The poisoning effect of mercury complexes with an anionic exchange membrane used in an electrodialysis process: a Raman study

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Poisoning of an ion exchange membrane is one of the most important problems encountered in the electrodialysis process. The poisoning of an anion exchange membrane, used in an electrodialysis process to purify and reconcentrate an hydrochloric acid solution containing mercury chloride, has been investigated. Raman spectroscopic analysis of the contaminated material, combined with electrodialysis results, are presented and discussed. The stoichiometry of the poisoning mercury complex and its action as a counter ion inside the membrane are determined. Moreover, a strong interaction between the membrane fixed sites and the mercury complex is pointed out.

Etude par spectrométrie Raman de l'empoisonnement d'une membrane échangeuse d'anions, par des complexes mercuriques, au cours d'un procédé d'électrodialyse. L'empoisonnement d'une membrane échangeuse d'ions lorsqu'elle est utilisée dans un procédé d'électrodialyse constitue un handicap majeur. Nous avons étudié l'empoisonnement de la membrane prototype AW11 utilisée dans un procédé d'électrodialyse destiné à purifier et à reconcentrer de l'acide chlorhydrique à partir d'une solution aqueuse de ce dernier contenant une faible teneur en chlorure mercurique. Les résultats obtenus au cours de l'électrodialyse associés à l'étude spectrale de la membrane contaminée, en diffusion Raman, sont présentés et discutés. Nous avons pu mettre en évidence la stoechiométrie et le rôle joué par le complexe mercurique majoritaire constituant, ici, l'agent empoisonnant. En outre nous montrons aussi que ce complexe entre en interaction forte avec les sites fixes de la membrane contaminée.

Electrodialysis is a powerful technique for the treatment of many waste acids. However, some important problems can be encountered if poisoning of the ionic exchange membrane occurs. This is the case in the purification and concentration process of hydrochloric acid solutions containing zinc, cadmium or mercury chlorides, because metallic complex formation gives rise to an important poisoning effect of the membranes used.

Our group has studied ionic fluxes across anion exchange membranes and it appears that a considerable loss of permselectivity for the sodium ion takes place in the presence of zinc complexes.[1] So we have undertaken an electrodialysis experiment, coupled with a Raman investigation, to obtain information on the poisoning of an anionic exchange membrane by metallic complexes. We have already emphasized the important advantages of Raman spectroscopy in the study of immersed ion exchange membranes in aqueous solutions. By this useful technique we have obtained valuable information on ion exchange membranes.[2–8]

Here, we have chosen to work with a hydrochloric acid solution containing mercury chloride for the following reasons: (*i*) mercury chloride complexes are more stable than the zinc or cadmium ones and (*ii*) there are only anionic complexes with mercury.

Experimental

Electrodialysis experiment

The electrodialysis operation is shown schematically in Fig. 1. Compartment 2 (0.3 M NaCl) and compartment 4 (0.1 M HCl) correspond to the concentrated stream whereas compartment 3 (0.3 M HCl + 10^{-3} M $HgCl_2$) correspond to the diluent stream. Compartments 1 (0.25 M H_2SO_4) and 5 (0.5 M HCl) are used to rinse off the electrodes.

In compartment 3 $HgCl_4^{2-}$ is indicated as it is preponderant compared to $HgCl_3^-$ and $HgCl_2$, taking into account the given composition.

The apparatus is made of polytrifluorochloroethylene (KEL-F) and each compartment is 12 mm thick. In these compartments the stream speed is about 5.8 cm s^{-1}. The initial volume of the diluent stream is equal to 5 l whereas those of the concentrated streams are equal to 0.5 l. The membrane pieces used in the process have an area of 40 cm^2 and the applied electric current density is equal to 0.05 A cm^{-2}. The electrodes are made of platinised titanium and are fixed with nylon screws.

Membranes

The cationic exchange membranes (CEM) used in the experiment are the CMV selemion membrane from Asahi Glass whereas the anionic exchange membranes (AEM) are the prototype membranes AW11 produced by Solvay. The AW membranes are composed of poly(4-vinylpyridinium) chains (in acidic solution) grafted onto an ETFE (ethylenetrifluoroethylene) polymer matrix and crosslinked with divinylbenzene. This kind of membrane has a low proton leakage and is therefore very well suited for acid reconcentration.

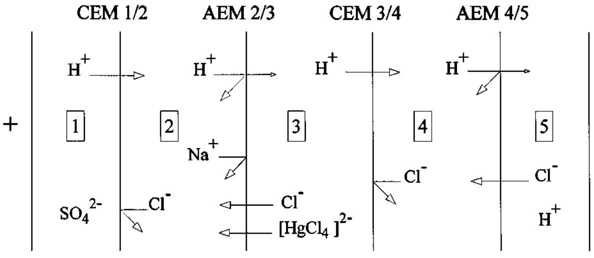

Fig. 1 Diagram of the electrodialysis process experiment

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Raman measurements

Raman spectra were obtained by excitation with 514.5 nm radiation from an argon ion laser (Spectra Physics model 2020-03) operated at about 300 mW. The spectra were recorded with an OMARS 89 multichannel spectrometer (Dilor, France). The detector is an intensified 1024 photodiode array. The membrane was kept flat between two optical glass plates that were pressed together. Two slots in the plates facing each other allowed the Raman spectrum of the membrane to be recorded without that of the plate material. The glass plates and the membrane can be immersed in various aqueous solutions contained in an optical cell (Hellma). The laser beam was focused onto the edge of the sample and the scattered light was collected at right angles to this beam. The Raman spectra were recorded at 23 °C.

