

# NEW TECHNIQUES FOR EVALUATION OF IONIC CONDUCTIVITY OF ION EXCHANGE MEMBRANES USED IN THE ELECTRODIALYSIS PROCESS

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**Abstract.** *New techniques for the determination of ionic conductivity of acrylic ion exchange membranes, as well as the electrochemical system used are presented in this paper. The electrochemical cell used in electrochemical impedance spectroscopy (EIS) investigation consisted of two plan-parallel platinum disk electrodes, with the acrylic membrane investigated placed between the electrodes. This configuration is placed inside the disk of a digital precision micrometer, which is able to determine very precisely the membrane thickness during the plotting of the electrochemical impedance spectra. The electrochemical impedance spectroscopy measurements were carried out with a Voltalab 40 potentiostat. According to the data obtained from the Nyquist and Bode diagrams, knowing the real thickness of the membrane during the measurements, were calculated the values of ionic conductivity. The chemical stability of this type of membranes was investigated by Fourier transformed infrared spectroscopy.*

**Keywords:** *electrochemical impedance spectroscopy, ionic conductivity, FT-IR spectroscopy*

## 1. INTRODUCTION

In present ion exchange membranes are receiving considerable attention and are successfully used in various industrial processes such as: electrolysis, electro-dialytic concentration of seawater to produce edible salt, desalination of saline water by electrodialysis, separation of ionic materials from non-ionic materials by electrodialysis, recovery of acid and alkali from wastewater by diffusion dialysis, dehydration of water-miscible organic solvent by pervaporation, removal of undesirable ions from wastewater, especially to extract toxic metal ions, etc. [1, 2].

Ion exchange membranes are membranes with fixed anionic or cationic exchange groups that are able to transport cations or anions [3].

Electrochemical impedance spectroscopy is a powerful and useful method to investigate the mechanisms of electrochemical reactions, to measure the dielectric and transport properties of different materials, to investigate passive surfaces, to study electrical properties of different materials and is often used to characterize a wide variety of electrochemical phenomena in porous materials, solid state, liquid electrolytes, synthetic and biological membranes etc. [3 -5].

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Electrochemical impedance spectroscopy was applied to investigate the influence of the pure membrane resistance, the ionic transfer resistance through the electrical double layer and the diffusion boundary layer resistance on the total measured resistance [3].

In general, this method can be used to provide more information on the functional and structural characteristics of different membrane systems [1 - 6].

In this paper the new techniques for the determination an ionic conductivity of acrylic ion exchange membranes, as well as the electrochemical system used was presented. The chemical stability of acrylic ion exchange membranes was investigated by Fourier transformed infrared spectroscopy.

## 2. MATERIALS AND METHODS

### 2.1. MEMBRANES

The experiments were conducted by using two different types of bicomponent ion-exchange membranes prepared with ion exchangers (Purolite C150 and Purolite A100) (Purolite Romania). The membranes were prepared from a mixture of 80% acrylic copolymer (90% acrylonitrile : 10% vinyl acetate) and 20 % polyvinyl alcohol in dimethyl sulfoxide (DMSO), by dissolving the both polymers, in the presence of 5% ion exchange resin (A100 or C150), calculated to the polymer mixture.

The polymer solution was cast at room temperature onto a glass plate and a draw-down technique was used to produce films of wet thickness 200  $\mu\text{m}$ . After few seconds, the plate was immersed in a coagulation bath containing 90% isopropanol: 10% water and left there for a half of hour.

These ion-exchange membranes were prepared at ICECHIM (Polymer Department, Bucharest, Romania).

Purolite C150 is a macroporous poly(styrene sulphonate) strong acid cation exchange resin with excellent resistance to both osmotic and thermal shock.

Purolite A100 is a macroporous polystyrenic weak base anion exchange resin with excellent resistance to osmotic shock as well as being physically resistant to mechanical breakage.

The acrylic cation exchange membrane type Purolite C150 contains sulfonic acid groups as fixed charges and the acrylic anion exchange membrane type Purolite A100 contains tertiary amine groups as fixed charges.

