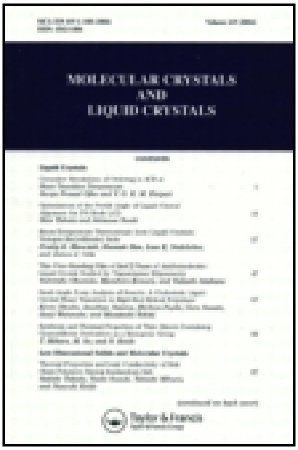

# Molecular Crystals and Liquid Crystals

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# FACILITATED TRANSPORT OF CATIONS (COPPER, SILVER, ZINC) BY SOLID DENSE MEMBRANES

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*For the removal of heavy metals, such as copper, zinc and silver from industrial effluents specific membranes have been developed containing carriers that are capable to transport these ions at a high rate by a facilitated transport mechanism. The carriers (crown ethers) are coupled to a polymer resulting in a fixed carrier membrane. We investigated the transport of silver, copper and zinc ions by sulfonated polisulfone and polyether ether ketone membranes modifies with crown-ether.*

## INTRODUCTION

Environmental pollution is one of the major problems that mankind is facing today. Severe pollutants such as heavy metals (cadmium, lead, copper, zinc, nickel) are on a so-called 'priority list', which means that these compounds should not be present in our eco-system. However, there are still many industrial effluent streams, such as from the metallurgical industry, which constitute still severe pollution problems. New separation techniques are required with a high separation performance and at low energy

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In Memoriam. Dr. Eng. M.H.V. Mulder. Address correspondence to Mihaela Emanuela Craciun, politehnica University of Bucharest, Polizu Street, no 1, Bucharest, Romania. E-mails: m_craciun@chim.upb.ro or me_craciun@yahoo.com consumption capable of removing heavy metals very specifically. Membrane technology can be employed using the concept of carrier mediated transport [1]. Liquid membrane technique was a solution to recovery and separation of cations from waste water. In the course of time different solutions were studied to improve the stability of the liquid membranes. A new approach was studied to fix the carrier in a polymeric membrane. Following the same procedure we studied the transport of cations (copper, zinc and silver) through fixed site polymeric films.

## MATERIALS AND METHODS

All chemicals used in experiments were of analytical purity and used as supplied if not stated otherwise. The transport device was washed with $HNO_3$ 0.5 M after the transport experiments in order to remove all the traces of metal ions that might deposit on the glass and plastic tubes, and flushed several times with demineralised and distilled water. The prepared membranes were kept in a $NaN_3$ solution 0.1% and flushed with demineralised and distilled water for several times before using them in the transport experiments. The re-used membranes were washed with $HNO_3$ 0.5 M, then with demineralised and distilled water.

The analytical determination was done with atomic absorption SOLAAR 969 AA.

The **synthesis of the carrier (EC)** [*2,3,11,12-bis*(*11-aminoundecylcarbonyl*)*-18-crown-6*] ($DB18C6COC10NH_2$) was done by [2]. ***Sulfonated polysulfone*** (PSS) was prepared according to [3] and characterized by standard characterization methods such as ion exchange capacity, electrical resistance, permselectivity [4].

***Sulphonated polyether ether ketone*** (*SPEEK*) was prepared according to [5,6]. The polymer was characterised by standard characterisation methods such as ion exchange capacity, electrical resistance, and permselectivity.

***The fixed site carrier membranes*** were prepared as follows:

A 25% polymer (sulphonated polyethersulfone and polyether etherketone) solution in N methyl pyrrolidone (NMP) containing an equivalent quantity of carrier is prepared. The quantity of carrier is calculated from the number of $SO_3H$ groups present in the polymer. To each two groups one molecule of carrier is added. For nonsulfonated polymer we kept the same quantity of carrier as for the sulfonated ones in order to have a comparison in behavior between the two membranes.

