Contribution of Raman Spectroscopy to the Comprehension of Limiting Phenomena Occurring with a Vinylpyridinium Anion Exchange Membrane during the Electrolysis of Cr(VI) Solutions

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Limiting phenomena occur during the recovery of chromic acid solutions by electrodialysis using a poly(4-vinylpyridinium) anion exchange membrane (AEM). An increase of the cell electrical resistance appears as the current is applied. As for other AEMs, the inner acid concentration is very high compared to that of the equilibrating solution. Raman spectroscopy shows the presence of polychromate ions. Moreover, a competition takes place between the dichromate ions and the poly(4-vinylpyridinium) exchange sites toward protons. The deprotonation of the sites and the very low mobility of the polychromate counterions explain the increase of the electrical resistance.

1. Introduction

The treatment of spent acids containing heavy metals represents a major environmental issue, affecting every industrialized country in the world.[1−4] These toxic effluents are generated by a number of industrial processes, such as steel treatment, metal refining (zinc and copper), pigment production (titanium), surface treatment (chromium and nickel), and chemical production (alkylation and catalysts).

Chromic acid is widely used for the electroplating of chromium on various substances in order to obtain a corrosion-resistant surface.[5] The process generates effluents that still contain anionic chromic species. Other anionic and cationic species may be also present. Hexavalent chromium, Cr(VI), is one of the most toxic materials discharged in the environment.[6] In the United States, many local water districts require the chromium discharge level to be virtually zero.[7] Owing to the solubility and high toxicity of the Cr(VI) oxo anions, the effluents are submitted to a chemical reduction that converts the Cr(VI) oxo anions to the inert Cr(III) cations. If processes based on the direct elimination of Cr(VI) by fixing it on appropriate resins are used on an industrial scale,[8] much interest is shown in the selective recovery and recycling of Cr(VI).[9] Liquid−liquid extraction and liquid membrane techniques have also been explored and found to be able to concentrate Cr(VI).[10−13] In recent years, substantial progress has been made in the use of neutral crown ethers not only for the extraction of metallic cations and metallic salts but also for the extraction of more complex ion pairs where the metallic species are included in a complex anion.[14−17]

Among the possible alternatives to the treatment of industrial spent acids, membrane technology offers many advantages that correspond to the general tendencies in matters of resources and energy management in the world. Because of their modularity and profitability at a small scale, membrane techniques in general, and electromembrane techniques in particular, are well suited to the treatment of the pollution at its source.[18−21] Electrodialysis (ED) offers the advantages that the acid can be recovered at a high concentration that is more likely to be useful in the pickling operation. ED is a membrane separation technique based on the selective migration of aqueous ions through ion selective membranes. ED accomplishes the deionization of an aqueous stream producing a deionizated stream (dialysate) and a concentrated stream (concentrate) and is a process of choice when the acid concentration in the feed is low.[22−24] However, this method presents limits that are related to the nature of the anion exchange membrane (AEM). The first one is the transport of hydrogen ions through AEM in contact with acid solutions; the second is the chemical resistance of AEM in contact with oxidizing acids. In the literature, few papers have been devoted to the treatment of Cr(VI) solutions by electrodialysis.[25−27] A problem that is direcly related to the reduction of the proton leakage by increasing the cross-linking of the membrane is the chemical composition of the interstitial solution of the membrane. Owing to the weak water content of such membranes, the inner solution becomes very concentrated. For example, when an ARA (from Solvay Co.) or an AAV (from Asahi Glass Co.) anion exchange membrane is in contact with a 6 M HCl solution, the inner HCl concentration is close to 18 M while it is only 1 M for a perfluorosulfonic cation exchange membrane.[28] So, molecular species or complex forms can appear within the membrane.[29,30] The study of the inner composition of the membrane is therefore important to get a better understanding of the transport phenomena during electrodialysis. To this end, Raman spectroscopy appears as a powerful tool for investigating ion exchange membranes owing to the easy measurement of fundamental vibrational spectra of the mem-