### 2.2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The electrochemical impedance spectroscopy measurements were carried out using a VoltaLab 40 Dynamic Electrochemical System in conjunction with VoltaMaster 4 software containing integrated data processing regression package to obtain electrochemical impedance spectra characteristic parameters. The electrochemical cell consisted of two plan-parallel platinum disk electrodes with a diameter of 11 mm (electrode area of 0.9503  $\text{cm}^2$ ) having as electrolyte an acrylic ion exchange membrane placed between these electrodes [7, 8]. This arrangement is placed between the disks of a precision digital micrometer (Mitutoyo) that is able to measure very precisely the membrane thickness during the plotting of the electrochemical impedance spectra, minimizing the associated errors (Fig. 1).



**Fig. 1. The electrochemical cell used for the determination of ionic conductivity of acrylic ion exchange membranes.**

The electrochemical impedance spectroscopy measurements were carried in the frequency range of 100 kHz and 1 Hz using a potential amplitude perturbation of 10 mV.

By using a circular regression procedure, the ionic conductivity is calculated from the value of normalised impedance,  $R_1$ , ( $\text{ohm}\cdot\text{cm}^2$ ), obtained from intersection with the real impedance axis in the high frequency area of Nyquist plot and from the actual value of the membrane thickness displayed on the digital micrometer during the determination (see Eq. 1):

$$\sigma = \frac{d}{R_1} \quad (1)$$

where:  $\sigma$  - the ionic conductivity,  $\text{ohm}^{-1}\cdot\text{cm}^{-1}$ ;  $d$  - actual membrane thickness, cm;  $R_1$  - the intersection of experimental curve with the real impedance axis,  $\text{ohm}\cdot\text{cm}^2$ .

### 2.3. INFRARED SPECTROSCOPY

Using a Fourier transforms infrared spectrometer (Tensor 37 from Bruker) FT-IR spectra were measured in transmission mode (ATR) using the Golden Gate unite. The Fourier transform infrared spectroscopy method was used in the investigations of removal process of copper ions using the weakly basic anion exchanger and strongly acid cation exchanger, respectively. The spectra of the acrylic ion exchange membranes were recorded in the spectral range of  $400 - 4000 \text{ cm}^{-1}$ .

