Emulsion Membranes Iodine Separation
Iodine Separation with Emulsion Membranes Based on Cyclohexanol II

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Among non-metals, iodine, as molecular iodine but also as iodide anion, is of particular importance for regenerative separations, justified by the technological importance, but especially by the biological importance, including the nuclear accidents (radioactive aerosol generation). In this paper is presented the regenerative separation of iodine from dilute aqueous solutions using emulsion liquid membranes based on cyclohexanol. For the study, a technical variant of emulsified liquid membranes was approached, with a membrane (M) less dense than water, based on cyclohexanol, in which the aqueous and receiving phase were dispersed. Synthetic feed solution (FS) simulates the composition of aerosols generated by: borehole water or seawater and has an iodine content of 20-200ppm. For the amplification of mass transfer through cyclohexanol based membranes the iodide ion conversion to molecular iodine was investigated using two available oxidants: hydrogen peroxide and molecular chlorine.The comparative results of iodine separation from low concentrations solutions (50 ppm iodine ion) by transforming iodide ion into molecular iodine as a result of an oxidation reaction taking place in the source phase, indicates a significant increase of iodine separation with increasing the amount of oxidant dosed in the source phase up to 50-60 ppm, followed by a slow, but significant decrease.

Keywords: iodine separation, emulsion membranes, hydrogen peroxide, molecular chlorine, oxidant

Global economic conditions - in which refurbishment and experimenting new processes in both chemical industry and other productive sectors are necessary - require the study of some concentration methods and techniques with high efficiency [1-3].

These methods and techniques are generally directed for the recovery of useful substances existing in poor sources or for effluents treatment [4-7].

Separation and concentration of multicomponent liquid mixtures is one of the most important processes applicable in several areas: manufacturing, agriculture, ecology, medicine [8-11].

Real aqueous systems with complex composition should be studied by methods that are able to ensure both regenerative remediation and separation and concentration of valuable compounds [12-16].

The choice for *membrane techniques*, amongst many separation techniques, methods and processes was based on several considerations [17-21]:

- possible applicability in pre-analytical determinations step (separation and concentration of solute in order to bring the sample to the parameters required by the analysis method);
- possible applicability in the industrial effluent containing harmful heavy metals treatment processes;
- the successfully already use of membrane processes applied for the separation of chemical compounds in various fields: chemical and petrochemical, environmental protection, metallurgy, biotechnology, agro-food, transport, bio-medicine.

Concentration and separation using liquid membranes have experienced an explosive growth both for metal ions and organic substances recovery, in contrast to the separation, and in particular, the regenerative separation of anions or non-metals [21-25].

Among non-metals, iodine, as molecular iodine but also as iodide anion, is of particular importance for regenerative separations, justified by the technological importance, but especially by the biological importance, including the nuclear accidents (radioactive aerosol generation) [26-30].

In this paper is presented the regenerative separation of iodine from dilute aqueous solutions using emulsion liquid membranes based on cyclohexanol.

For the study, a technical variant of emulsified liquid membranes was approached, with a membrane (M) less dense than water, based on cyclohexanol, in which the aqueous and receiving phase were dispersed.

Synthetic feed solution (FS) simulates the composition of aerosols generated by: borehole water or seawater and has an iodine content of 20-200ppm.

The experiments were aimed to establish the conditions that allow the development of a technological process in order to concentrate the iodine from poor sources such as: borehole water (from oil extraction), mining (salt or metal) using emulsion membrane based on cyclohexanol.

Experimental part

Materials and equipment

In the study of iodine concentration using emulsion membrane based on cyclohexanol were used:

-source phase - aqueous solutions containing 20 and 120 ppm iodine (in the form of iodide anion);

-receiving phase - aqueous solution containing sodium thiosulfate, lead or silver ion;

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-membrane phase – cyclohexanol (Merck);
-emulsion stabilizers SPAN 20 (Sigma-Aldrich) and SPAN 80 (Sigma-Aldrich).