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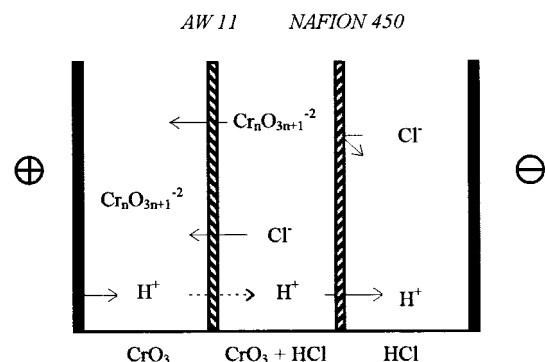*J. Phys. Chem. B, Vol. 103, No. 51, 1999* **11367**

Figure 1. Electrochemical cell for the transport number measurements.

brane constituents when these materials are immersed in various aqueous solutions.[31-35]

Limiting phenomena occur during the recovery of chromic acid by ED. The oxidizing nature of the chromate, the possible formation of chromate complexes due to the specificity of the chromate chemistry, and the possible occurrence of fouling phenomena are doubtless at the origin of this limit. The aim of this work is to apply Raman spectroscopy to understand the transfer of chromate species through a vinylpyridinium anion exchange membrane.

2. Experimental Section

2.1. Materials. The ion exchange membranes used for this study were as follows.

(i) For the anion exchange membrane, the AW 11 (from Solvay Co). It consists of poly(4-vinylpyridinium) chains (in acidic solution) grafted onto a ETFE matrix 150 μm thick (poly-(tetrafluoroethene-*co*-ethene)). Its exchange capacity is 0.9 mequiv·g^{-1}. It was chosen for its low proton leakage in acidic solutions.

(ii) For the cation exchange membrane, the Nafion 450 (from Du Pont de Nemours). It is a reinforced membrane fabricated from perfluorinated sulfonic acid polymer of equivalent weight 1100. This is a durable, general purpose membrane and probably the choice for initial studies of a new electrolytic process. It is used for the manufacture of 30-35% KOH as well in cells for synthesis, chromic acid regeneration, and effluent treatment.[36]

The reagents, CrO$_3$, NaCl, and H$_2$SO$_4$, were obtained from Merck Suprapur Products.

2.2. Electrochemical Measurements. The ac membrane electrical resistance was measured using the clip-cell method already described,[37] in solutions containing NaCl, CrO$_3$ + HCl, and HCl. The surface electrical resistance R_s (in Ω cm^2) is related to the specific conductivity κ (in Ω^{-1} cm^{-1}) through

$$\kappa = e/R_s \tag{1}$$

where e (in cm) is the thickness of the membrane.

The transport number of chromate species through the anion exchange membrane was determined using a three-compartment electrolysis cell depicted in Figure 1. The central compartment (the donor) contained 150 mL of a mixed solution of CrO$_3$ (0.1 M) + HCl (10^{-4} M). These concentrations are close to those of rinsing solutions of the electroplating plants. The volume chosen was sufficient to neglect concentration variations with regard to the amount of current crossing the cell. The anodic compartment was filled with 50 mL of 0.1 M CrO$_3$. The cathodic compartment was filled with 150 mL of 0.1 M HCl. The working area of each membrane was 7 cm^2. Glass paddle stirrers ensured the homogeneity of solutions. The temperature was

maintained at 25 $\pm$ 0.5 °C. During the electrolysis, anionic chromate species migrated from the donor to the anodic compartment. They competed with protons crossing the anion exchange membrane in the opposite direction. The transport number of chromate species is given by

$$t_{Cr} = (z_{Cr}J_{Cr}F)/j \tag{2}$$

where z_{Cr} and J_{Cr} are the positive value of the valency and the flux (in mol cm^{-2} s^{-1}) of the anionic chromate species (z_{Cr} = 2), respectively, F is the faraday constant, and j is the current density (in A cm^{-2}). The galvanostatic mode allows the application of a constant current. The Cr(VI) concentration in the anodic compartment was followed by a UV spectrophotometer (UVIKON 923, wavelength 432 nm).