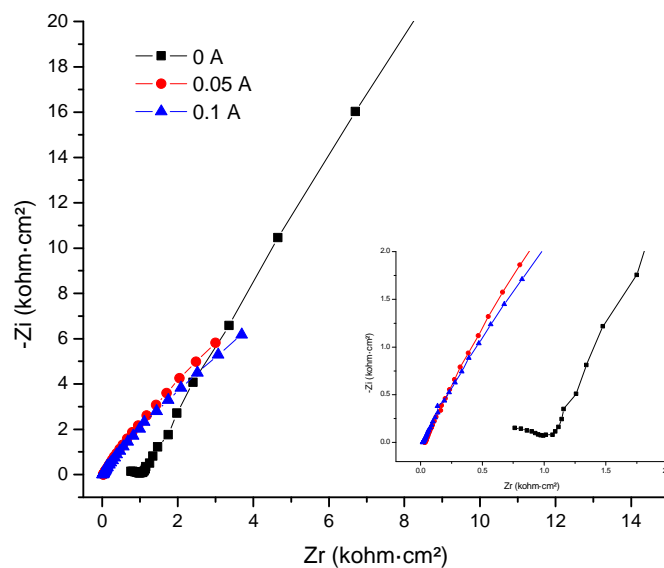
## 3. RESULTS AND DISCUSSION

### 3.1. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

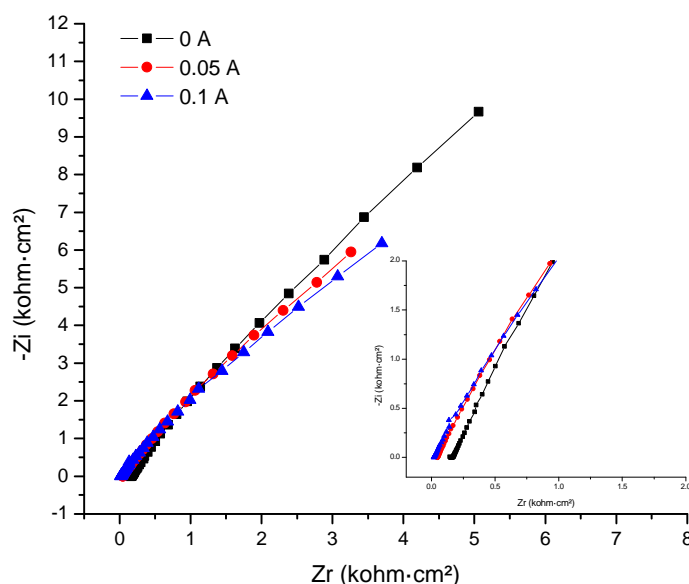
By representing the electrochemical impedance spectra in the form of Nyquist plots for the investigated membranes (Figs. 2 and 3) one is now able to determine the characteristic parameters and the corresponding ionic conductivity (Tables 2 and 3).

Impedance data are typically depicted in Nyquist and Bode plots.

Fig. 2 displays such a Nyquist plot, which shows the real part  $Z_r$  and the imaginary part  $-Z_i$  of the impedance  $Z$ .



**Fig. 2. Impedance spectra of the acrylic anion exchange membrane (Purolite A100) at various values of current.**



**Fig. 3. Impedance spectra of the acrylic cation exchange membrane (Purolite C150) at various values of current.**

Figs. 2 and 3 show the impedance spectra for the acrylic anion exchange membranes and respectively for acrylic cation exchange membranes, at two different values of current and at zero current.

As it can be observed, for investigated anion and cation membranes under initial state (absence of imposed current), the Nyquist plots present two capacitive loops: a small loop at high frequencies followed by a larger one at low frequencies. A more detailed view of the loop observed at high frequencies is also shown in Figs. 2 and 3. Moreover, a linear behavior is clearly observed at the beginning of the second capacitive loop [9-12].

The beginning part of the capacitive loop in Figs. 2 and 3 represents the pure resistance of the solutions and the membrane at zero phase angle. The shift of the capacitive loops toward lower real impedance is due to the decrease in solution resistance. It is well known that resistance of ion-exchange membranes should be independent of solution

concentration due to the electroneutrality between the counter-ions and the fixed exchangeable sites. It is noted that a change in the diameter of loops also occurs: the diameter decreases as the imposed dc current increases. Thus it can be deduced that there appear another impedance to restrict ionic transport from the solution to the membrane (i.e., heterogeneous transport) [9-17].

The complex plane plots of the impedance of membranes under a galvanostatic mode show indeed the same features: a single semicircle at high frequencies with a slope of nearly 45° turning into a vertical line. In both cases the charge-transfer semicircle is seen [14-16].

This linear behaviour is maintained in the entire explored domain in the case of acrylic anion and cation exchange membrane. The low-frequency behavior of impedance could be attributed to process characteristics. The overall current densities  $i = I/A$  at steady state include the contributions  $i_w = I_w/A$  and  $i_c = I_c/A$ , where  $A$  is the membrane working area. The principal contribution  $i_w$  is produced by the water-splitting mechanism in the membrane which yields the amount of  $H^+$  and  $OH^-$  ions transported by the current. The second contribution  $i_c$  corresponds to the co-ion leakage current through the membrane. Thus, in our case, the latter effect is due to  $Cu^{2+}$  ions transport from the base compartment to the acid compartment and  $SO_4^{2-}$  ions transport in the opposite direction [10].