All reagents used in order to achive the source and receiving aqueous phases are analytical grade: I_2 (Merck), KI (Merck), $AgNO_3$ (Merck), $Pb(NO_3)_2$ (Merck), NaCl (Merck), $HClO_3$ (Merck), solutie HCl (Merck), KOH(Merck), H_2O_2 (Merck).

Equipment and analysis

The determination of the iodine content in the foam, after extraction in hexanol, was performed spectrophotometrically using a Cary double-beam 50 spectrophotometer at optimal wavelength = 510 nm.

The determination of iodine concentration in emulsion membrane system phases was carried out with a CAMSPEC spectrometer with the following characteristics: local control software - includes all methods, basic mode - absorbance measurements, % T and concentration; quantitative – can be used down to 10 standard solutions for one calibration; wavelength scanning - 200-800 nm; multiple wavelengths - up to 10 wavelengths, performance validating – for GLP according to laboratory.

Results and discussions

Sea, well and/or mine waters have a complex composition containing a variety of components in the form of soluble and insoluble ionic, molecular and colloidal species with variable concentrations, which are slowing the separation, removal or recovery [31,32].

Such aqueous systems require the application of available separation methods that allow the separation and/or recovery of useful components [33].

Between these methods: ion exchange, adsorption, reverse osmosis, ultrafiltration and liquid membranes have been intensively studied [31-34].

Emulsion membranes separation was rarely approached mainly to recover the heavy metal cations [35,36].

The objectives of the experiments regarding iodine concentration from poor sources made in this paper are as following.

Determining the volume ratio between source and receiving phase (SP/RP)

The role of the receiving phase is to collect, in a volume as small as possible, the useful component from the source phase, in this case: iodine.

Starting from the results regarding the maximum stability of the receiving phase emulsion in cyclohexanol, at 1:1 volume ratio, it is found that varying the source phase to the receiving phase ratio from 15: 1 to 150:1 (fig. 1), the iodine extraction efficiency remains relatively constant up to 120:1. The results were obtained using a source phase with a composition of 20 to 100 ppm I_2, the receiving phase consisted of 1M sodium thiosulfate, cyclohexanol membrane, a stabilizing agent 1.5% SPAN 80, and an emulsion-source phase contact time of 20 minutes.

From a practical point of view, it may be recommend as optimal an ratio SP / RP = 100:1, which would provide a concentration factor close to two orders of magnitude.

The decrease of separation efficiency with increasing the volume ratio between source and receiving phase can be determined by the increase of iodine concentration in source phase and thus a smaller collection capacity of the emulsion caused by concentration gradient decrease.

In the particular case of iodine poor sources may be ensured that a threshold of more than 1 g I_2/L is reached,

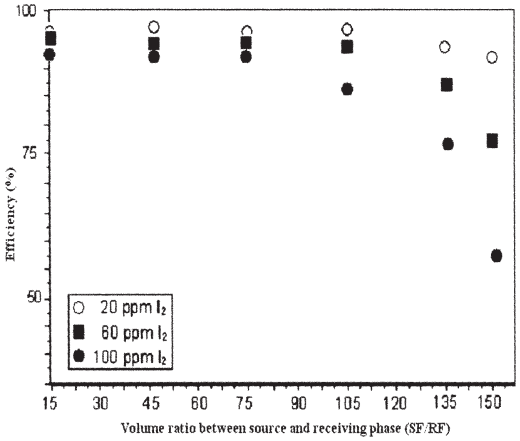

Fig.1. The iodine separation efficiency in cyclohexanol membrane system according to source/receiving phase volume ratio (SP/RP)

which enables the practical usage of the iodine resulted from the conventional technologies.

Determining the optimal pH in the source phase

The real systems from which iodine comes have a *p*H between 6 and 10 in the case of probe waters and under 4, in the case of mine waters.

