Iodine Separation by Ionic Flotation

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In this paper we present an ion flotation study for iodine recuperative separation from dilute aqueous synthetic solutions (20-120 ppm). In the presence of surfactants, cationic collectors, flotation assisted by polyethyleneglycol or crown ethers, iodine separation efficiency was at least 50% in a single stage operation.

Keywords: ionic flotation, iodine, cationic collectors, surfactants, crown ethers

Sea, bore and/or mine water have a complex composition, containing a variety of components, in the form of soluble and insoluble iono-molecular and colloidal species, with variable concentrations, making separation, removal and recovery more difficult [1-4]. Such aqueous systems require the application of available separation methods, which may allow separation and / or recovery of useful components [5-7]. From these methods: ion exchange [8,9], adsorption [10,11], reverse osmosis and ultrafiltration [12-15], liquid membranes have been extensively studied [16,17]. Ion separation by flotation was rarely addressed, mainly to recover the heavy metal cations [18-20].

In this paper we present an ion flotation study for iodine recuperative separation from dilute aqueous synthetic solutions (20-120 ppm), simulating properly sea, bore or mine water.

The aim consists in regenerative iodine separation as iodide ion (I^-) or 3-iodide (I_3^-) from aqueous solutions, using the ion flotation as separation method, in the presence of cationic surfactants as surfactants collectors, and normal alkyl alcohols, polyethylene glycols or crown ethers as coligande.

Experimental part
Materials

Experiments were performed on synthetic solutions containing iodine, with concentrations ranging from 20-120 ppm, obtained by dissolving in deionized water an appropriate volume of standard iodine-iodide 1N solution (special analysis reagent, REACTIVUL Bucharest). These types of solutions exist in nature as bore or mine water, but laboratory tests were performed with synthetic solutions.

The collectors used were cationic type: dodecyl pyridinium chloride (DDP), tetradecyl pyridinium chloride (TDP), octadecyl pyridinium chloride (ODP) and Hyamina 10 (chloride, benzyl trimethyl ammonium p-alkyl) (H10), provided by Merck .

The coligands used were: polyethylene glycols 300, 1000, 2000, 4000, 10000 D, ether 18C6 and dibenzo ether 18C6, from Merck.

Analysis and equipment

Foam iodine content, after extraction into hexanol, was determined spectrophotometrically using a Cary 50 double beam spectrometer at optimum wavelength l = 510 nm.

Figure 1 shows the laboratory set-up operating in discontinuous mode used to determine the iodine separation efficiency with foaming bubbles, and table 1 shows technical characteristics of laboratory set-up. The installation is relatively simple, versatile and does not require special precautions because gas (air) feed system consists of a compressor connected to the installation lens. Synthetic solutions containing iodine were placed in the flotation column made of glass with a 1500 cm³capacity. Air dispersion was achieved throught porous plate, and air flow control has been achieved using a dosing system equipped with pressure and flow reducer.

Piston air compressor operating at 2 to 3 atm is connected to the flotation column through air tap.

The foam that is forming at the surface of the solution in the column is passed to the intermediary vessel and then in the receiving vessel. What remains in the column is considered a waste product.

Samples taken from initial, collected (float) and residual solutions were analyzed at the spectrophotometer.

Determining the nature and concentration of the collector

Essential step in promoting separation by flotation, determining the nature and concentration of surfactants collectors, is based on the maximum foam production, depending on air flow that is passed through the column.

In the first part of the experiments it was aimed to establish the optimum airflow in order to ensure getting a maximum foam production without piercing feed solution or destabilize the separation column.
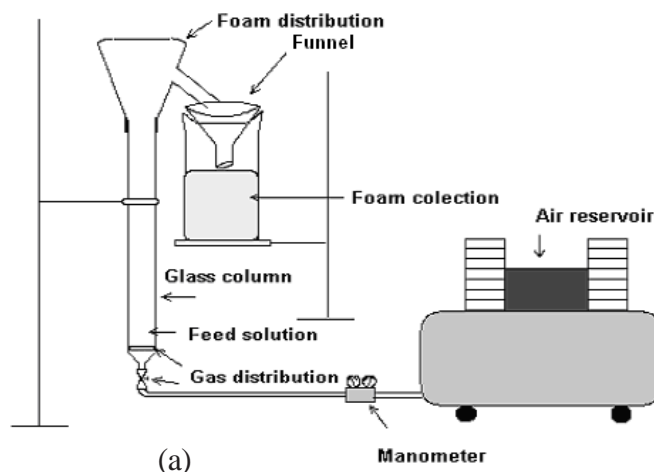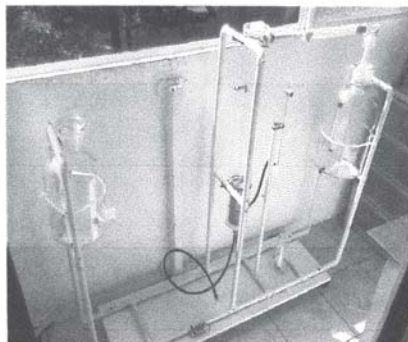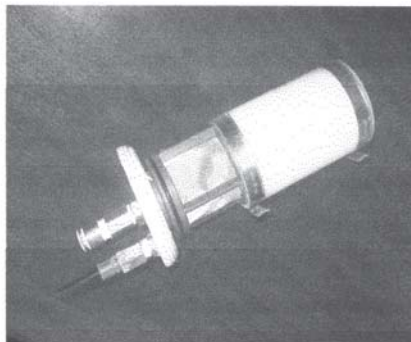
Fig.1. Laboratory installation for ionic flotation
a) schematic representation