After de-aeration, the solution was cast in a thin film of 0.2 μm on a glass plate using a doctor blade knife. The film was dried for 24 h at 70°C and then immersed in a deionized water bath (to facilitate the removal of the film from

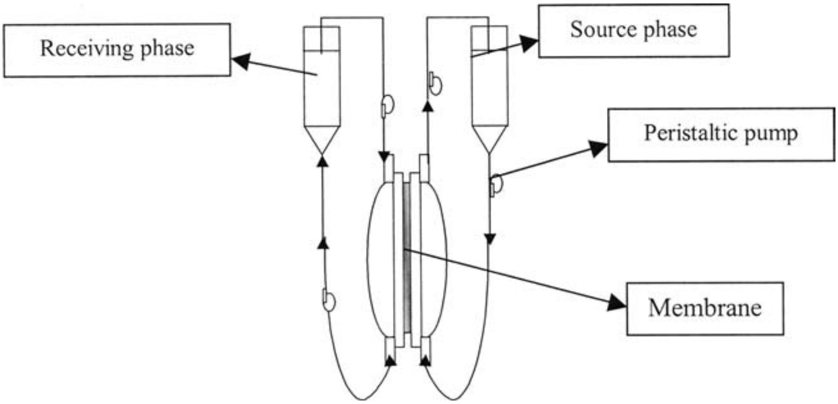

**FIGURE 1** Schematic experimental device for the transport experiments.

the glass plate). In order to study the transport of ions through the above-prepared membranes an experimental device according to Figure 1 was used.

The main device consists of two glass compartments that are separated by the membrane. In order to keep membrane and avoid any leakeage the glass necks are polished. The device has also two peristaltic pumps that are recirculating the source and receiving phase from two storage glass vessels. The flow on the membrane surface is counter current. All the experiments were carried out at 20°C and the same geometrical conditions.

The *experimental conditions* were:

- Active surface of the membrane: 17.34 cm$^2$;
- Cell volume: 500 ml.

## TRANSPORT EXPERIMENT

The silver, copper and zinc transport was carried out at two different initial concentrations 0.025 M and 0.1 M in the source phase. The receiving phases used were: $NH_3$ 1 M, $H_2O$, $HNO_3$. The mixtures transport was copper and silver (with the initial concentration 0.025 M $Cu(NO_3)_2$ and 0.025 M $AgNO_3$ in the source phase) and zinc and copper (with initial concentration 0.025 M $ZnSO_4$ and 0.025 M $CuSO_4$ in the source phase); the receiving phases used are: $NH_3$ 1 M, $H_2O$, $HNO_3$.

## RESULTS AND DISCUSSIONS

Transport experiments with a mixture of metals ($Cu^{2+}$, $Zn^{2+}$, $Ag^{+}$) were performed with the ion-exchange membranes. Three different receiving phases were investigated; ammonia solution 1 M, water and an acid solution 1 M (sulphonic acid and nitric acid). In addition bulk experiments were carried out to determine the association constant of metal ion and carrier. The carrier used in the transport experiments was suitable for silver and less for copper and zinc. This is due to the dimensions of the various species (the cavity of the 18-crown-6 ether carrier $d_{\text{18-crown-6}} = 3.2\,\text{Å}$ and $dCu^{2+} = 0.96\,\text{Å}$, $dZn^{2+} = 1.2\,\text{Å}$ and $dAg^{+} = 3.2\,\text{Å}$, respectively). Copper and zinc ions are transported through the ion exchange complexant membranes through a typical ion exchange mechanism via the $SO_3H$ groups. Figures 2 and 3 show that for two different sulphonated polymers the influence of the carrier of the transport of zinc is insignificant.

From Figures 2 and 3 it can be seen that in the case of water the zinc flux is the lowest. This is due to the fact that with water no counter-current transport takes place and the zinc flux is related to zinc gradient across the membrane as driving force. In the case of sulphuric acid counter-current transport takes place and the zinc flux is now driven by the proton gradient across the membrane. With ammonia as receiving phase a flux decline can be observed which is due to the precipitation of zinc hydroxides at the membrane surface. For copper the same behaviour occurs as for zinc as can be seen in Figures 4 and 5.