Results and Discussion

Electrodialysis

In Fig. 2A the acid concentration *versus* time is given for compartments 2 and 4. One can see that a greater increase in acid concentration is observed in compartment 4. Moreover, in Fig. 2B the acid concentration yield has been plotted *versus* time and a significant difference occurs between these two compartments. The acid concentration yield is about 20% higher in compartment 4 than in compartment 2, whereas the concentration yield is the same in these two compartments when the electrodialysis is carried out under the same conditions without any $HgCl_2$. Finally, Fig. 2C shows that mercury species are present in compartment 2 while we do not detect this element in compartment 4.

Obviously, AEM 2/3 (see Fig. 1) is affected by mercury species in contrast to AEM 4/5. The low proton leakage of AEM 2/3 is certainly lost by the poisoning effect due to the presence of a mercury chloride complex inside this material.

Raman spectra

First we have measured Raman spectra of aqueous solutions containing NaCl and $HgCl_2$ at various compositions. The molar fractions of mercury complexes depend on the free chloride concentration, the ionic strength of the solution and the different equilibrium constants of formation.[9] So, we have calculated the percentage of $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ as a function of the free ligand concentration[10] (see Fig. 3A). We cannot obtain an aqueous solution giving spectra where the bands of $HgCl_3^-$ are preponderant whereas this is possible for $HgCl_4^{2-}$ and $HgCl_2$. However, it is to be noted that in these spectra each complex gives rise only to the most intense and characteristic band (*i.e.*, the ν_1 totally symmetric stretch of Hg—Cl) as can be seen in Fig. 3B. The observed wavenumbers are in agreement with the work of Waters and coworkers,[11] although their spectra were measured in tributylphosphate extracts from concentrated aqueous solutions.

We have then recorded Raman spectra of the AW11 membrane immersed in water, before and after the electrodialysis operation. The stong ν_1 band located at 272 cm^{-1} (Fig. 4A, curve a), which is absent in Fig. 4A, curve b, indicates essentially the presence of $HgCl_4^{2-}$ inside the anionic membrane used in the process. Furthermore, while keeping this last membrane immersed in water for several days and recording Raman spectra from time to time we have noticed that the $HgCl_4^{2-}$ complex remains in this material (see Fig. 4B). It thus appears that the $HgCl_4^{2-}$ complex is acting as a counter ion of the poly(4-vinylpyridinium) fixed sites of the membrane, as we cannot detect co-ions inside this material under these conditions (Donnan's rule). Moreover, as the concentration of the free chloride ions is very low, it is evident that the stability of the mercury complex involves a strong electrostatic interaction with the fixed sites.

In Fig. 4B and Fig. 4C two bands are located by arrows and labeled Pyr and Pyr^+ since these last two bands are characteristic of the poly(4-vinylpyridine) and poly(4-vinylpyridinium) grafts.[4] When the membrane is immersed in water (coming from an acidic solution) deprotonation of the grafts

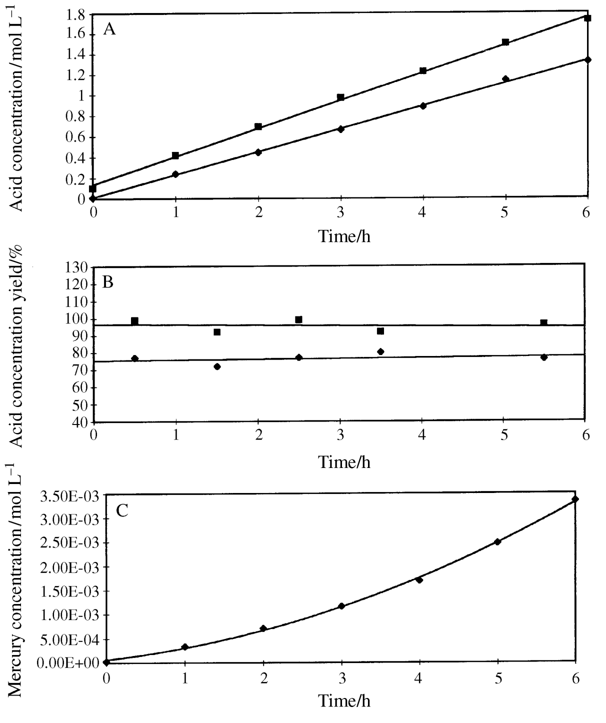

Fig. 2 Main results of the electrodialysis in compartments 2 (◆) and 4 (■)

