Regenerative iodine recuperation using medium saturated alcohols - based liquid membranes

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Abstract

This paper presents the regenerative separation of iodine from diluted aqueous solutions using liquid membranes, with and without carrier, based on medium saturated alcohols. For the study approach was used a technique variant of volume liquid membrane, with membrane (M) less dense than water, based on n-hexanol, n-octanol or n-decanol, in which source and receiving aqueous phases were dispersed. Synthetic feed solution (FS) simulates sea water or well (probe) water composition and has an iodine content of 20-200ppm. Receiving aqueous solution (FR) contains chemical species able to fix iodine as iodide ion (aqueous solution containing sodium thiosulfate and/or metal ions). Regenerative separation variable parameters were: dibenzo 18 crown 6 ether concentration and the nature of the alcohol that forms the membrane, iodine concentration, silver or lead ions concentration in receiving phase for invariable composition of the source phase (pH=0 and oxidizing agents K2Cr2O7). The results show a regenerative separation between 81.7 and 98.3%, with the best results, regardless of the concentration of iodine in feed solution, for hexanol, as the membrane phase and silver ion in the receiving phase.

Keywords: iodine separation, liquid membranes, regenerative recuperation, saturated alcohols

Introduction

Liquid membranes separation has seen explosive growth both for recovery of metal ions and organic substances, in contrast with separation, and in particular, with regenerative separation of anions or non-metals. From non-metals, iodine, as molecular iodine, but as well as iodide anion is of particular importance for regenerative separation, justified by the technological importance, but especially the biological one, including nuclear accidents. Because of its chemical properties, iodine is a bactericidal, sporicidal, protoacid, cisticid and virucide agent, aspects that give it application in various scientific and technical fields [1-3].

Iodine and its compounds are used in medicine, photography and various industries. Iodine is also biological involved, being an essential trace element for human body, involved in thyroid hormone synthesis.

Radioactive iodine emissions from nuclear disaster are affecting the thyroid and the administration of potassium iodide prevents the uptake in the gland.

Although iodine is not an abundant element, and iodine are very poorly soluble in water, the element is still present in relatively high concentrations in sea water or groundwater [2-4].

All the above considerations lead to the need of separation and recovery of iodine from various sources, using regenerative separation techniques.
Membrane techniques have become the main means of separation, concentration and recovery of important elements and substances from poor or difficult workable sources [5-9].

In this way, liquid membranes have opened up ways for separation and recovery of noble metal ions (Au, Ag, Pt, ...), but also metals of technological interest (Co, Ni, Cr, Cd, Zn, Cu, ...) from industrial effluents with economic and social purposes, but thus, also contributing to reducing their environmental impact [10-16].

Relatively little used in the separation and concentration of non-metals [17-23], membranes will be evaluated in this work for iodine regenerative separation from poor sources.

From the covered sources, sea water, well and mine water with contents from 20 to 200 ppm represent the main objects of the study, reason for which synthetic solutions research addressed in this paper fall or close to these limits.

Materials and Methods

Materials

All reagents used for prepraration of source and receiving aqueous phases are analytical purity: KI (Merck), AgNO₃ (Merck), Pb (NO₃)₂ (Merck), crown polyether dibenzo-18C-6 (Merck), H₂SO₄ (Merck) K₂Cr₂O₇ and Na₂S₂O₃ (CHIMPAR Bucharest).

As membrane solvent were used the following medium saturated alcohols: n hexanol (Merck), n octanol (Merck), n decanol (Merck).

Liquid membrane experimental setup

Experimental laboratory setup was built in order to match the experimental strategy of maximizing the contact surface between the aqueous and membrane phases (Figure 1) and (Figure 2). Liquid membrane (based on C6-C10 alcohols) is immobile and aqueous phases, source and receiving are dispersed in the form of micrometer drops inside the membrane. The experimental setup has two reservoirs in which the source and receiving phases are placed.

Flows of these phases are determined from the ratio of the volume and the duration in which the volume was accumulated in cylinders and are maintained constant with Boyle Mariott vessels.

Figure1. Experimental setup: a) overall; b) permeation cell details.
Source and receiving phases are dispersed in the membrane through nozzles ($\Phi = 50$-$100$ mm) of identical construction. The two phases are recirculated in the system until the iodide ion from source phase is consumed [17-20].