Comparatively with zinc transport the $NH_3$ 1 M as receiving phase has a stronger effect on the copper transport. When $NH_3$ is used as receiving phase and PSS membranes the flux is decreasing very quickly due to the transport of $NH_3$ towards the source phase. Also for this system a precipate at the membrane surface could be observed which causes a flux decline. The copper flux is higher for $NH_3$ 1 M in the receiving phase for the first 2 hours. This can be explained by the formation of a very stable complex

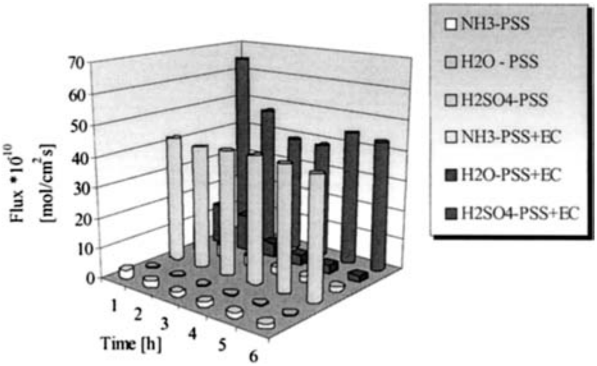

**FIGURE 2** The flux of zinc for: sulfonated polysulfone (PSS) membrane and crown ether sulfonated polysulfone (PSS-EC) membrane.

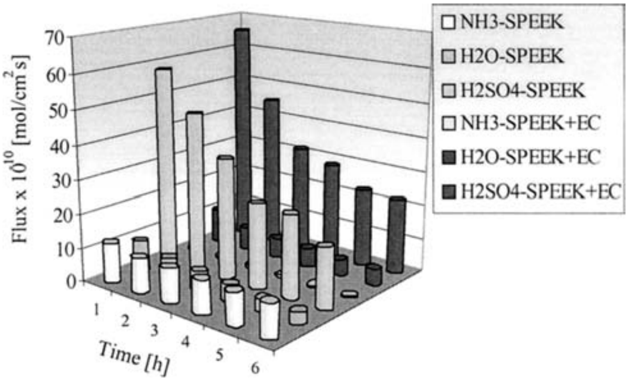

**FIGURE 3** The flux of zinc for: sulphonated polyether ether ketone (SPEEK) membrane and crown ether sulphonated polyether ether ketone (SPEEK-EC) membrane.

($pK_{2Cu(NH_3)^{2+}} = 13.5$). During this time a precipitate is formed on the feed site of the membrane, precipitate that is increasing the thickness of the membrane and in consequence in decreasing the flux.

The difference in transport observed between the two ions zinc and copper for $NH_3$ 1 M as receiving phase can be due to solubility of the precipitates that are formed on the source phase side of the membrane. For copper a complex is formed where for zinc a hydroxide that becomes soluble only when an excess of $NH_3$ is present. As a result the transport properties on the source phase side are different depending on the precipitated that is present on the surface.

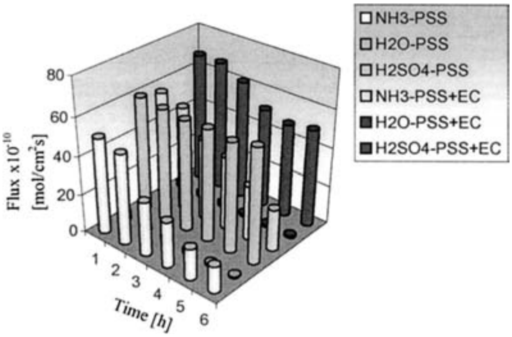

**FIGURE 4** The flux of copper for: sulfonated polysulfone membrane (PSS) and crown ether sulfonated polysulfone membrane (PSS + EC).

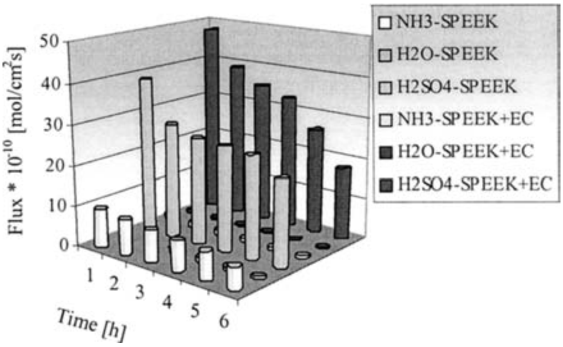

**FIGURE 5** The flux of copper for: sulphonated polyether ether ketone membrane (SPEEK) and crown ether sulphonated polyether ether ketone membrane (SPEEK-EC).