2.3. Raman Spectroscopy Measurements. *Raman Measurements.* Raman spectra were obtained by excitation with 632.8 nm radiation from an He-Ne laser operated at about 17mW (~12 mW on the sample). The spectra were recorded, at 25 °C, with an LABRAM 1B confocal Raman spectrometer (Horiba-Dilor, France). The detector is an two-dimensional array of MPP-CCD (1024 $\times$ 256 pixels) TE cooled at about -65 °C. This spectrometer can be used in macroscopic or microscopic configuration.

Solutions Spectra. Raman spectra were obtained in the macroscopic mode. An optical system mounted on the turret of the microscope allows one to work with the laser beam perpendicular to the microscope optical axis. This device accepts all the microscopic and macroscopic objectives to work horizontally. In the macroscopic mode, the laser beam was focused on the sample by a 50 mm focal lens, and in this case the volume of the illuminated solution was constituted by a cylinder (diameter, 250 μm; height, 10 mm). The solutions were contained in optical parallepipedic cells filled with 0.2 mL of liquid.

Membranes Spectra. Membrane spectra were obtained in microscopic mode using the device described above. Pieces of membranes were maintained vertically between a cover glass and an optical cell face. Then, this cell (5 $\times$ 5 $\times$ 2 cm) contained the membrane, always immersed, in the solution. We used a long work distance (10.6 mm), objective (50$\times$, NA = 0.50), to record Raman spectra through the cell. Bearing in mind that our membranes were about 150 μm in thickness, the microscope confocality allows one to record, only, the light scattered by the membrane sample, because in our experimental conditions, the analyzed membrane depth was about 50 μm.

3. Results and Discussion

3.1. Electrochemical Measurements. When a current density of 30 mA cm^{-2} was applied to the cell, the applied voltage increased after 5 min. A value of 10 mA cm^{-2} led to the same increase after about 10 min. In the potentiostatic mode (where the voltage is monitored), the value of the current intensity decreases with time as depicted in Figure 2. Under these conditions, the measurement of the transport number was impossible. The problem was therefore to identify the cause of the increase in electrical resistance of the electrochemical cell. By means of electrical resistance measurements of the membranes, it was checked that this increase was not due to the Nafion 450 membrane. The values of the surface electrical resistance of the anion exchange membrane equilibrated 24 h in 0.2 M NaCl and in 1 M HCl were 11 and 6 Ω·cm^2, respectively. After 24 h in CrO$_3$ (0.1 M) + HCl (10^{-4} M), the values were close to 1500 Ω·cm^2. The AW 11 membrane was

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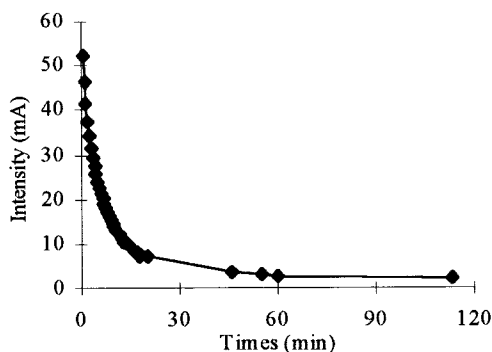
Figure 2. Current−time dependence of the electrochemical cell.

