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INFLUENCE OF THE CARRIER (DIBENZO-18 CROWN-6) ON LIQUID MEMBRANE IODIDE SEPARATION

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A fost studiat mecanismul de transport al anionului iodură prin membrane lichide de cloroform, tetraclorură de carbon cu dibenzo-18-coroană-6 Experimentele s-au efectuat într-o instalaţie dublu jet ce constă dintr-o fază sursă (ce conţine dicromat de potasiu, acid sulfuric şi iodură de potasiu), membrana (cloroform şi tetraclorură de carbon) şi faza receptoare (soluţie de tiosulfat de sodiu). Efectul pozitiv al eterului coroană asupra transportului de iod a fost remarcat pentru ambii solventi dar în mod special s-a remarcat acţiunea faţa de solventul nepolar, tetraclorura de carbon.

Iodide anion transport mechanism of liquid chloroform and carbon tetrachloride membrane with dibenzo - 18-crown-6 has been studied.. Experiments were carried out in a double jet installation consist of source phase (containing potassium dichromate, sulphuric acid and potassium iodide), membrane (chloroform and carbon tetrachloride) and receiving phase (sodium thiosulfate solution). Experiments were conducted in a double-jet installation. Iodine concentration shave been monitored. The crown ether has positive effect on the iodine transport in both solvents but especially in the non-polar solvents as carbon tetrachloride.

Keywords: liquid membranes, iodide separation, transport mechanism

1. Introduction

Crown ethers are of interest for the selective extraction of ions and organic molecules from aqueous solution. Experiments on the introduction of carriers in liquid membranes, for the activation of anions mass transfer have been reported for amino acids [1-3].

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Economic advantages and efficiency of the liquid membranes recommend them as solutions of metal (Ag, Pt, Au, etc) and toxic products (phenol, cyanide, etc) recovery [4, 5].

Supported liquid membranes have been used to the remove iodide anion from aqueous solution. The removal of ions has growing importance to the environmental problems. Liquid membranes have shown a great potential for iodine recovery from low concentrated solutions. The advantages of liquid membrane transport against conventional separation techniques are low costs, small space requirements and low energy consumption. Vural et al. [6, 7] used bulk liquid membrane with calixarene as carrier to extract iodine at low concentrations in feed solution. [8].

We studied the iodide anion membrane transport mechanism of supported liquid membrane with a chloroform and carbon tetrachloride membrane and dibenzo - 18 –crown ether-6 as carrier.

2. Experimental part

Reagents and materials

Reagents used were of analytical purity. In the preparation of the source phase potassium dichromate (Merck), sulfuric acid (Merck) and potassium iodide (Merck) were used and for preparation of receiving phase was used sodium thiosulfate (Merck).

Chloroform and carbon tetrachloride used as the transport membrane (Chimopar) was used after a preliminary purification by distillation followed by saturation with water.

Membrane system

The experiments were carried out with the help of a double jet installation presented in Fig. 1. The installation function as follows: the source phase and the receiving one are introduced in the separation dropping funnels. In the permeator, the chloroform membrane was introduced and the aqueous phases are collected in graded cylinders so that the working flow rate can be evaluated. Crown ether was added to membranes at concentrations of 10^{-3} M. Membrane with crown ether is contacted for 48 hours with 1M potassium iodide solution to remove the saturation time of membrane in iodide.

More information about the experimental installation set-up and work procedure was presented in a previous paper [9, 10].

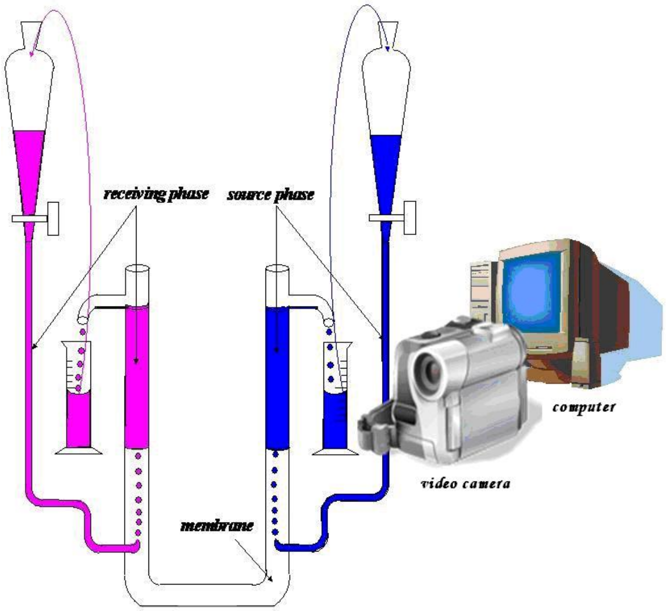


Fig.1. Schematic experimental installation

Analysis methods

The iodine content in the aqueous membrane system was determined spectrophotometrically with CAMSPEC^R apparatus, at $\lambda = 510$ nm.