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Fig.1. Laboratory installation for
ionic flotation
b) overview of the components;
c) air lens

(b)

(c)

Table 1
LABORATORY CHARACTERISTICS OF THE INSTALLATION

Components	Properties
Column	Standard length = 1200 mm
	Outside diameter = 60 mm
	Inside diameter = 50 mm
Porous plate	Diameter = 50 mm
	µm order pore diameter
Compressor	Operating pressure = 2-3 atm

The standard experiment consists in introducing feed solution in the flotation column, air flow adjustment, collection and breaking (collapse) the foam. The duration of the standard experiment was 60 min, and in order to determine the productivity depending on air flow it was used a test solution of sodium oleate 10^{-4} M and the air flow was varied in the range 0.2-2.0 L/min.

In order to determine the ideal colector concentration, feed aqueous solutions with 10^{-6}, 10^{-5} and 10^{-4} M collector concentrations were used at an air flow ranging from 0.2 to 2.0 L/min. The feed solution volume was 1000 mL in all cases.

Determination the efficiency of ion flotation in iodine separation

In the second part of the experiments the aim was to determine the efficiency of iodine recuperative separation by ion flotation.

For the experiment were chosen the following constant parameters: air flow = 0.8 L/min; collector concentration = 10^{-4} M; the nature of collectors (cationic surfactants type).

The iodine separations from aqueous solutions process variables have been: feed solution concentration = 20-120 ppm; the coligande nature: polyethylenglycol 300, 1000, 2000, 4000 and 10000 D, 18C6 ether and 18C6 dibenzo ether.

Results and discussions

The approach of iodine recuperative separation by ionic flotation is based on three arguments: the reduced consumption of materials, the reduced investment and the possibility to apply the separation process for dilute solutions [21-23]. Generally, the separation by ionic flotation is realized by using a simple equipment [22-29]. There are several types of ionic flotation, but each one may fall within the principle scheme from figure 2, which contains the following components: 1- gas input system; 2 - sample input system; 3 - collector input system; 4 - separator device (flotation cell); 5 - capture foam system (containing the sublate); 6 - liquid waste disposal system [30-35].

Gas supply system includes: high pressure source or compressed air line, mechanical and chemical gas purification system, control and gas flow measurement system.
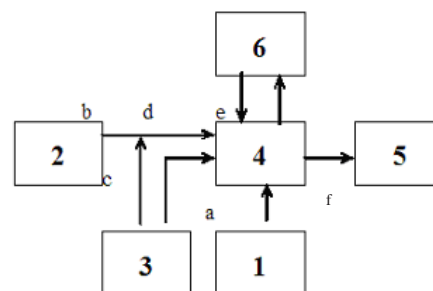

Fig.2. Components of an installation for ionic flotation
a) gas, b) initial sample, c) collecting solution, d) and e) foam
sublate f) inferior product (effluent)

The sample introducing system is necessary only in the continuous iono-molecular flotation process and contains a micro-pump and a rotameter.

The collector introducing system allows its introduction into the inlet line of the analyzed solution or directly in the separator device. The collector is usually introduced as a dilute aqueous solution, and the other components in concentrated solutions, so after mixing, the solution introduced into the cell should have the desired composition. The collector inlet block contains, in this case, a micro-pump and a rotameter.

In precipitate flotation case, an input block of precipitated reagent is provided. The foam capture system is different for each variant of adsorptive bubble separation technique.

In flotation, the foam can be mechanically removed, with a spatula or a scraper, can be aspirated with a micropump or captured in a water-immiscible organic solvent.

Liquid waste disposal system is only required for the continuous process. The installation must also contain a system to maintain constant the initial solution level in the separator device.

The experimental set-up (fig.1) allows the study of flotation main operational parameters: air flow, nature and concentration of surfactants, colectors and coligands, for synthetic aqueous solutions with iodine concentrations range imposed in feed solution. Foam production variation curve depending on air flow is presented in figure 3 and has the following characteristics:

- zone I, of exponential increase at flow ranging from 0.2 to 0.8 L/min;
- zone II, with the allure of landing, between 0.8 and 1.2 L/min, with foam production relatively constant;
- zone III - exponential decrease of foam amount, between 1.2 and 2.0 L/min.