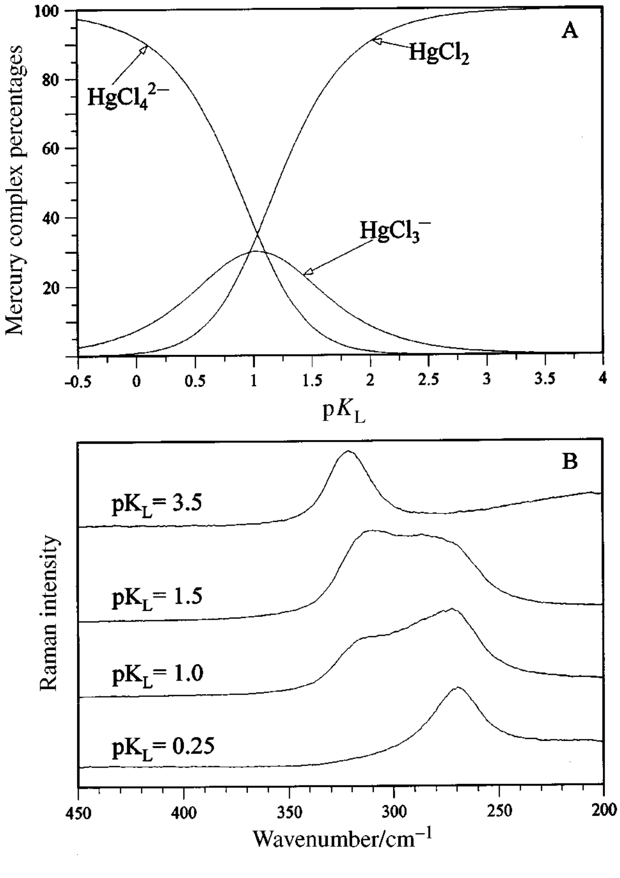

Fig. 3 (A) Percentages of mercury complexes as a function of pK_L = $-\log(L)$ where L is the free ligand concentration. (B) Raman spectra of (NaCl + $HgCl_2$) aqueous solutions for different pK_L values, with an ionic strength equal to 1. The intensities are on an arbitrary scale

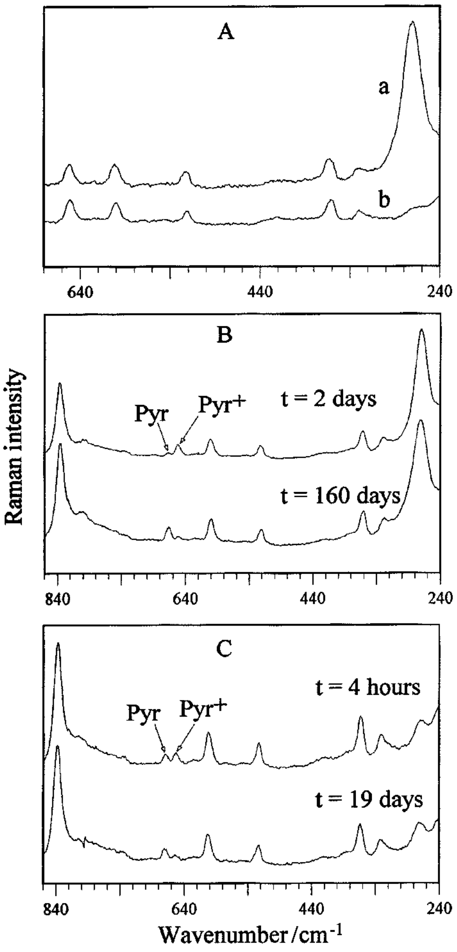

Fig. 4 (A) Raman spectra of the AW11 membrane immersed in water: curve a after 6 h of electrodialysis; curve b before electrodialysis. (B) Raman spectra *versus* time of the AW11 membrane containing $HgCl_4^{2-}$. (C) Raman spectra *versus* time of the AW11 membrane without $HgCl_4^{2-}$. The intensities are on arbitrary scales

occurs with time and the intensity of the Pyr band increases whereas it decreases for the Pyr^+ band. However, the rate of variation of the intensities with time is very different between a clean membrane and one containing the mercury complex. If we compare the spectra of Fig. 4B with those of Fig. 4C, it can be seen that the deprotonation rate is much lower when the mercury complex is inside the membrane. Our previous results[4] concerning the deprotonation kinetics for this kind of membrane have indicated that the reaction half-life increases markedly when the membrane grafting rate is reduced. Thus, it can be deduced that there are fewer accessible sites in the presence of mercury complex ions. This provides confirmation of the presence of the mercury complex as counter ions inside the membrane and that some fixed sites continue to be neutralized by chloride ions. Fixed sites neutralized by $HgCl_4^{2-}$ ions are then protected against deprotonation by the hydroxide ions present in water.

Finally, although some of the initial mercury complex is lost, there is always some present in the used membrane, even after an immersion time as long as 450 days. It is also to be noted that $HgCl_4^{2-}$ is always involved as the counter ion because fixed poly(4-vinylpyridinium) sites appear in the Raman spectrum, whereas no more fixed sites are present for a clean membrane immersed in water for the same time.

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