The iodine transfer monitoring was done spectrophotometrically using a Cary 50 double beam spectrophotometer, at $\lambda = 510$ nm.

3. Results and discutions

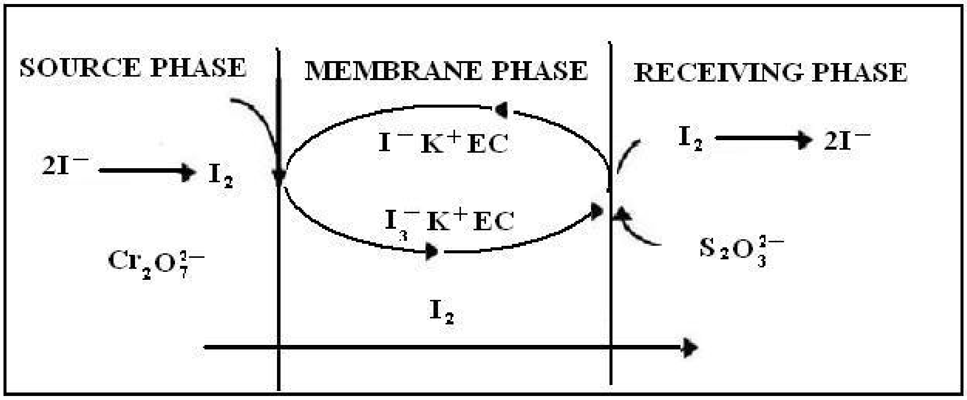
In the first phase of the study, chloroform and carbon tetrachloride were successively used as liquid membrane. The volume of membrane phase is 25.0 cm^3. The separation system, classical permeate cell, requires two separate compartments by organic solvent (liquid membrane), which is in contact with two aqueous phases. The interface is about 10 cm^2 and the amount of liquid membrane of 25.0 cm^3. 25.0 cm^3 sodium thiosulfate solution was used as receiving phase. The transport experiments were carried out in a transport cell, (fig. 1) described in detail in a previous paper [10, 11].

The iodide content from the source phase was determined by oxidation of potassium iodide with potassium dichromate in the presence of sulfuric acid to elemental iodine, followed by its extraction in chloroform. The iodine content of the membrane was determined spectrophotometrically from samples taken each half an hour. Iodide content of the receiving phase was established from the mass balance.

Iodide ion is oxidised in the source phase with potassium dichromate in acid catalysis (in the presence of sulfuric acid) to molecular iodine, which is transferred into the chloroform membrane. Iodide concentration is constant in the membrane, is transferred only molecular iodine. Iodine is transported through the membrane by diffusion mechanism.

Thus, the equilibrium translocation towards the way of the iodide anion transfers from the source phase in the receiving phase of the membrane system.

In the presence of dibenzo-18-crown-6 (EC) used as a marker, there is an improvement of the iodide ion transport.



Scheme 1

Experiments were conducted to see if the transport in presence of EC is enhanced and in order to evaluate each step of the iodine transport mechanism (Scheme 1):

- iodide ion is oxidate to molecular iodine in the source phase.

$$2I^- - 2e^- \rightarrow I_2$$

- molecular iodine penetrates the source phase – membrane interface being picked up as triiodide co-ion of potassium complexed crown ether.

$$K^+EC\ I^- + I_2 \rightarrow K^+EC\ I_3^-$$

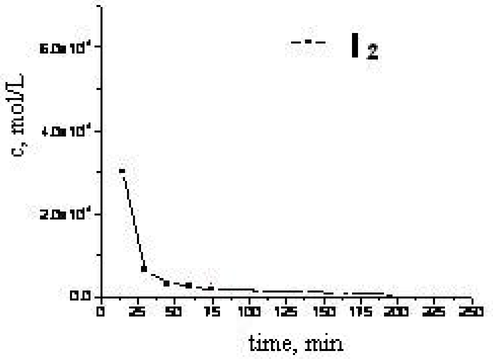
- chemical complex species $K^+EC\ I_3^-$, neutral and soluble, diffuses through membrane.
- iodine penetrates the membrane – source phase interface being taken by the aqueous phase in which occurs the reduction of iodine to iodide.

$$I_2 \rightarrow 2I^- + 2e^-$$

The two oxidation-reduction reactions in the source phase and receiving phase is the driving force of iodine transfer from source phase to receiving phase.