therefore responsible for this increase in electrical resistance, which was already observed in the case of fouling or deprotonation of this kind of exchanging group (poly(4-vinylpyridinium)), which decreases the exchange capacity, or both.[35,38] The study of the ionic composition of the anion exchange membrane in contact with chromic acid solutions is therefore the way to understand this phenomenon.
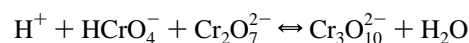
3.2. Raman Spectroscopy. In the electrodialysis process, involving the AW11 membrane, solutions containing CrO_3 (0.1 M) and HCl (0.1 M) were used. As shown by Samartis et al.,[39] the dominating particles of the solution (pH ≤1) within a wide range of Cr(VI) concentration are the polychromate ions (mainly $Cr_3O_{10}^{2-}$ ions). So, at first we measured Raman spectra of aqueous solutions of CrO_3 (1 M) with increasing acidity. This concentration of CrO_3 in aqueous solution was chosen to obtain Raman bands with appreciable intensity. The acid used was HNO_3 (from 1 to 6 M) to avoid oxydo−reduction reaction at high concentration. Our spectra, as shown in Figure 3, are similar to those measured by Machiroux and Cahay.[40] The main features are the increasing intensity of the 846 cm^{-1} [$\nu_{as}(Cr-O-Cr)$] versus acidity. This band is the only one, with appreciable intensity, absolutely characteristic of the trichromate ion. Several other bands are due to the trichromate ions but are located very near the dichromate ions bands as indicated by arrows in Figure 3. Assignment of the trichromate ion bands was given many years ago by Mattes[41,42] and has been confirmed by Pressprich et al.[43] The wavenumber corresponding to this [$\nu_{as}(Cr-O-Cr)$] band's summit, as given by Machiroux and Cahay, is decreasing versus acidity. However, we have completed the deconvolution of the Raman bands in the range 200−1200 cm^{-1}, and it appears that there is no significant shift of this last band regardless of the solution studied.

Then, we put a piece of AW11 membrane in solutions containing CrO_3 with different concentration (from 1×10^{-5} to 0.5 M) and fixed concentration of HCl (0.1 M). The materials were immersed for 1 week, to reach the equilibrium between each solution and the membrane. The HCl concentration was chosen like that existing in the rinse bath treated by electrodialysis, whereas we used a scanning of Cr(VI) concentrations.
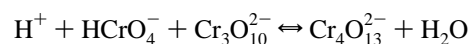
Confocal Raman microspectrometry allows one to record spectra inside the membrane in equilibrium with the solution mentioned above. As it can be seen in Figure 4.1, the spectrum (a) of the AW11 immersed in HCl solution only (clean membrane) is compared with all the other spectra (b−g) of the AW11 membrane immersed in Cr(VI) acid solutions. Obviously new bands are observed in these last spectra. For Cr(VI) solution of concentration 1×10^{-5} M (b), only dichromate ion bands are present, whereas for 1×10^{-4} M up to 0.5 M (c−g) bands that are characteristic of polychromate ions appear with increasing intensities (see arrows). It is to be noted that we have not

recorded new bands that could be due to complexes involved via some bond between Cr and N atoms. The deconvolution of all the recorded spectra for the spectral range 700−1000 cm^{-1} (see Figure 4.2−4.4) has been obtained following some reasonable assumptions. First we have done the deconvolution of the clean membrane (Figure 4.2). Then each membrane band's parameters were fixed (positions, half-width, intensity bands ratios, profiles) when deconvolution of contaminated membranes were performed. Here again the best fit is reached with only one band (rather broad) taking into account the presence of polychromate inside the membrane (see Figure 4.3−4.4). This last band shifts slightly (from 850 to 864 cm^{-1}), and the intensity ratio R of the polychromate band to a membrane one (at 838 cm^{-1}) is globally increasing when the external Cr(VI) concentration increases. However, R undergoes a slight decrease when the external Cr(VI) concentration changes from 1×10^{-3} M to 1×10^{-2} M, and then R increases again. This intensity behavior can be explained.