**Table 1. The value of ionic conductivity for acrylic anion exchange membrane at various values of current.**

Current, $A$	$R_1$ , $\Omega cm^2$	$d$ , $cm$	$\sigma \cdot 10^3$ $\Omega^{-1} cm^{-1}$
0 (until the electro dialysis)	996.40	0.0114	0.011
0.05	32.07	0.1960	6.112
0.10	12.62	0.1630	12.916

**Table 2. The value of ionic conductivity for acrylic cation exchange membrane at various values of current.**

Current, $A$	$R_1$ , $\Omega cm^2$	$d$ , $cm$	$\sigma \cdot 10^3$ $\Omega^{-1} cm^{-1}$
0 (until the electro dialysis)	160.20	0.0186	0.116
0.05	43.23	0.2010	4.650
0.10	29.70	0.1830	6.162

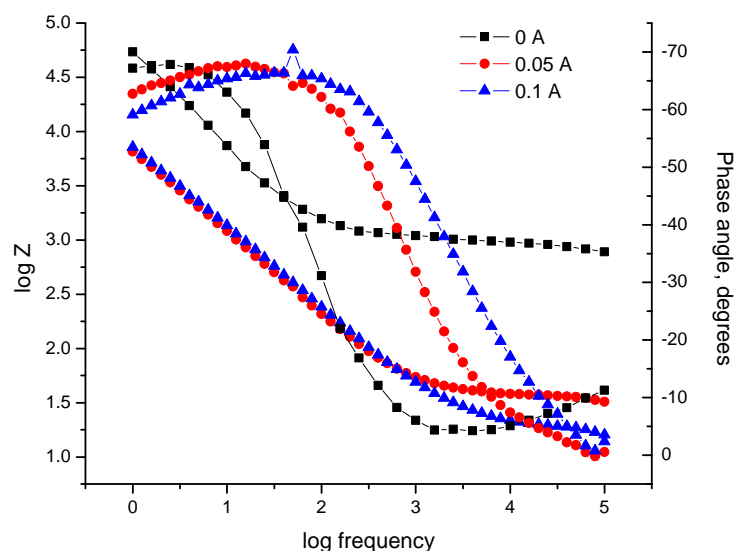
From Tables 1 and 2 it can be seen that the value of ionic conductivity increases with increase of current values. The ionic conductivity of acrylic anion exchange membrane is higher comparative with acrylic cation exchange membrane, in particular at value of current of 0.10 A, due to the low resistance  $R_1$ .

The EIS response did not change significantly with applied dc potential. This means that changes in electrode polarization and current distribution were negligible in the range of applied dc potential, as expected. Higher polarizations should drastically change the impedance spectra [10-14].

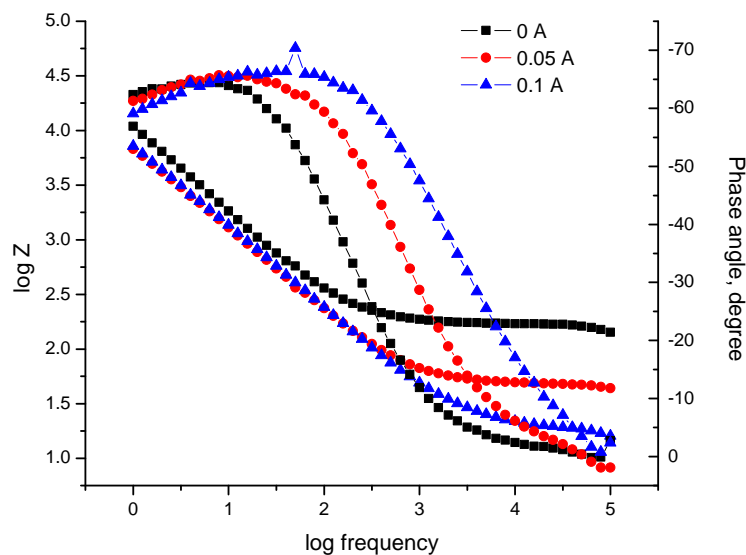
The collected data indicates that the ohmic drop in the membranes accounts for the principal ohmic drop in the electro dialysis cell, even at low polarization. The results obtained demonstrate that the electrochemical impedance spectroscopy technique can be used as a tool to predict the performance of electro dialysis membranes, without the need for high polarizations and currents.