This wide range of pH for source phases imposes the study of iodine separation efficiency in the given circumstances of the membrane system parameters:

- source phase of 50 ppm I_2;
- receiving phase 1 M sodium thiosulfate solution;
- volume ratio between source and receiving phase 100:1;
- membrane phase cyclohexanol;
- stabilizer SPAN 20 and SPAN 80 1.5%;
- contact time of 15 min.

The efficiency of iodine separation from weakly basic (fig.3), respectively acidic iodine containing solutions (fig. 2) shows that source phase *p*H value affects insignificantly the results.

In the case of all basic source solutions, the iodine separation efficiency is superior, fact which is explained by two cumulative favorable factors: the first one consists in the increase of receiving phase/cyclohexanol stability at *p*H increase and the second one, is related to the fact that basic *p*H is achieved with potassium hydroxide, which allows the amplification of triiodine ion formation whose transport through membrane is facilitated.

However, in the case of the stabilizer SPAN 20 low *p*H greatly reduces the efficiency of iodine separation, most likely caused by the co-transport of water.

Throughout the *p*H range the stabilizer SPAN 80 is superior for iodine separation by emulsion membranes based on cyclohexanol.

The study of the oxidant additives influence in source phase

The iodine sources considered to be useful in terms of the concentration and recovery of iodine rarely contain molecular iodine, the main chemical species in such sources being iodide ion.

For the amplification of mass transfer through cyclohexanol based membranes the iodide ion conversion to molecular iodine was investigated using two available oxidants: hydrogen peroxide and molecular chlorine.

The conditions of iodine concentration from poor sources (the average concentration of sources known as viable was chosen):

-source phase, 50 ppm iodide ion;
-receiving phase sodium thiosulfate 1M solution;
-cyclohexanol membrane stabilized with 1.5% SPAN 80;

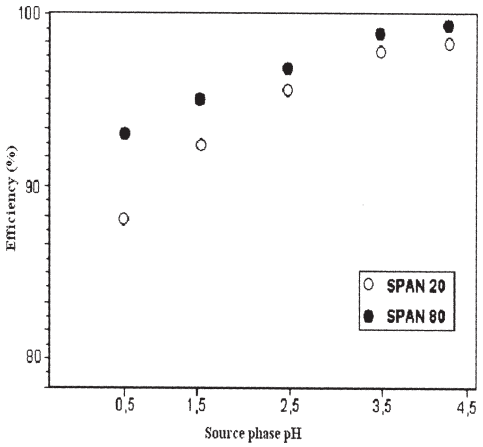

Fig. 2. Iodine separation effciciency in membrane system with cyclohexanol according to acid source phase pH

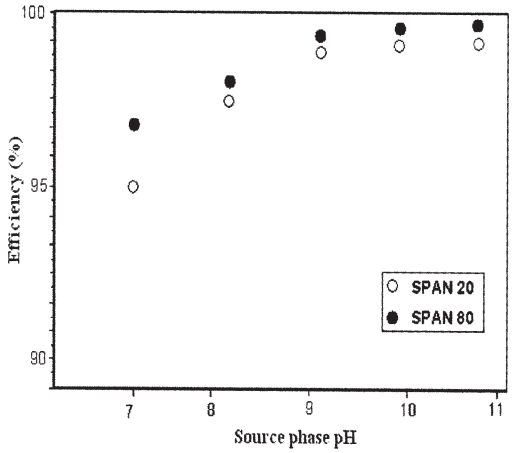

Fig. 3. Iodine separation effciciency in membrane system with cyclohexanol according to basic source phase *p*H

-oxidants: hydrogen peroxide and chlorine 10-100 ppm dosed in source phase;

-source phase/receiving phase ratio 100:1;

-contact time 15 min.

The comparative results of iodine separation from low concentrations solutions (50 ppm iodine ion) by transforming iodide ion into molecular iodine as a result of an oxidation reaction taking place in the source phase, indicates a significant increase of iodine separation with increasing the amount of oxidant dosed in the source phase up to 50-60 ppm, followed by a slow, but significant decrease. (fig. 4).