Some years ago, we studied poly(4-vinylpyridinium) membranes.[31] We assigned several vibrational bands due to pyridinium or pyridine cycles of the grafted functional chains. These last bands appear in a function of the pH value of the solution where the membranes were immersed. In particular, two well-defined bands are, respectively, due to the pyridinium (at 652 cm^{-1}) and to the pyridine (670 cm^{-1}) cycles. It can be seen in Figure 4.1 (zoomed region) that some deprotonation occurs (apparition of the 670 cm^{-1} band) when the external Cr(VI) concentration is equal or superior to 1×10^{-2} M. In other words, some fixed charged pyridinium sites are lost, and for this reason some polychromate counterions (see text hereafter) have, also, disappeared. Actually, the equilibrium[39] involved for the formation of the polychromate ions can be written in the following way:

$$H^+ + HCrO_4^- + Cr_2O_7^{2-} \leftrightarrow Cr_3O_{10}^{2-} + H_2O$$

and

$$H^+ + HCrO_4^- + Cr_3O_{10}^{2-} \leftrightarrow Cr_4O_{13}^{2-} + H_2O$$

Then, the deprotonation of the poly(4-pyridinium) membrane is certainly due to the interaction of the $Cr_2O_7^{2-}$ ions with the pyridinium sites (Pyr$^+$) when there is a lack of acid to produce polychromate ions. Actually, the following equilibrium can occur:

$$Pyr^+ + Cr_2O_7^{2-} \leftrightarrow HCr_2O_7^- + Pyr$$
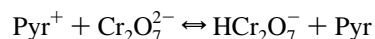
To confirm this assumption we have recorded Raman spectra of the AW11 membrane in equilibrium with solution where the Cr(VI) concentration is fixed (0.2 M) but with different acid concentration (from no acid to HNO_3 at 0.1, 0.5, 1, and 2 M). As can be seen in Figure 5.1a, although some deprotonation of pyridinium fixed sites occurs, there is no formation of polychromate in the absence of acid. However, in the presence of acid the typical vibrational broad band (see deconvolution) of polychromate ions is visible in all the spectra (for instance, see Figure 5.3). In the same way Raman spectra (not reported here) of Cr(VI) solutions with a fixed concentration of 2 M show that deprotonation of the pyridinium sites occurs (without formation of polychromate ions inside the membrane) not only in the absence of acid but also for 0.1 M acid solution.

Finally, we have desorbed in water, over 3 days, a piece of membrane contaminated by an acid Cr(VI) solution. The Raman spectrum of the desorbed membrane shows clearly that the