In terms of the ohmic drop, the membrane with the smallest electrical resistance and thus with the lowest energy consumption in the tested electro dialysis system is anion exchange membrane Purolite A100.

Figs. 4 and 5 shows the corresponding Bode plot which shows the relation between the impedance, the frequency and the phase angle.



**Fig. 4.** Change of the imaginary impedance part of the anion exchange membrane (Purolite A100) system with respect to the reciprocal of frequency, at different value of current.



**Fig. 5.** Change of the imaginary impedance part of the cation exchange membrane (Purolite C150) system with respect to the reciprocal of frequency, at different value of current.

It is well known that resistance of ion-exchange membranes should be independent of solution concentration due to the electroneutrality between the counterions and the fixed exchangeable sites. The impedance values at zero phase angles represent the pure resistance of the solution and membrane [10 - 12].

In Figs. 4 and 5 it was observed that the value of the resistance of the system at the limit of zero frequency decreases as current increases. This behavior was observed when studying the stationary electrical properties of these systems due to a decreasing in the steady state electric current in response to an increasing in the electric potential perturbation. The capacitive low frequency behavior results from the finite diffusion hindrance of the electrochemical charge transfer.

The real part of the impedance at the intersection point between the geometric and diffusional arcs is obtained from the relative minimum value of the imaginary part of the impedance at low frequencies. The influence of the electric current on the geometric arc was very small. This behavior may be due to the variations of the ionic concentrations not only in the diffusion boundary layers but also in the bulk of the membrane. Also the membrane seems to be strongly charged, which could explain that the changes in the value of the impedance for acrylic cation exchange membrane with current are very small. Thus, an increase in the value of the electric current leads to a decrease in the peak frequency of the geometric arc. This behavior may be due to the variations of the ionic concentrations into the diffusion boundary layers [9 - 13].

With increasing value of current, the resistance of depleted diffusion boundary layers increases, while that of enriched diffusion boundary layer decreases. At the same time, the conductivity term contribution in the depleted diffusion boundary layer increases [5, 11].

The resistances of the diffusion boundary layer and the interfacial ionic charge transfer through the double layer for anion exchange membranes are lower than for cation exchange membranes. This is due to the difference in ion mobility between  $\text{SO}_4^{2-}$  ions and  $\text{Cu}^{2+}$  ions [3, 5].

### 3.2. INFRARED SPECTROSCOPY

The chemical structure of acrylic anion- and cation-exchange membranes (non-used membranes and used membranes at different values of current) was investigated by the FT-IR spectroscopy (see Figs. 6 and 7). The samples were examined before and after exposure to electro dialysis process.