The explanation for these behaviours lies in the transformation of a portion of iodide ion from source phase in molecular iodine and the transfer through cyclohexanol membrane as tri-iodide ion and molecular iodine. The oxidant excess leads to the transformation of whole iodide ion amount in molecular iodine, which leads to a decrease and then capping of the separation efficiency is observed.

The results show that if it aims to increase the iodine separation efficiency from iodide solutions, the appropriate dosing of the oxidizing agent should be considered in order to not exceed the optimal threshold, which in this case is 50-60 ppm.

The study of receiving phase composition influence

The data presented in the previous chapter, and the results obtained at iodine concentration by volume liquid membranes based on medium saturated alcohols show that receiving phase must contain chemical species which immobilize iodine.

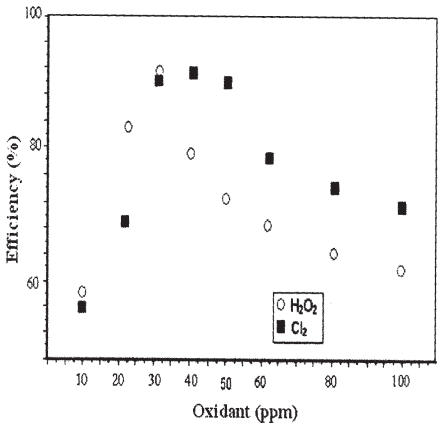

Fig. 4. Iodine separation effciciency in membrane system with cyclohexanol according to oxidants concentration from source phase

In the previous experiments as chemical species for iodine immobilization were used:

-thiosulfate ion, which entirely transforms iodine in iodide ion;

-lead ions, which sets the iodide as lead iodine, hardly soluble;

-silver ions, that form silver iodide or an anionic complex, depending on the amount of iodide ion transfered.

The study of iodine concentration with emulsion membrane based on cyclohexanol aimed to establish the influence of iodide ion fixing agent in the receiving phase, and the chemical speciation of iodine from source phase (iodine, iodide ion or tri-iodide ion).

Iodine separation data (fig. 5-7) under similar working conditions:

-source phase iodine 20-120 ppm;

-receiving phase thiosulfate, lead or silver ions 1M solution;

-cyclohexanol membrane stabilized with 1.5% SPAN 80;

-source phase/receiving phase ratio 100:1;

-contact time 15 min

indicates a superior extraction efficiency for receiving phase containing silver ion, on the whole range of source phase concentrations (20-120 ppm).

Iodine speciation in the source phase is important for all fixing agents from receiving phase, but the largest variations are found at iodine concentration from source phase containing iodide ion. For a superior concentration of iodine, it turns out that iodide ion must be oxidized, at least in part, to molecular iodine in source phase.

Full transformation of iodide ion from source phase in molecular iodine is beneficial for solubilization in

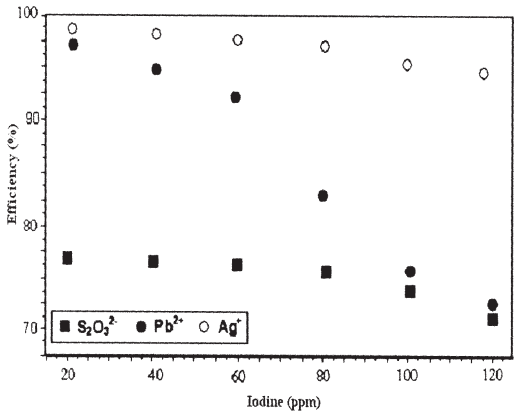

Fig. 5. Iodine separation effciciency in membrane system with cyclohexanol according to receiving phase composition, source phase with iodide ion