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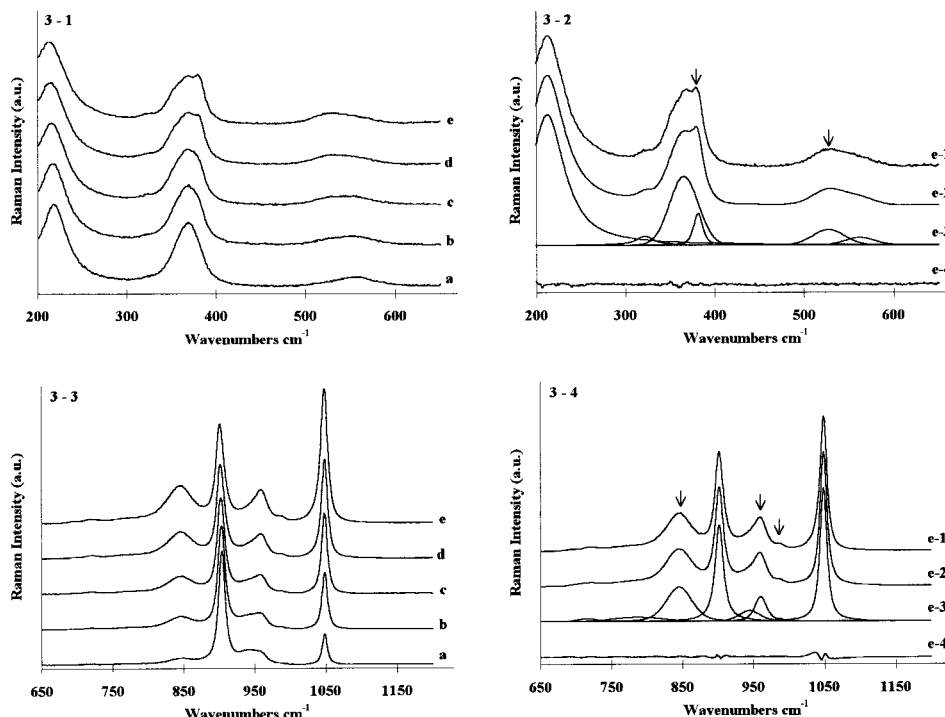
Figure 3. Raman spectra of Cr(VI) acidic solutions. (1) (lowest region) and (3) (highest region) Raman spectra as a function of HNO_3 concentration [(a) 1 M HNO_3, (b) 2 M HNO_3, (c) 3 M HNO_3, (d) 4 M HNO_3, (e) 6 M HNO_3] (2) (lowest region) and (4) (highest region). Deconvolution of the e Raman spectrum (e.1 experimental spectrum, e.2 calculated spectrum, e.3 individual determined bands by deconvolution of the experimental spectrum, e.4 difference between calculated and experimental spectra).
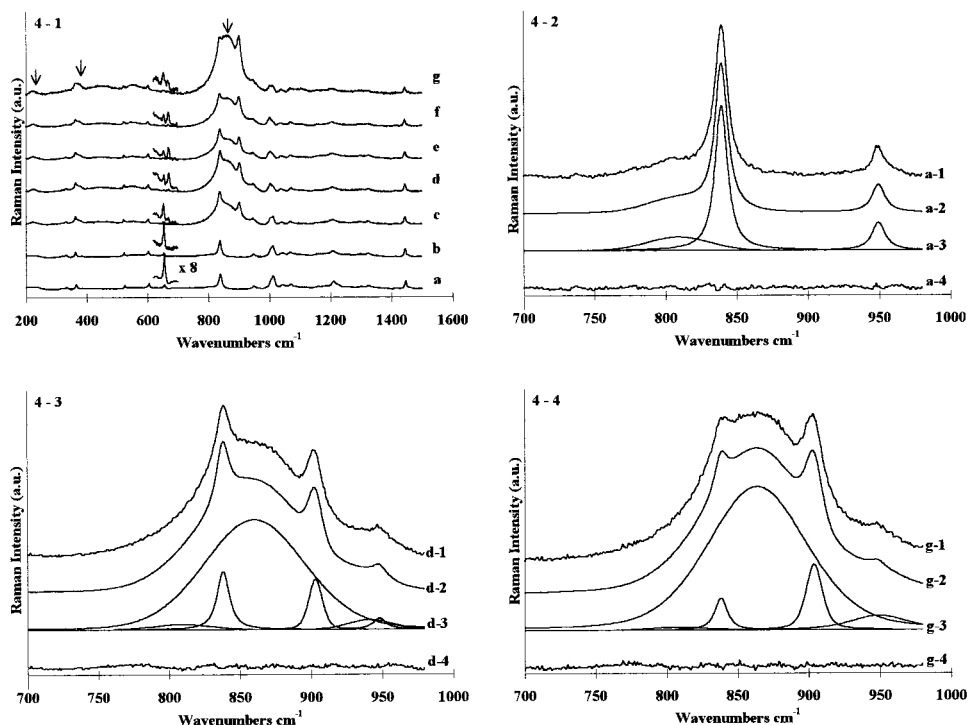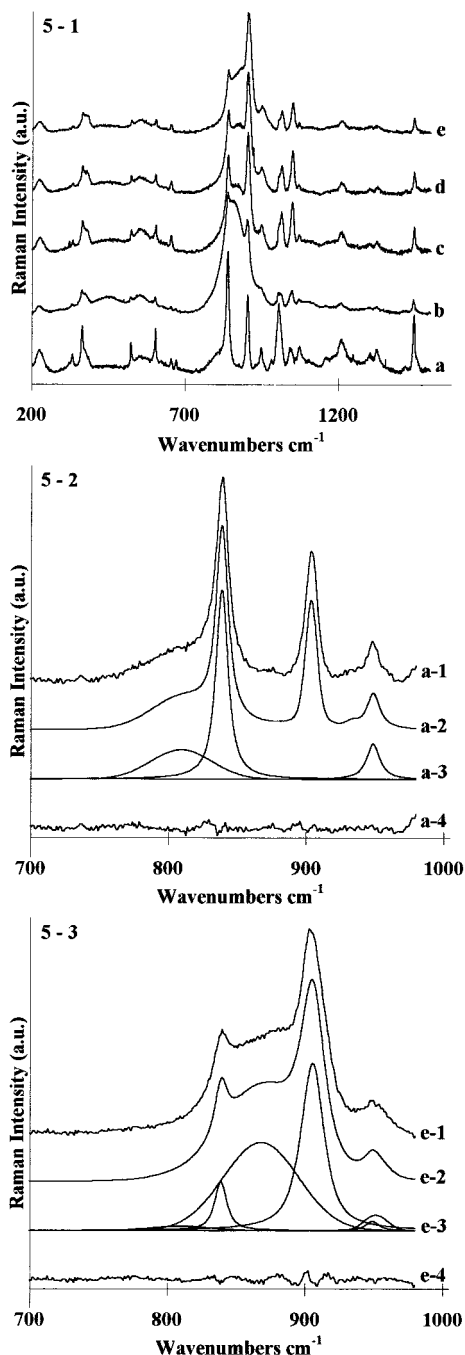