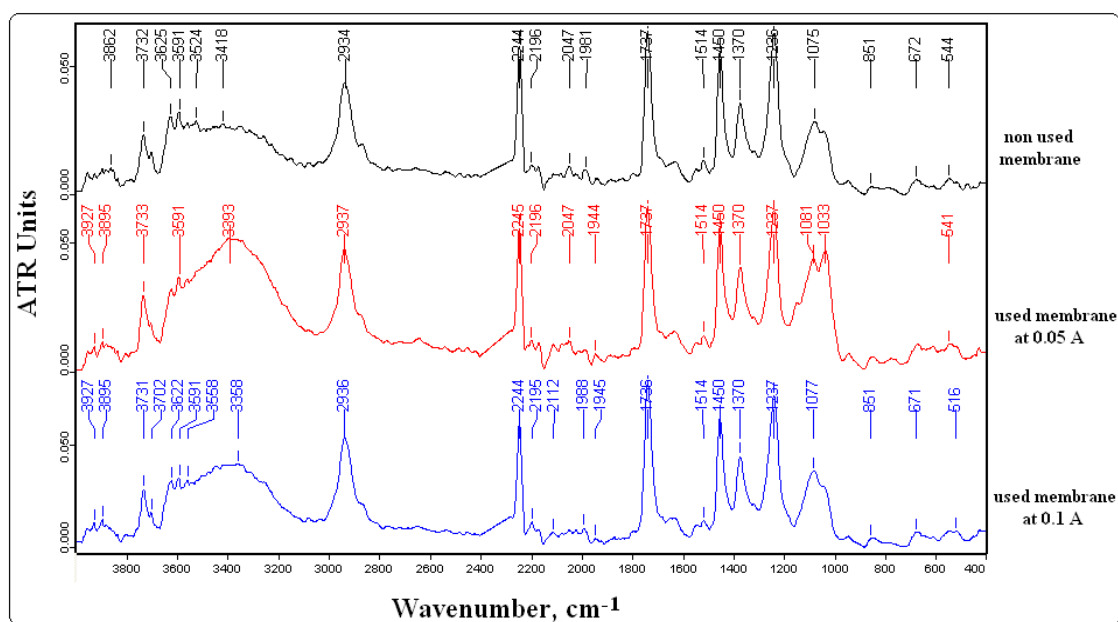


Fig. 6. FT-IR spectra of acrylic anion exchange membranes, for different values of current.

After evaluation of FT-IR spectra of acrylic anion-exchange membranes (fig. 6), were not observed significant modification between the samples, indicating that the membranes were not damaged during the electro dialysis, after one hour.

It was observed that in case of the spectra of the loaded anion exchangers, the peak that appears at  $3393\text{ cm}^{-1}$  is shifted to lower wave numbers ( $3358\text{ cm}^{-1}$ ) (used membrane) and is due to stretching vibration of O-H.

The peaks that appear at  $2934\text{ cm}^{-1}$  is shifted to higher wave numbers and can be assigned to N-H (stretching vibration). The peak that appears at  $2244\text{ cm}^{-1}$  may be due to -OCN stretching vibration.

Peak observed at  $1737\text{ cm}^{-1}$  may be due to C=O stretching vibration from acrylic component. This fact shows that new chemical bonds are formed between the acrylic component and ion exchanger (Purolite A100).

The peaks that appear at  $1450\text{ cm}^{-1}$  can be assigned to asymmetrically N=N-O stretching vibration and peaks that appear at  $1370\text{ cm}^{-1}$  may be due to C-N stretching vibrations.

The peaks that appear at  $1075\text{ cm}^{-1}$  is shifted to higher wave numbers ( $1081\text{ cm}^{-1}$ ) and may be due to aromatic =C-H in-plane deformation vibrations [18, 19].