To evaluate the results were presented graphically as individual data, each experiment (Fig. 2 and 3). Crown ether used in membranes (dibenzo 18 - crown 6) in 10^{-3} M concentration increased membrane transport of iodine in all experiments. Was observed that the yield transfer improved and the time of transport was reduced.

In carbon tetrachloride the shape of iodine concentration curves is similar as in chloroform, but the parameters are different. There is a spectacular growth performance of the iodine transport yield observed in the presence of carbon tetrachloride from 84.8% in the absence of crown ether to 97.4% in its presence. This behaviour is consistent with the decrease polarity of the solvent in case of carbon tetrachloride in respect with chloroform.



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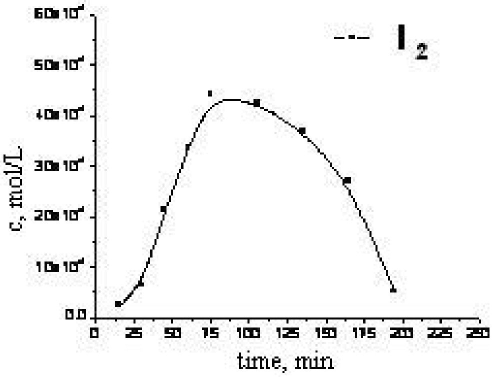

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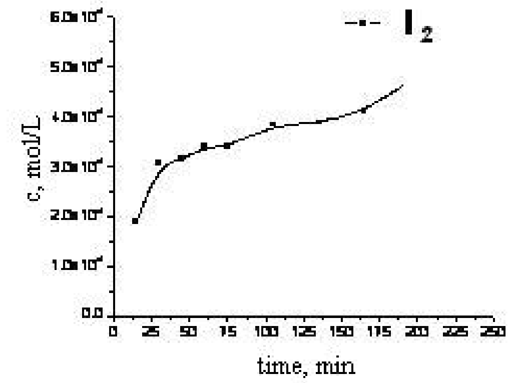

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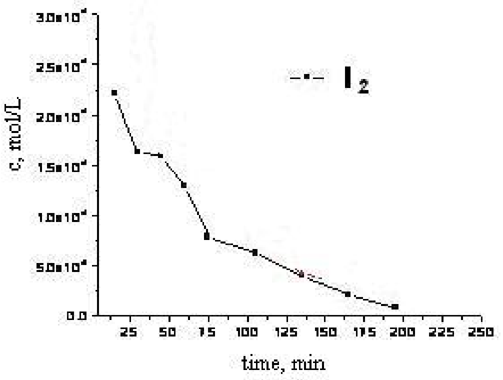
Fig.2. Concentration of iodine in the system phases with a membrane of chloroform and dibenzo-18-crown -6 (10^{-3}M). A- source phase; B- membrane; C- receiving phase.



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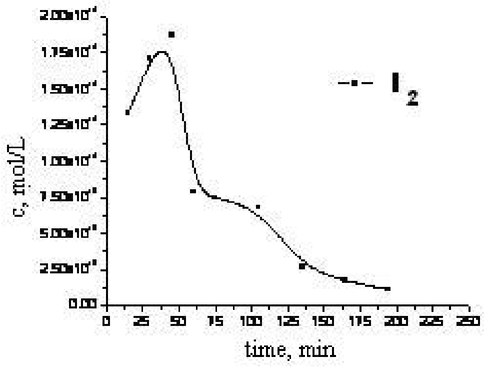

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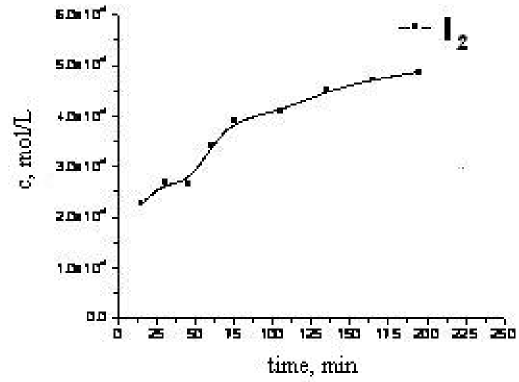

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Fig.3. Iodine concentration in the system phases with a membrane of carbon tetrachloride and dibenzo-18-crown -6 (10^{-3}M). A- source phase; B- membrane; C- receiving phase.

4. Conclusion

The influence of ether crown on iodide ion transport in membrane systems of source phase with chemical reaction type / chlorinated solvents and receiving phase, connected with the presence of carrier and the mass transfer mechanism is determined by solubilisation of iodine in the membrane solvent, but also with the formation of a complex form $\mathbf{I_3^-}$ ion and the crown ether which would increase the transport. The positive effect of the crown ether is remarkable for a non-polar solvent, as carbon tetrachloride.

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