**Measurement of the main hydrodynamic parameters of the two-phase system drops - continuous phase**

In this paper, photographic method was used to measure hydrodynamic parameters. This method, due to the development of commercially available digital imaging equipment and software to process them, is one of the most used methods to measure these parameters. Measurement of droplets characteristics consists of photographing the drops from the column and then measure of their size and shape based on a landmark. The required number of processed drops is very high, between 1000 and 3000 drops, and on one photo can be measured between 2 and 5 drops. The method is nonintrusive, so is not disturbing the two-phase system and provides supplementary useful information regarding the drops layer structure and the flow regimes adjacent phenomenon. The method is laborious because for only one result are measured over 1000 replicated and requires experience in the sampling and sample size to reduce measurement error and increase the reproducibility of the results.

An experiment takes place as follows:

- with a digital camera, stuck to the wall column, to reduce the errors caused by glass curvature, were made photo captures with a frequency depending on the experiment duration;
- video captures were transferred to a computer, where they were fragmented with a specialized program, and for ease of data processing, the film is fragmented in one minute pieces;
- with a specialized program, film fragments lasting 1 minute were divided into frames, for each minute of film were obtained between 600 and 700 images;
- on these images by means of an image processing program were measured and determined by 'filling', drop area and form factor, then the program calculated the droplet equivalent diameter (Feret diameter) and its volume;
- actual real size of the droplet was established using the landmark shown in the photo above through which were calibrated previous paragraph measurements.
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The tests regarding the conditions which the measured drops sample must fulfill in order to obtain reproducible results with an average error of less than 2% indicate that it is necessary to measure over 900 drops for an experiment in order to fulfill those conditions [17, 19,20].

**The calculation of total mass transfer coefficient relative to dispersed phase**

Experimentally was measured iodine concentration variation in the dispersed phase. This concentration is the result of the difference between the amount of iodine generated by the chemical reaction and the amount of iodine transferred into the membrane, relative to the volume of effluent used.

Simultaneous pursuit of the two processes interrelates them and this fact requires the use of a size that characterizes the overall intensity of the process labeled "process rate" which is calculated as follows:

\[ n = \nu_p \cdot a_{sp} \cdot (C - C_m) \]  

(1)

where:

- C = iodine concentration in disperse phase, mol/L;
- C_m = iodine concentration in membrane near the interface; mol/L, C_m = 0
- asp = specific area, m²/m³,
- n = transferred iodine flow, mol/min.

n is calculated using the following formula:

\[ n = \frac{dC}{dt} \cdot V \]  

(2)

The volume of effluent used in an experiment was noted with V. Because the amount of iodine transferred is low, this amount is considered to remain constant during the transfer process.

Experimental data processing for total mass transfer coefficient calculation was done based on the following hypotheses:

A. the process takes place in non-stationary regime;
B. the upward movement of the droplet through liquid is approximated with displacement model;
C. the motion induced by the continuous phase droplets is approximated by perfect mixing model;
D. iodine mass transfer process from drops to continuous phase is controlled by membrane iodine transport;
E. droplet interface has no mass transfer resistance.

Under these conditions, the equation that describes iodine mass transfer from drop to continuous phase is:

\[ \frac{dC}{dt} = -K_L a_{sp} \cdot (C_s - C) \]  

(3)

Equation (3) has the following analytical solution:

\[ K_L = \frac{1}{t \cdot a_{sp}} \ln \frac{C_s - C}{C_s - C_0} \]  

(4)

where:

- \( K_L \) = mass transfer coefficient reported to source phase, m·min⁻¹;
- \( a_{sp} \) = interfacial specific area, m²/m³;
- \( C_s \) = iodine saturation concentration in source phase, mol/l;
- \( C_0 \) = iodine initial concentration in source phase, mol/l;
- \( C \) = iodine concentration at time \( t \) in source phase, mol/l;
- \( t \) = time, min.

In order to calculate \( K_L \) with equation (4) time variation of iodine concentration \( C \), \( C_0 \), and \( a_{sp} \) are experimentally measured. They show that in the flow field in which the
experiments were done the distribution curve is unimodal and can be approximated by the normal distribution. With increasing effluent flow curves moves to lower values of diameter and degree of dispersion of values diameter increases.

**Determination of iodine and iodide concentration in membrane phases**

The monitoring of transfer process was performed spectrophotometrically using a Cary 50 double beam spectrophotometer at $\lambda = 510$ nm. Thereby, iodide content in source phase was determined by oxidation of potassium iodide with potassium dichromate in sulfuric acid to elemental iodine, followed by its extraction into hexanol. Iodine content of the membrane was spectrophotometrically determined. From mass balance was established iodide content of the receiving phase [18,19].

Also, in order to confirm the data, for determination of iodine from source phase was used Dr. DAQ interface for data acquisition [20].