The transport of copper and zinc through the ion exchange membranes with and without carrier takes place via an ion exchange mechanism. In consequence is expected that no difference should occur when the two ions are in mixture in source phase. Indeed as it can be clearly seen form the results represented on Figures 6 and 7 no real difference appears between the fluxes for copper and zinc when using two different membranes.

The results should be totally different when silver is used in the source phase. As explained earlier silver fits well in the cavity of the carrier so the presence of the crown ether is inducing facilitation in the transport. Indeed the best transport results were obtained (Figs. 8 and 9) when membranes

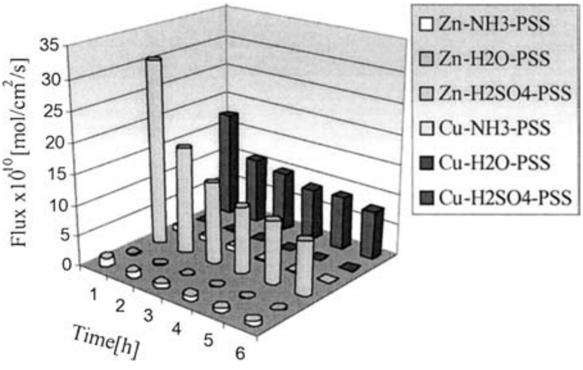

**FIGURE 6** The flux of Copper and Zinc through sulfonated polysulfone membrane (PSS).

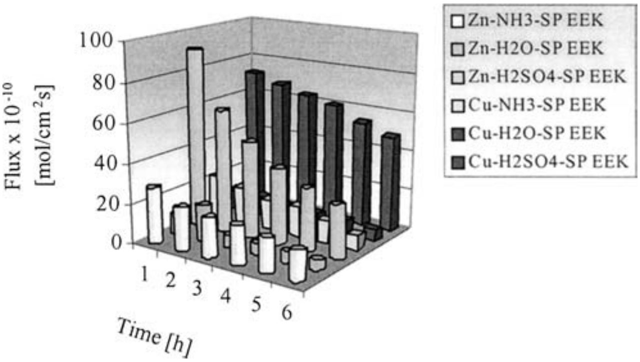

**FIGURE 7** The flux for Copper and Zinc through sulphonated polyether ether ketone membrane (SPEEK).

contained crown ether and the receiving phase was nitric or sulphuric acid. When $NH_3$ is used as receiving phase a complex is formed between $NH_3$ and silver ions, complex with high stability ($pK_{s\,Ag(NH_3)^{2+}} = 6.5$). Normally such complex should enable the transport of silver across the membrane. On the other hand others phenomena are taking place related to a possible precipitation of silver due to the presence of $HO^-$ ions that are transported across the membrane.

Frequently the receiving phases with sulphuric acid show a higher flux than with ammonia or water. Since protons have the highest transport rates across ion-exchange materials it is expected that in counter-current

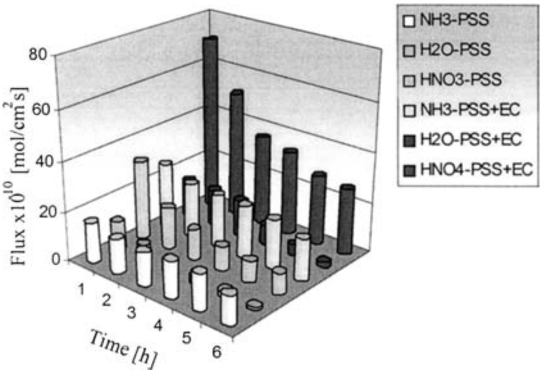

**FIGURE 8** The flux of silver for: sulfonated polysulfone membrane (PSS) and crown ether sulfonated polysulfone membrane (PSS + EC).