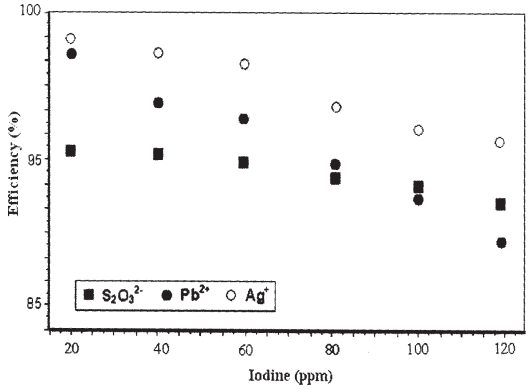

Fig. 6. Iodine separation effciciency in membrane system with cyclohexanol according to receiving phase composition, source phase with tri-iodide ion

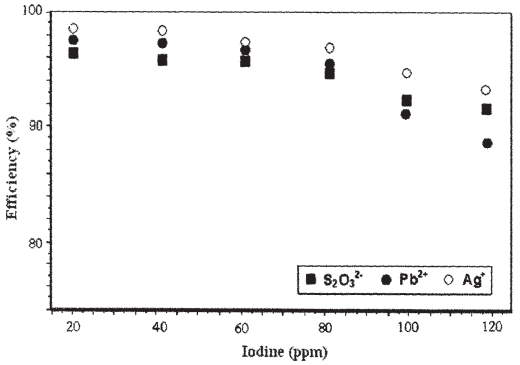

Fig. 7. Iodine separation effciciency in membrane system with cyclohexanol according to receiving phase composition, source phase with moleculare iodine

cyclohexanol based membranes, but raises fixing problems in receiving phase.

Membrane transport mechanism is diffusion and therefore, in all cases, it is recommended the transformation of iodide from source phase in molecular iodine, but on the other hand, this reaction requires a reduction reaction in the receiving phase, which usually is excellent ensured with thiosulfate ions.

Unfavorable iodine separation efficiency variations at higher concentrations (80-120 ppm) can be explained by the formation of precipitates at the interface of emulsion membrane / receiving phase in the case of metal ions and the decrease of thiosulfate concentration, hence the concentration gradient, in the case of fixing as iodide ion in the receiving phase.

Working with sodium thiosulfate as receiving phase will be followed by re-oxidation of iodide ion to iodine after breaking the emulsion, and when is fixed as silver or lead iodide, the iodine will be used under the form of these salts.

Determining the optimum contact time between emulsion and source phase

The optimum contact time between the source phase and the receiving phase/cyclohexanol emulsion can be determined appealing to the study of iodine separation efficiency depending on time, but also studying the effect of membrane swelling (receiving phase/cyclohexanol emulsion).

Operating conditions for establishing the optimum contact time between the source phase and the receiving phase/cyclohexanol emulsion:

- source phase of 50 ppm I_2;
- receiving phase 1 M sodium thiosulfate solution;

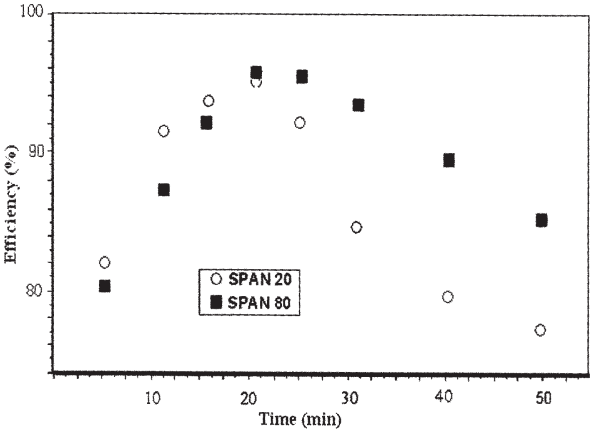

Fig. 8. Iodine separation effciciency in membrane system with cyclohexanol according to the contact time between phases