Experimental equipment used for automatic data acquisition consists of:

- drDaq type interface for data acquisition under dataloging regime;
- software for data recording and processing;
- laptop type unit of account equipped with wireless communication module;
- uninterruptible power supply UPS (1000W);
- electrodes for the measurement of interest parameters in the proposed aim;
- adapter for external sensors, when a sensor is connected to such a socket, the software automatically detects the scale of measurement and sensor type;
- in our case, the iodide ion selective and reference electrode Ag|$\mid$AgCl, Cl$^-$ from Mettler Toledo;
- data were acquired from 10 to 10 seconds.

Experimental data obtained (concentration of iodine and iodide, iodine amount transferred, the transfer efficiency) are presented for each of the four types of membranes based on medium aliphatic alcohols.

**Results and Discussions**

**The influence of the membrane solvent**

In all cases the transport of iodide anion was performed. The iodine concentration (20-200 ppm) was spectrophotometrically determined from source phase, receive phase, and membrane. The following diagrams present this data and also the transferred iodine quantity and the transfer efficiency. The considered membrane volume was 10.0 mL, with a contact surface membrane/aqueous phases 100 cm$^2$.

In each case, the iodine respective iodide concentration, was graphically represented in all membranary system phases (Figure 3), (Figure 4), and (Figure 5).

Practically, this section aims to highlight the influence of the liquid membrane’s chemical nature on the process performance. For this end the following membranes were chosen, correspondent series of hydroxilic by-products with normal saturated hydracarbonated chain: hexanol, octanol and decanol. The main physical properties of the used liquid substances are presented in Table 1.

The results comparison was performed based on the diagrams presented in (Figure 3), (Figure 4) and (Figure 5).

As it is observed in these figures, the membrane nature insignificantly influences the time evolution of iodine concentration in dispersed phases. The result is not unexpected because the variation domain of the main physical property that influences the drop’s transfer specific surface ranges in a limited domain (Table 1), except hexanol.
Table 1. The chemical properties of membrane solvents.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>C₆</th>
<th>C₈</th>
<th>C₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index (nD₂₀)</td>
<td>1.4178 (20°C)</td>
<td>1.428-1.431</td>
<td>1.434-1.445</td>
</tr>
<tr>
<td>Density (d²₀) (g/cm³)</td>
<td>0.8136</td>
<td>0.8240</td>
<td>0.8297</td>
</tr>
<tr>
<td>Water solubility (20°C)</td>
<td>0.59 g/100 ml</td>
<td>0.3 g/L</td>
<td>12 ppm or 0.0037g/l 25°C</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>158</td>
<td>195</td>
<td>232.9</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>-46.7</td>
<td>-16</td>
<td>6.4</td>
</tr>
<tr>
<td>Molar mass (g/mol)</td>
<td>102.17</td>
<td>130.23</td>
<td>158.28</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>63°C</td>
<td>81°C</td>
<td>108°C</td>
</tr>
<tr>
<td>Self-ignition point (°C)</td>
<td>290</td>
<td>270</td>
<td>255</td>
</tr>
<tr>
<td>Explosive limit</td>
<td>0.3-1.2 % vol</td>
<td>0.8% vol</td>
<td>-</td>
</tr>
</tbody>
</table>

The different behaviour in the case of the n alcohols membrane can be due to the different range of concentrations at which the experiment was conducted.

The membrane nature influence is important in the transport phase as it can be observed in (Figure 3), (Figure 4) and (Figure 5). In this case, the diffusion molecular mechanism of iodine between phases is mainly influenced by the molecule size, by the continuous phase density and tack.

The larger the molecule and the lower the tack are the iodine transport will be favoured. The presented experimental measurements results highlight that in the case of the hexanol membrane the best results are obtained.

Figure 3. Iodine concentration on hexanol membrane system (SP-Source Phase; M-Membrane; RP-Receiving Phase).

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Figure 4. Iodine concentration on octanol membrane system
(SP-Source Phase; M-Membrane; RP-Receiving Phase).

Figure 5. Iodine concentration on decanol membrane system
(SP-Source Phase; M-Membrane; RP-Receiving Phase).

It is observed that in the iodine concentration measure point, next to the receiver phase, iodine is transported the fastest towards this phase, accumulates in this area and then in transferred the fastest in the receiver phase.

The presented data highlight that the continuous phase tack is important for the iodine transfer through the receiver phase drops. This leads to the conclusion that the mass transfer resistance in this case is represented by the liquid film adjacent to the membrane.

The lower the liquid’s tack is the lower the thickness of the liquid film adjacent to the membrane is and the resistance to mass transfer is lower. Thus, a larger quantity of iodine will be transferred into the membrane if the continuous phase tack is lower.
The analyzed cases recommend the hexanol membrane for the iodide ion recovering process.