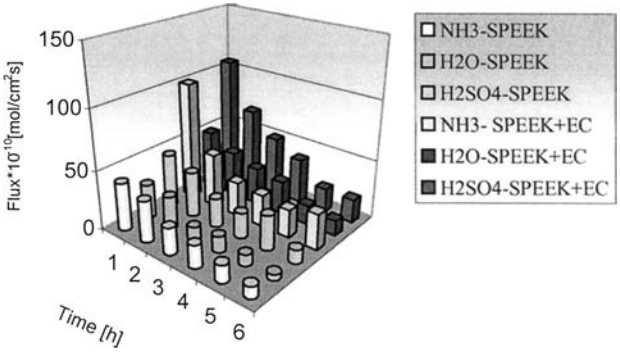

**FIGURE 9** The flux of silver for: sulphonated polyether ether ketone membrane (SPEEK) and crown ether sulphonated polyether ether ketone membrane (SPEEK-EC).

transport with a strong acid as receiving phase a much higher metal ion rate will occur compared to water as receiving phase. With ammonia often a flux decline is observed which is caused by the precipitation of metal-ammonia complexes that induce an additional resistance.

Silver was transported by a different mechanism: facilitated via the carrier and an ion exchange mechanism.

As it can be clearly seen in Figure 10 the presence of carrier in sulphonated polysulphone dense membranes is facilitating the transport of silver against copper and zinc.

The selectivity for complexing sulphonated polysulfone with carrier for silver towards copper was $S_{Ag^+/Cu^{2+}} = 118$ after 6 hours with $HNO_3$ 1 M as receiving phase, and $S_{Ag^+/Cu^{2+}} = 42$ after 6 hours with $NH_3$ 1 M as receiving phase.

## TRANSPORT MECHANISM FOR COUPLED FACILITATED TRANSPORT

In case sulphuric acid or nitric acid is used as receiving phase there are two fluxes in opposite directions and the transport is so-called counter-currently. This is shown schematically in Figure 11.

The metal ion transport is driven by the proton transport and the metal ions may diffuse against its own concentration gradient. On the other hand if water is used as receiving phase there is no counter-transport and in this case we have 'an ordinary facilitated transport' of copper and zinc. The ion-exchange membranes can be considered as fixed site carrier membranes and as has been shown the presence of the crown ether does hardly affect

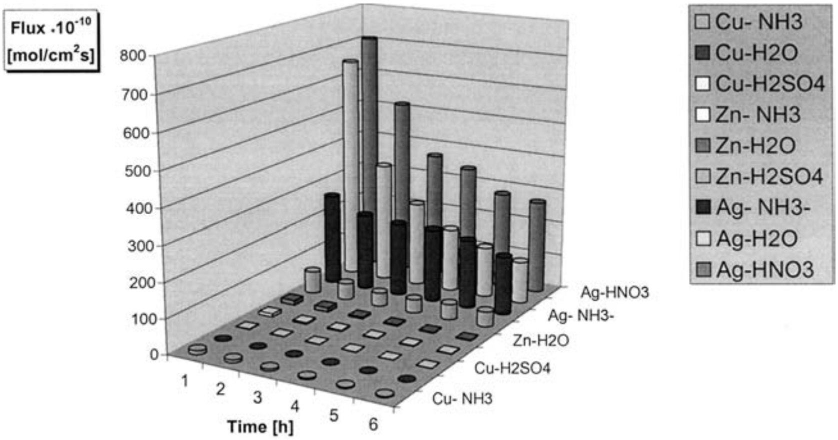

**FIGURE 10** Flux of copper, zinc and silver in sulfonated polysulfone membrane (PSS) with carrier and ammonia, sulphuric acid and water as receiving phase.

the transport of copper and zinc ions, only in case of silver a strong facilitation occurs.

For zinc and copper the same mechanism takes place and in the following only copper will be considered. The reaction of the process is:

$$Cu^{2+} + 2\ RH \leftrightarrow R_2Cu + 2H^+$$

R represents a sulphonic acid group. The reaction is driven by the protons forcing metal ions to transport counter-currently since electroneutrality should be maintained. In addition, the reaction proceeds much faster than the diffusion process. If it is assumed that the ion transport