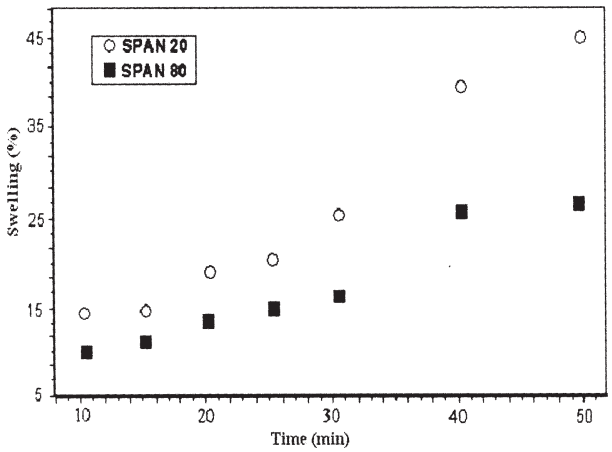

Fig. 9. Membrane swelling (cyclohexanol / receiving phase) according to the contact time between phases

- volume ratio between source and receiving phase 100:1;
- membrane phase cyclohexanol;
- stabilizer SPAN 20 and SPAN 80 1.5%.

The iodine separation efficiency from solutions with a concentration of 50 ppm in optimal operating conditions, increases in the range of 5 to 25 min, after which stagnates and then decreases sharply (fig. 8).

Emulsifiers SPAN contribute much to effective iodine concentration (fig. 8) as follows:

-in the first operation period SPANU 20 is more effective;

-in the second part of the concentration, the efficiency greatly decreases in the case of the same emulsifier.

Basically, an operation in which the negative effects are related to the breaking of the emulsions in time, requires a working range between 10 up to 25 min.

The decrease of concentration efficiency in time is due to swelling and then due to primary emulsion, receiving phase/cyclohexanol breakage.

The variation of emulsion swelling is more pronounced for SPAN 20, but it is not negligible even for SPAN 80, at contact times with source phase over 30 min (fig. 9).

Swelling and then breaking the receiving phase / cyclohexanol primary emulsion is the main cause of concentration and separation efficiency decrease in the case of emulsion type membrane. This phenomenon occurs due to the osmotic water effect, but also because chemical species carry water at the transfer from source to receiving phase.

If the operating time does not exceed an optimum, experimentally established, the emulsion swelling has no negative consequences, and in the case of SPAN 20, it can

be said that even an efficiency increase is observed due to emulsifier participation in transport.

Conclusions

The experiments aimed establishing the conditions that allow the development of a technological process for iodine concentration from poor sources such as: water probe (from oil extraction), those from mining (salt or metal) using emulsion membrane based on cyclohexanol .

From a practical point of view it may be recommend as the optimum a ratio SP/RP = 100:1, which would provide a concentration factor close to two orders of magnitude.

The decrease of separation efficiency with increasing the source phase/receiving phase volume ratio can be determined by the increase of iodine concentration in the source phase and thus, a smaller collection capacity of the emulsion caused by the concentration gradient decrease.

The efficiency of iodine separation from weakly basic (fig.2), respectively acidic iodine containing solutions (fig. 3) shows that source phase *p*H value affects insignificantly the results.

However, in the case of the stabilizer SPAN 20 low *p*H greatly reduces the efficiency of iodine separation, most likely caused by the co-transport of water.

Throughout the *p*H range the stabilizer SPAN 80 is superior for iodine separation by emulsion membranes based on cyclohexanol.

For the amplification of mass transfer through cyclohexanol based membranes the iodide ion conversion to molecular iodine was investigated using two available oxidants: hydrogen peroxide and molecular chlorine.

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Unfavorable iodine separation efficiency variations at higher concentrations (80-120 ppm) can be explained by the formation of precipitates at the interface of emulsion membrane / receiving phase in the case of metal ions and the decrease of thiosulfate concentration, hence the concentration gradient, in the case of fixing as iodide ion in the receiving phase.

Working with sodium thiosulfate as receiving phase will be followed by re-oxidation of iodide ion to iodine after breaking the emulsion, and when is fixed as silver or lead iodide, the iodine will be used under the form of these salts.

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