Figure 4. Raman spectra of the contaminated AW11 membrane. (1) Raman spectra of AW11 membrane immersed in acidic solutions (0.1 M HCl) of different Cr(VI) composition [(a) clean membrane, (b) 1×10^{-5} M CrO_3, (c) 1×10^{-4} M CrO_3, (d) 1×10^{-3} M CrO_3, (e) 1×10^{-2} M CrO_3, (f) 1×10^{-1} M CrO_3, (g) 5×10^{-1} M CrO_3]. (2−4) Deconvolution of a−g Raman spectra (a.1−g.1 experimental spectra, a.2−g.2 calculated spectra, a.3−g.3 individual determined bands by deconvolution of each experimental spectrum, a.4−g.4 difference between calculated and experimental spectra).

polychromate ions act predominantly as counterions in the membrane. The existence of these polychromate ions in this condition is certainly due to the electrostatic interaction with the pyridinium sites. Actually, we have already found a similar phenomena with mercury chloride or zinc chloride complexes[30,44] acting as counterions in the AW membrane type. The

intensity ratio R' of the typical polychromate ions band (at 860 cm^{-1}) to another band due to dichromate and polychromate ions (CrO_3 groups at 903 cm^{-1}) increases in the desorbed membrane (Figure 6.2) compared with the original contaminated membrane (see Figure 6.1). This fact confirms that dichromate ions are not the predominant counterions in the AW11 membrane under

Figure 5. Raman spectra of the contaminated AW11 membrane. (1) Raman spectra of AW11 membrane immersed in Cr(VI) (0.2 M) solutions with different HNO_3 concentration [(a) no acid, (b) 0.1 M HNO_3, (c) 0.5 M HNO_3, (d) 1 M HNO_3, (e) 2 M HNO_3]. (2) Deconvolution of a–e spectra. (a.1–e.1 experimental spectra, a.2–e.2 calculated spectra, a.3–e.3 individual determined bands by deconvolution of each experimental spectrum, a.4–e.4 difference between calculated and experimental spectra).

this condition. Besides, we put desorbed pieces of membrane in HCl and HNO_3, 1 M, solutions (1 day), and it appears that the polychromate ions are exchanged by the chloride or nitrate ions (see Figure 6.3). This last point corroborates the fact that there is no complex formation in the membrane between polychromate ions and the pyridinium sites.