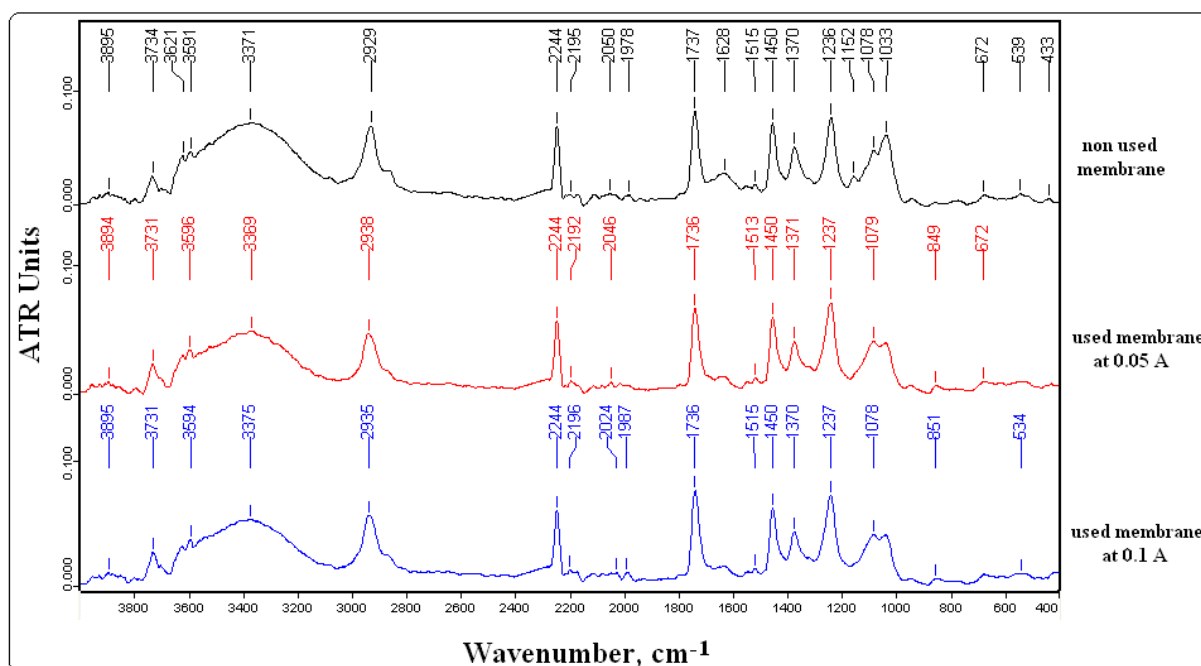


Fig. 7. FT-IR spectra of acrylic cation exchange membranes, for different values of current.

After evaluation of FT-IR spectra of acrylic cation-exchange membrane (fig. 7), also were not observed significant modifications between the samples, indicating that these membranes were not damaged during the electro dialysis, after one hour.

From Fig. 7 it was observed that in case of the spectra of the loaded cation exchangers, the peak that appears at  $3371\text{ cm}^{-1}$  is shifted to higher wave numbers ( $3375\text{ cm}^{-1}$ ) and can be assigned to O-H stretching vibration.

The peak that appear at  $2929\text{ cm}^{-1}$  is shifted to higher wave numbers ( $2935\text{ cm}^{-1}$ ) and may be due to the asymmetrically  $\text{CH}_3$  stretching vibration.

Peak observed at  $2244\text{ cm}^{-1}$  is due to CN.

The peak that appear at  $1737\text{ cm}^{-1}$  can be assigned to C = O bond (stretching vibration) and the peak that appears at  $1450\text{ cm}^{-1}$  can be assigned to C=C stretching vibration.



A medium intensity band is observed in all spectra at  $1370\text{ cm}^{-1}$  and is due to O-H deformation and C-O stretching vibration interaction.

Asymmetrically  $\text{SO}_3$  stretching vibration was observed at  $1237\text{ cm}^{-1}$  and may be due to the sulphonic acid group.

The peak that appear at  $1078\text{ cm}^{-1}$  can be assigned to S=O stretching vibration [18, 19].

## CONCLUSIONS

From the investigations in electrochemical impedance spectroscopy for acrylic ion-exchange membrane systems the following results have been obtained:

- the difference between the impedance values was an increase in the impedance magnitude due to the ohmic behavior of the pronounced concentration polarization by an increase of current;
- the value of ionic conductivity increases with increasing values of current. The ionic conductivity of acrylic anion exchange membrane is higher comparative with acrylic cation exchange membrane, in particular at value of current at 0.10 A, due to the low value of resistance  $R_1$ .
- the value of the resistance of the system at the limit of zero frequency decreases as current increases;
- with increasing value of current, the resistance of depleted diffusion boundary layers increases, while that of enriched diffusion boundary layer decreases. At the same time, the conductivity term contribution in the depleted diffusion boundary layer increases;
- the resistances of the diffusion boundary layer and the interfacial ionic charge transfer through the double layer for anion exchange membranes are lower than for cation exchange membranes. This is due to the difference in ion mobility between  $\text{Cu}^{2+}$  ions and  $\text{SO}_4^{2-}$  ions.

After evaluation of FT-IR spectra of acrylic anion and cation-exchange membranes were not observed significant modification between the samples, indicating that the membranes were not damaged during the electrodialysis, after one hour.

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