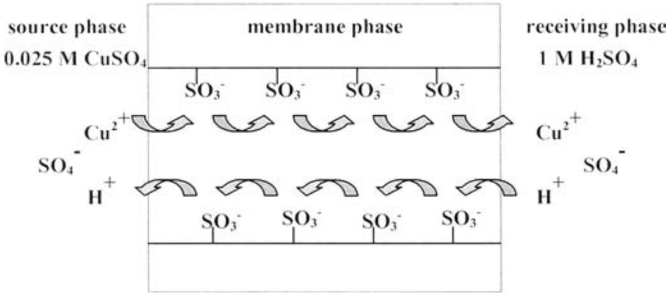

**FIGURE 11** Counter-current transport of $H^+$ and $Cu^{2+}$ across a sulphonated polymeric membrane.

(of both protons and metal ions) proceed by the active site (sulphonic groups) only and no free diffusion takes place then the proton flux in a counter-current process is given by:

$$\begin{aligned} J_{tot,H^+} = {} & k_l \cdot D_{H^+}/1 \cdot (c_{R-} \cdot [H^+]^r \cdot K_1(1 + k_2 \cdot [Cu^{2+}]^s \cdot K_2)/ \\ & (1 + k_1 \cdot [H^+]^r \cdot K_1 + k_2 \cdot [Cu^{2+}]^s \cdot K_2) \\ & - k_1 \cdot D_{H+}/1 \cdot (c_{R-} \cdot k_1 \cdot [H^+]^r \cdot K_1 k_2 \cdot [Cu^{2+}]^s \cdot K_2) \\ & \times (1 + k_1 \cdot [H^+]^r \cdot K_1 + k_2 \cdot [Cu^{2+}]^s \cdot K_2) \end{aligned} \tag{1}$$

Subscripts 1 and 2 refer to proton and copper ions respectively and superscripts r and s stands for receiving phase and source phase, respectively. Equation 1 clearly shows that the fluxes are coupled and that copper has a retarding effect on the diffusion of protons as indicated by the second term on the right hand side.

In order to compare the copper/zinc fluxes with either sulphuric acid or water as receiving phase we will consider binary diffusion only. The proton complexation can be given by:

$$[H^+] + [RSO_3^-] \leftrightarrow [RSO_3H] \tag{2}$$

or

$$[RSO_3H] = K_1 \cdot [H^+] \cdot [RSO_3^-] \tag{3}$$

The average number of sulphonic acid groups is given by

$$c_{R-} = [RSO_3^-] + [RSO_3H] \tag{4}$$

in which the first term at the right side represent the uncomplexed sulphonic acid groups and the second term the complexed sulphonic acid groups.

Substitution of Eq. (2) into Eq. (3) gives

$$c_{R-} = [RSO_3H]/[H^+] \cdot K_1 + [RSO_3H] \tag{5}$$

or

$$c_{R-} = ([RSO_3H](1 + [H^+] \cdot K_1))/[H^+] \cdot K_1 \tag{6}$$

and

$$[RSO_3H] = c_{R-} \cdot [H^+] \cdot K_1/(1 + [H^+] \cdot K_1) \tag{7}$$

The total proton flux is given by

$$J_{tot,H^+} = J_{H^+} + J_{H^+}^{comp} \tag{8}$$

assuming that tranport only takes place along the sulphonic acid groups Eq. (8) becomes.

$$\begin{aligned} J_{tot,H^+} &= -D\,d[RSO_3H]/dx = -D\,d \\ &\times (c_{R-} \cdot [H^+] \cdot K_1/(1 + [H^+] \cdot K_1))/dx \end{aligned} \tag{9}$$

integration across the membrane and introducing a distribution coefficient $k_1 = [H^+]^r/[H^+]$ where $[H^+]^r$ is the proton concentration in the receiving phase gives

$$\begin{aligned} J_{tot,H^+} &= -D\,d[RSO_3H]/dx \\ &= -D_{H^+}/1 \cdot (c_{R-} \cdot k_1 \cdot [H^+]^r \cdot K_1/(1 + k_1 \cdot [H^+]^r \cdot K_1))/dx \end{aligned} \tag{10}$$

integration across the membrane gives

$$J_{tot,H^+} = D_{H^+}/1 \cdot (c_{R-} \cdot k_1 \cdot [H^+]^r \cdot K_1/(1 + k_1 \cdot [H^+]^r \cdot K_1)) \tag{11}$$

the copper flux is given as

$$J_{tot,Cu2} = D_{Cu2^+}/1 \cdot (c_{R-} \cdot k_2 \cdot [Cu^{2+}]^r \cdot K_2/(1 + k_2 \cdot [Cu^{2+}]^r \cdot K_2)) \tag{12}$$

