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SELECTIVE EXTRACTION OF BROMIDE WITH LIQUID ORGANIC MEMBRANE

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ABSTRACT

A novel separation technique for bromide in the presence of various anions with a liquid membrane was reported. Initially, bromide ion was oxidized by sodium dichromate in acidic media (aqueous or source phase), followed by a continuous chloroform extraction (organic phase). Next, a back-extraction of bromine into a second aqueous phase (receiving phase) containing nitrite ions was conducted in order to reduce bromine into bromide. Parameters affecting the transport efficiency as well as the influences of potential interfering ions in this bromide extraction method were studied. After a 70-min extraction period, 91.4 ± 1.2% of the bromide ions were transported across the liquid membrane. The developed extraction method was used for the detection of bromide ions in seawater.

Key Words: Extraction; Bromide; Liquid membrane.

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INTRODUCTION

In recent times, intense research of transport phenomena has been carried out in the field of chemistry and biology. Nevertheless, the separation of less lipophilic anions, such as bromide, by means of extraction is a relatively new area of research. Up to this date, relatively few anion carriers have been reported (1). Out of these lipophilic carriers, the most commonly used carriers are copper complexes (2,3) and a lipophilic complex of UO_2^{2+} (4), used for the extraction of dihydrogen phosphate anions. Other research groups have reported the application of the oxidized form of *N,N,N′,N′*-tetramethyl *p*-phenylenediamine (TMPD) as a picrate transporter (5). Vitamin B_{12} derivatives (6), quaternary ammonium or phosphonium salts (7), and triaryl cations (8) have also been used as carriers, but the latter carrier exhibits a relative selectivity for bromide. The successful extraction of bromide has already been reported (5,9), but the method exhibits low selectivity and long extraction periods, and in few cases transportation was carried out with oxidation–reduction couples. As far as we know, no reports have been made on the selective transport of bromide ions through a liquid membrane, using a redox couple.

In this paper we will demonstrate a selective extraction method for bromide that is based on an oxidation-reduction mechanism. With this method, bromide is quantitatively and selectively converted to bromine by dichromate ions, which are in turn extracted into the chloroform media. The bromine now present in the organic phase comes in contact with the second aqueous phase (receiving phase) that contains nitrite ions. Nitrite acts as a reducing agent that converts the bromine to bromide, which is easily extracted into the second aqueous phase (receiving phase). The amounts of bromide in the source and receiving phase have been determined by extractive–photometric determination of Br_2 with chloroform at 410 nm and by potentiometric titration using a standard silver nitrate solution, respectively. We will demonstrate that the transportation method is efficient, selective, and rapid and can also be used for the separation of bromide. This method will also be applied to separate trace amounts of bromide from seawater.

EXPERIMENTAL

Reagents

Double distilled water was used throughout all experiments. Stock solutions were prepared using KBr (Merck), sodium dichromate, $Na_2Cr_2O_7$ (Merck), and sodium nitrite. The sodium nitrite solution had a final concentration of 1.00 *M* and was prepared by dissolving 6.90 g $NaNO_2$ (Merck) in water in a 100-mL volumetric flask. Chloroform (Fluka) served as the liquid membrane for all experiments.

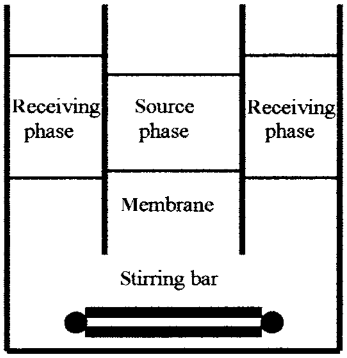


Figure 1. Schematic diagram of the apparatus used for the extraction of bromide with liquid membrane.

Apparatus

A homemade cylindrical glass cell (4-cm internal diameter) that vertically holds a glass tube (1.8-cm internal diameter) was used for all experiments (Fig. 1). The transport cell contains two immissible solvents (three phases). Water used, as the source is located within the inner glass tube, is separated from the aqueous receiving solution by an organic ($CHCl_3$) liquid membrane as shown in Figure 1. A conventional polymeric stopper for the source phase was used to prevent bromine evaporation from the aqueous solution. Transport processes through the different phases were carried out while the solutions were stirred with a magnetic stirring motor set at 250–300 rpm.

All potentiometric titration was made by using a Corning potentiometer (Model 435) with a silver wire as an indicator electrode and calomel reference electrode. A Perkin-Elmer spectrophotometer (Model 551) was used for all spectrophotometric and turbidimetric measurements. A Perkin-Elmer atomic absorption spectrometer (Model 2380) was used to determine all cations present in the source and receiving phases.