The behavior described for zone I is justified by the number and the surface of gas bubbles, which increases with increasing the air flow.

In this case, at a flow higher than 1.0 L/min, the bubbles begin to merge, leading to the formation of jets, or air

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columns, leading to flattening of the curve, suggesting a bubbles surface capping, determining the formation of zone II.

The zone III formation is justified by decreasing the contact surface between the air and the solution, due to column destabilization. The significant decrease of the foam production is a cause of flotation column destabilization by formation of large air bubbles which pass through the column, without dispersing and are acting like a piston.
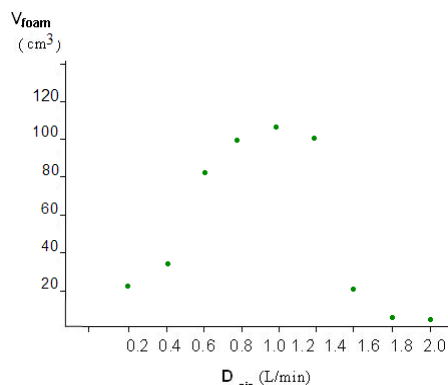

Fig. 3. The variation of foam production colected in 10^{-4} M sodium oleate solutions depending on air flow

The amount of foam collected increases with the air flow introduced in the flotation column, by 0.8-1.2 L/min area, after which, reveals a pronounced decrease in foam production. The optimum air flow must be correlated also with the concentration value and the collector nature.

In order to determine the optimal operation conditions with the four cationic collectors, imposed by the anionic species that must be separated: I⁻ and /or I³⁻, were performed the experiments which are presented in figures 4÷6.
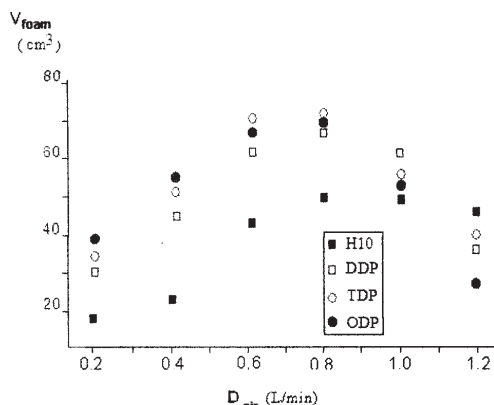

Fig. 4. The variation of foam production colected in 10^{-5} M sodium oleate solutions depending on air flow
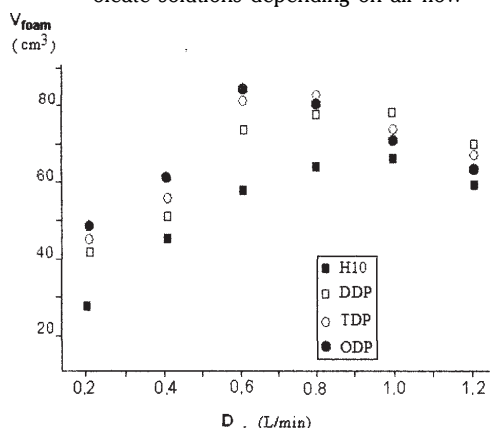

Fig. 5. The variation of foam production colected in 10^{-6} M sodium oleate solutions depending on air flow.
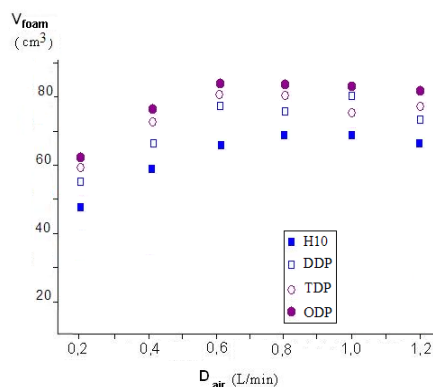

Fig. 6. The variation of foam production colected in 10^{-5} M collector solutions depending on air flow

The experimental results (figs 4÷6) show that the foam production increases with collector concentration increase, from about 10 cm³ for Hyamine 10, at a 20 L/min flow, up to about 85 cm³ for pyridinium chlorides, at flows ranging from 0.6 to 1.0 L/min.

At the same concentration value, for air flows up to 0.8 L/min, the productivity order increases as follows: H10<DDP<TDP<ODP. However, the interference phenomena decrease the foam production at flows exceeding 1.0 L/min.

The importance of the interference phenomena attenuates with collector concentration increase, but limitates the volume of foam collected, noticing the appearance of some levels, more obvious at 10^{-4} M.