The ratio of the two flux equations is given by

$$\begin{aligned} J_{tot,H^+}/J_{tot,Cu2} &= D_{H^+}/D_{Cu2^+} \cdot (k_1 \cdot [H^+]^r \cdot K_1/(k_2 \cdot [Cu^+]^r \cdot K_2) \\ &\times (1 + k_2 \cdot [Cu^{2+}]^s \cdot K_2)/(1 + k_1 \cdot [H^+]^r \cdot K_1) \end{aligned} \tag{13}$$

Assuming that the distribution coefficients and equilibrium constants of $H^+$ and $Cu^{2+}$ are more or less equal then Eq. (13) is simplified to

$$J_{tot,H^+}/J_{tot,Cu2} = D_{H^+}/D_{Cu2^+} \tag{14}$$

Since the diffusion coefficients of protons in ion-exchange materials is about one order of magnitude higher than of the copper and zinc ions it is expected that the metal flux with sulphuric acid as receiving phase is about one order of magnitude higher than with water as receiving phase. As can be seen from Figures 3–10 this is confirmed by experiments. In case of silver the effect of the crown-ether becomes dominant as can be seen from Figures 8 and 9. If only the binary case is considered then Eq. (12)

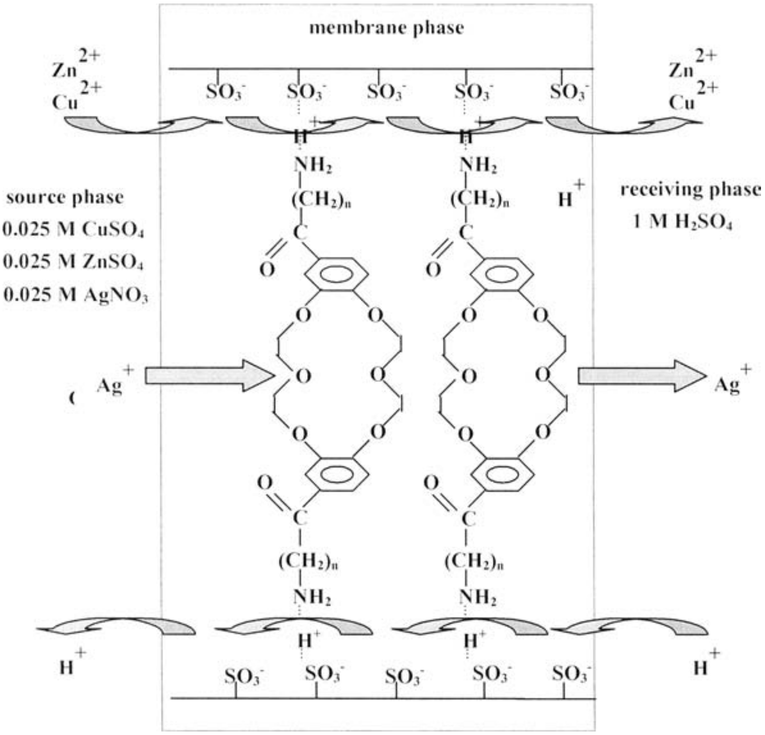

**FIGURE 12** Transport of copper, zinc, and silver across-an ion-exchange membrane with carrier.

also holds for silver and now the complexation constant or equilibrium constant K is very large since silver perfectly fits into the cavity of the crown resulting into a high flux. Figure 12 shows schematically the transport mechanism of copper, zinc and silver in one figure.

## CONCLUSIONS

The ion-exchange sulphonated polysulfone and sulphonated polyetheretherketone membranes developed in this project, showed excellent permeability properties for the removal of heavy metals such as copper, zinc and silver.

They offered an excellent alternative to support liquid membranes (SLM) due to a higher mechanical stability. The ionic fluxes were comparable to the ones in SLM's.

The effect of the crown-ether complexant had only a limited effect for Cu or Zn metal ions but it was significant for silver due to dimensional compatibility.

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