Practically this membrane has the distinct advantage of solvent recovery through vacuum evaporation at room temperature.

It can take into consideration the integral recovery of other components from membrane phase (e.g. transporters).

**The study of influence of dissolved transporter in membranary solvent**

The experiments regarding transporters introduction into liquid membranes for activating anions mass transfer have been reported for amino acids [24-26].

In the present case, the iodide ions transfer and/or separation through membrane systems with reaction of transformation of the anion into iodine would not impose a transporter use.

During this paragraph the results of iodide ion carrier study are presented with the membranes previously developed in presence of crown ether. Dibenzo-18-crown-6 was used as a marker. The crown ether was introduced in membranes at concentrations of $10^{-4}$ M.

The conducted experiments considered the transport enhancement and the testing of proposed transport mechanism.

![Figure 6. Iodine concentration on system phases with hexanol and ether dibenzo 18 crown 6.](image)

The general conditions of the experiment and the iodide ion and iodine concentration monitoring way are those presented in paragraph 2.

For the results assessment were graphically presented the individual data in the case of each experiment ((Figure 6), (Figure 7) and (Figure 8)).

The hypothesis that allowed the study of crown ether influence on the transport is the following transfer mechanism:

- Generating iodine from the iodide ion derived from potassium iodide, by oxidation reaction, in acid environment, using potassium dichromate;
- Iodine and iodide ion diffusion to the source phase interface with the membrane;
- Iodine solubilisation in the membrane solvent as well as of $I_3^-$ ion, as complex $K^+EC I_3^-$, that would practically enhance the transport;
- The molecular iodine and complex diffusion through the membrane, towards the interface with the receiving phase;
- Iodine transfer from the two chemical species in receiving phase.

![Graph](image1)

**Figure 7.** Iodine concentration on system phases with octanol and ether dibenzo 18 crown 6.

![Graph](image2)

**Figure 8.** Iodine concentration on system phases with decanol and ether dibenzo 18 crown 6.

The crown ether used in membranes (dibenzo 18 – crown 6) in $10^{-4}$ M concentration has enhanced the iodine transport in regard to the initial membrane, in all performed experiments. A transfer efficiency enhancement and a transport time decrease were observed.

The experimental measurements results show that the process was enhanced by the decrease of iodide ion transport duration through the membrane system.
Together with the transport time decrease, the efficiencies of iodine transfer through membranes improved.

The best results are obtained using hexanol as solvent, when the efficiency rises from 95.1% to 97.8%. The following is octanol, with an efficiency of 93.0%, and at a small distance is decanol, with an efficiency of 90.8% (Table 2).

Table 2. Membrane efficiency vs. the chemical properties of membrane systems.

<table>
<thead>
<tr>
<th>Receiving Phase</th>
<th>Membrane without carrier efficiency (%)</th>
<th>Membrane with dibenzo 18 – crown 6 efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n hexanol</td>
<td>n octanol</td>
</tr>
<tr>
<td>S_2O_3^2-</td>
<td>95.1</td>
<td>91.4</td>
</tr>
<tr>
<td>Pb^{2+}</td>
<td>96.4</td>
<td>92.3</td>
</tr>
<tr>
<td>Ag^+</td>
<td>97.8</td>
<td>93.0</td>
</tr>
</tbody>
</table>

However the most spectacular enhancement was observed in the presence of decanol from 90.8 % in the absence of crown ether at 97.0% in his presence. This observation is in accordance with the polarity of the used solvent.

The study of influence of crown ether on the iodide ion transport in membrane alcoholic systems, type source phase with chemical reaction/hydroxylic solvent receiving phase, shows that the transport is favoured by the transporter’s presence and the mass transfer mechanism is the one proposed.

The positive effect of crown ether using is remarkable in the case of the less polar solvent, decanol.

Conclusions

This paper presents the regenerative separation of iodine from diluted aqueous solutions using liquid membranes, with and without carrier, based on medium saturated alcohols. Regenerative separation variable parameters were: dibenzo 18 crown 6 ether concentration and the nature of the alcohol that forms the membrane, iodine concentration, silver or lead ions concentration in receiving phase for invariable composition of the source phase (pH=0 and oxidizing agents K_2Cr_2O_7). The results show a regenerative separation between 81.7 and 98.3%, with the best results, regardless of the concentration of iodine in feed solution, for hexanol, as the membrane phase and silver ion in the receiving phase. The positive effect of crown ether using is remarkable in the case of the less polar solvent, decanol.

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