Experimental data obtained (fig. 7) show that the experiment was successful and the ionic flotation can be considerate an efficient method for iodine or iodide ions separation and recovery from aqueous solutions, with over 50% efficiency in the presence of collectors: DDP, TDP, ODP, H10 and of coligands: PEG 300, 1000, 2000, 4000 si 10000 D, 18C6 ether and 18C6 dibenzo ether.

Iodine recuperative separation efficiency by ionic flotation with cationic collectors, PEG coligands and ethers is justified because the chemical predominant species in separation system are iodide (I⁻) and tri-iodide ($I^- + I_2$) ions.

Iodide and/or tri-iodide ion ($I^- + I_2$) form ionic aggregates with cationic surfactants in the foam, which justifies the increase of iodine separation efficiency over the entire concentration range (20-120 ppm), in order: H10<<DDP<TDP<ODP (fig. 7).

However, as iodine solution concentration increases, separation efficiency decreases for all the coligandes used.

The separation eficiency increase is notable in order: PEG 300 ≤ PEG 10000< PEG 1000< PEG 2000 < PEG 4000 (fig. 8).
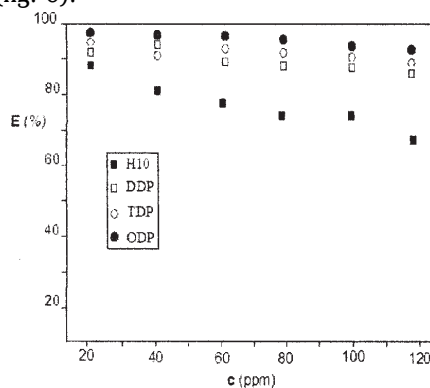

Fig. 7. The variation of iodine separation efficiency from solutions with variable concentration, in the presence of 18C6 ether and cationic collectors
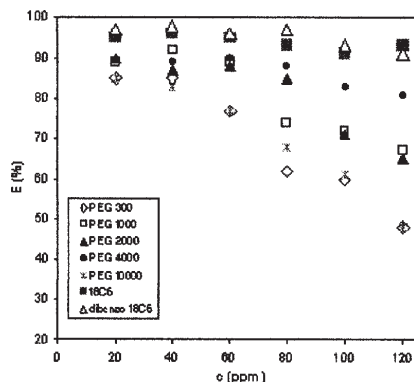
Fig. 8. The variation of iodine separation efficiency from solutions with variable concentration, in the presence of ODP collector and different colligands

Since from theoretically point of view, the interactions between iodide ion and /or tri-iodide (I^- and I_2) and polyethylene glycol could not be sustained, the only explanation for the increase of the separation efficiency is the foam stabilization capacity, with increasing molecular weight of polyethylene glycols used.

The decrease somewhat surprising of the eficiency in the case of PEG 10000 (fig. 8) can be explained by the lower solubility of this coligand in foam.

The 18C6 ether utilization in the system - iodide and tri-iodide shows that the separation eficiency increases (about 100%) and remains quasi-constant on the whole concentration domain, for alkyl pyridinium chlorides and significantly increases, compared with PEG's, in the H10 case (alchiylamoniu salt).

Since the 18C6 ether has no foaming effect and it does not stabilize the foam, the only explanation for the increase of separation efficiency lies in its ability to complex potassium ions which accompanies the iodide and/or tri-iodide ion in solution, so, improving their solubility in foam (fig. 8).

Conclusions

The approach of iodine recuperative separation by ionic flotation is based on three arguments: the reduced consumption of materials, the reduced investment and the possibility to apply the separation process for dilute solutions. The installation is relatively simple, versatile and does not require special precautions because the gas (air) introduction system consists of a compressor connected to the system lens. The determination of the nature and concentration of surfactant collectors is realized based on the maximum foam production, depending on air flow that is passed throught the column.

At the same concentration value, for air flows up to 0.8 L/min, the productivity order increases as follows: H10<DDP<TDP<ODP. However, the interference phenomena decrease the foam production at flows exceeding 1,0 L/min. The importance of the interference phenomena attenuates with collector concentration increase, but limitates the volume of foam collected, noticing the appearance of some levels, more obvious at 10^{-4} M.

The iodine separation by ionic flotation in the presence of surfactants, cationic collectors, assisted by polyetylene glycols or ethers, lead to efficiencies of at least 50%.

Using alkyl pyridinium derivates collectors allows the achivement of efficiencies over 95%, at small iodine solution concentrations, especially in the octadecyl pyridinium chloride case.

Polyethylene glycol type coligands contributes to increased separation efficiency with increasing the molecular weight, but should not exceed the 4000D limit.

The ethers are significantly improving the efficiency of separation on the entire range of iodine concentrations in supply. The 18C6 ether has the most favorable effect because is more soluble than 18C6 dibenzo ether.

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