4. Conclusion

Raman spectroscopy pointed out the presence of polychromate ions inside the AW11 membrane immersed in Cr(VI)
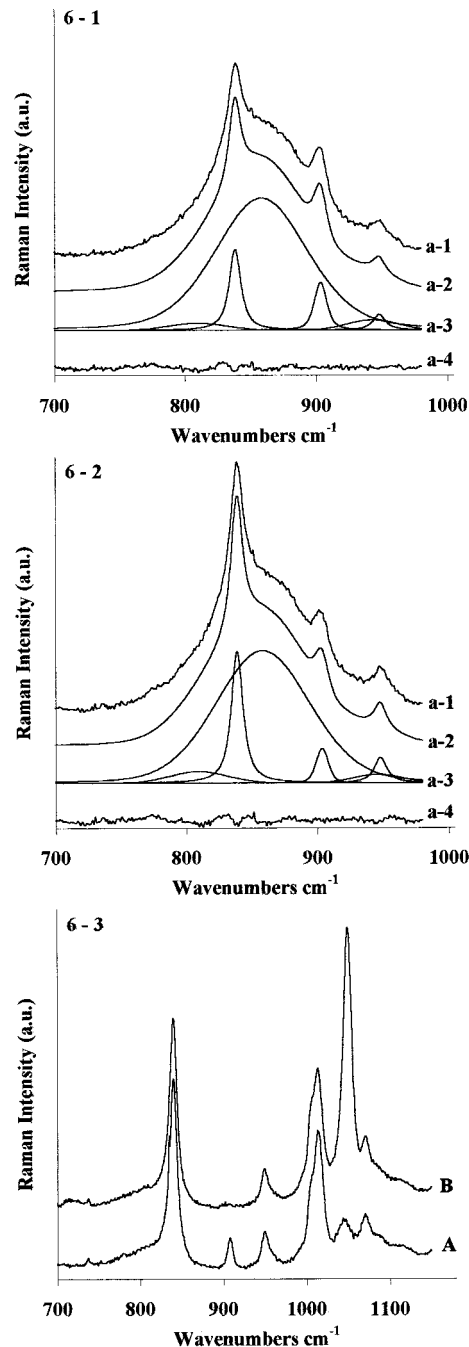
Figure 6. (1) AW11 membrane equilibrated with 1×10^{-3} M CrO_3 + 1×10^{-1} M HCl solution; (2) the same membrane desorbed in water after 3 days (a.1 experimental spectrum, a.2 calculated spectrum, a.3 individual determined bands by deconvolution of the experimental spectrum, a.4 difference between calculated and experimental spectra); (3A) the same membrane after 1 day immersion in 1 M HCl, (3B) the same membrane after 1 day immersion in 1 M HNO_3.

solutions. The very low mobility of this polychromate ions was at the origin of the resistance increases of the electrochemical cell. Furthermore, the presence of the polychromate ions inside the membrane, for very small concentrations of the Cr(VI) solutions, (as little as 5×10^{-5} M of CrO_3 in 0.1 M HCl) showed that the inner AW membrane solutions can reach, rapidly, very important species concentrations.

When the Cr(VI) solution concentration is of the order of 1×10^{-2} M (or more), a competition between the dichromate ions and the poly(4-vinylpyridinium) sites toward protons is observed. However, we did not observe any new vibrational bands that could be assigned to the formation of a complex

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between vinylpyridinium sites and Cr species. This point was confirmed by the exchange of polychromate ions by the chloride or nitrate ions, using 1 M HCl or HNO$_3$ solutions, for a contaminated membrane preliminary desorbed in water. The same study with anion exchange membranes bearing quaternary ammonium groups is presently in progress.

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