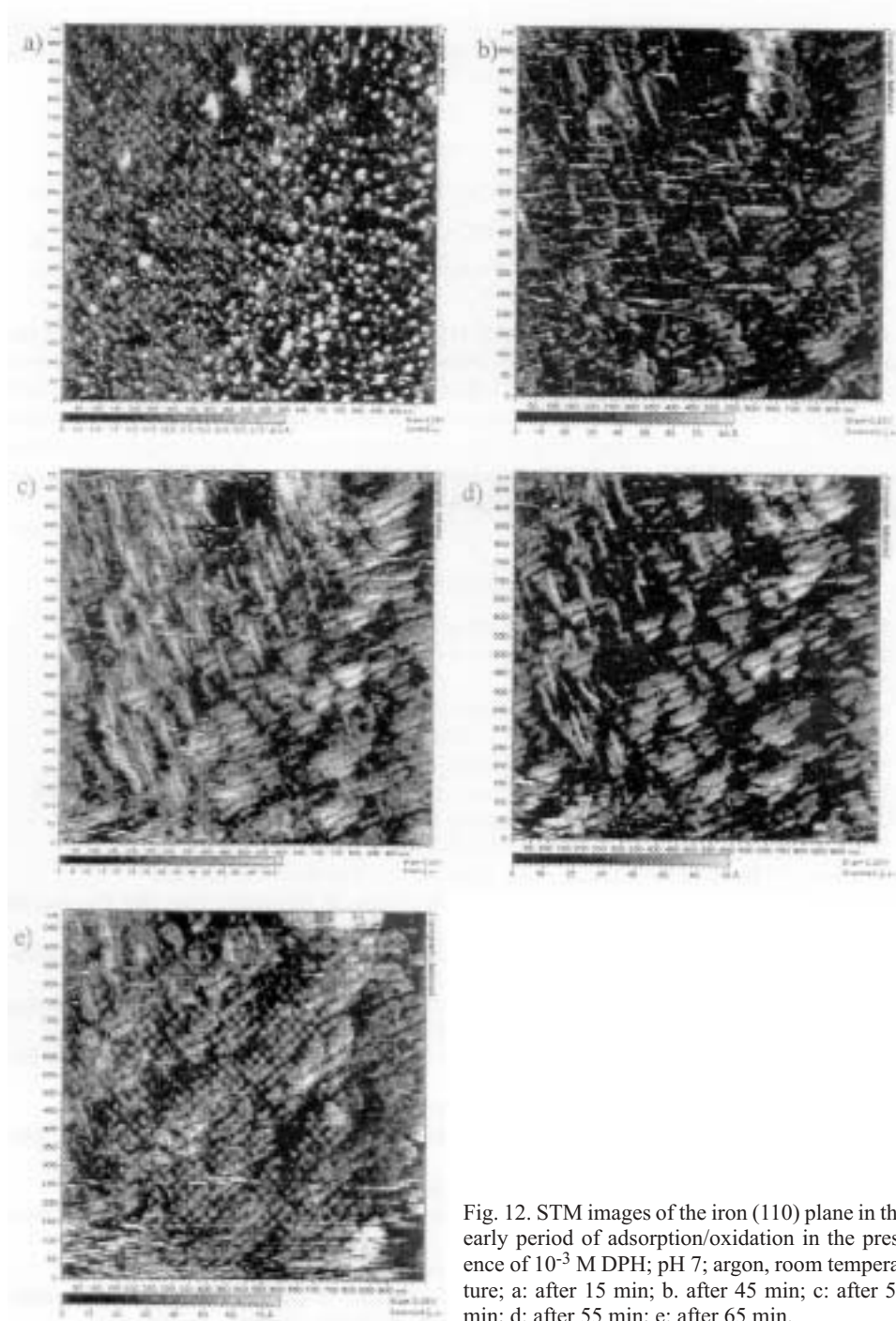
Fig. 12. STM images of the iron (110) plane in the early period of adsorption/oxidation in the presence of 10^{-3} M DPH; pH 7; argon, room temperature; a: after 15 min; b. after 45 min; c: after 50 min; d: after 55 min; e: after 65 min.

И З В О Д

ФОРМИРАЊЕ СЛОЈА 1,7-ДИФОСФОНО-ХЕПТАНА

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Површине поликристалног ARMCO гвожђа и Fe(110) монокристала модификоване су у раствору 1,7-дифосфоно-хептана (DPH). Промене особина површине проучаване су техникама SNIFTIRS, STM и SEI. Током излагања површине дејству DPH формирао се уређени мултимолекулски слој после неколико сати континуелне адсорпције. На оријентацију DPH молекула утиче основни електролит и потенцијал електроде. Третман у одсуству кисеоника резултовао је слабијим ефектом заштите од корозије у поређењу са дифосфонатним слојем формираним у атмосферским условима.

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