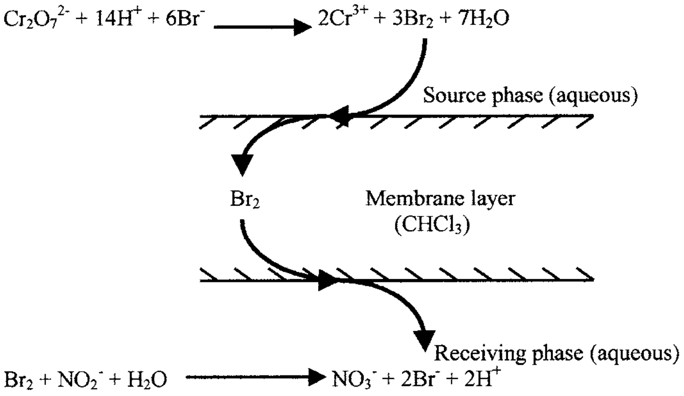
Procedure

All experiments were carried out at temperatures between 25 and 30°C (room temperature). A mixture of 1.0 mL bromide solution (0.400 *M*), 2.0 mL concentrated sulfuric acid (7.5 *M*), and 2.0 mL of sodium dichromate (0.63 *M*) was used as the source phase; the total volume of the source phase solution was 5 mL. The outer receiving solution contained 10 mL of 0.30 *M* sodium nitrite as a reducing agent (Fig. 1). The concentration of bromide in the source phase and receiving phase was determined by the following methods: For the receiving phase, 2.0 mL of the solution was mixed with 15 mL 0.02 *M* nitric acid prior to the potentiometric titration of bromide with a standard 0.0203 *M* $AgNO_3$ solution. For the source phase, 1 mL bromide sample was taken from the source phase and diluted five-fold with water. Next, 2.0 mL aliquots of the dilute bromide solution were treated with 2.0 mL of 0.040 *M* acidic permanganate solution (1.0 mL of 5 *M* sulfuric acid) in order to convert bromide to bromine. Subsequently, the produced bromine is extracted into 5 mL of $CHCl_3$, and the absorbance of the chloroform solution was measured at 410 nm. The bromine content was calculated by using the calibration graph obtained under the same conditions.

Several cations such as Mg^{2+}, Ca^{2+}, K^+, and Na^+ and anions such as Cl^-, I^-, $SO_4{}^{2-}$, and $PO_4{}^3$ were tested in order to investigate their effect on bromide transfer processes. Atomic absorption spectrophotometry was used to measure the amounts of cations in the source and receiving phases. Iodide was determined spectrophotometrically at 510 nm after the oxidation–extraction method was used to produce iodine as described for the bromide in the source solution. Determination of chloride was carried out by potentiometric titration with a standard 0.0203 *M* $AgNO_3$ solution. Phosphate traces were determined spectrophotometrically at 780 nm by implementing the phosphomolybdenum blue method (10). Sulfate contents were measured by turbidimetry after dilution with of 2.0 mL of the source solution or receiving solution and the treatment with alcoholic $BaCl_2$ solution (11).

RESULTS AND DISCUSSION

The proposed mechanism for the extraction phenomena can be seen in the Scheme 1. The initial reaction in the source phase is followed by the reaction at



Scheme 1.

the interphase (liquid membrane/receiving phase). The produced bromide is then extracted into the receiving phase.

The type of oxidizing agent in the source phase and type of reducing agent in the receiving phase are the most important factors for the selective oxidation–reduction reaction. We chose dichromate in sulfuric acid as the appropriate oxidant in the source phase, because of its inability to oxidize chloride under the above conditions. Nevertheless, bromide ions are subject to oxidation. In addition, the types of reducing agent present in the receiving phase affect the selectivity of the ion transfer through the interphase. Our studies showed that nitrite ions in a weak acidic, basic, and neutral media are a powerful reducing agent for rapid and quantitative reduction of bromine to bromide. It is also a selective oxidizing agent for iodide in acidic media to produce iodine. Thus, nitrite ions were selected as reducing agents for the receiving phase.

Optimization of the bromide extraction method involved varying dichromate and nitric concentrations at different pH levels within the three phases. Figure 2 shows the effect of dichromate concentration on the transport of 0.08 M Br^- in the source phase. Results show that the transport efficiency increases exponentially by increasing dichromate concentration up to 0.35 M. Dichromate solubility is limited and thus the studies at higher concentrations could not be performed. Consequently, all experiments were carried out using a concentration of 0.25 M dichromate.

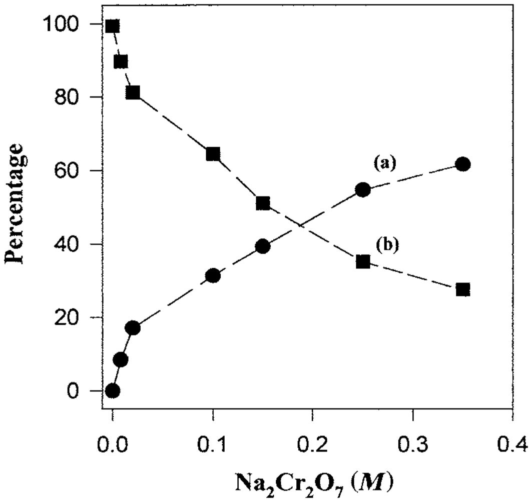


Figure 2. Effect of dichromate concentration on the bromide transport; Bromide found a) in the receiving phase and b) in the source phase. Conditions: 0.30 M NO_2^- in the receiving phase; 1.0 M H_2SO_4 in the source phase; 30 mL of chloroform as a membrane phase; and time of transport, 70 min.

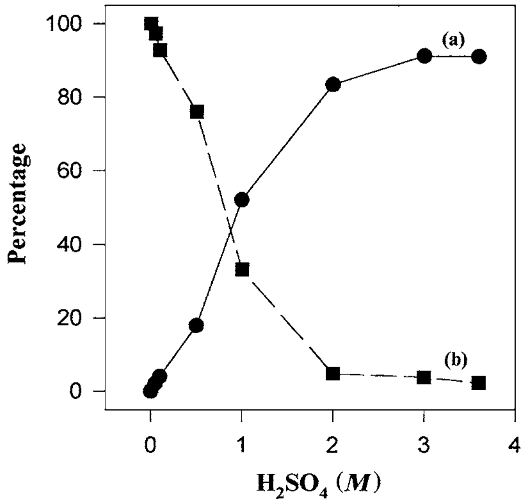


Figure 3. Influence of sulfuric acid concentration on the bromide transport; Bromide found a) in the receiving phase and b) in the source phase. Conditions: NO_2^-, 0.30 *M* in the receiving phase; 0.25 *M* $Cr_2O_7^{2-}$ in the source phase; 30 mL of chloroform as a membrane phase; and time of transport, 70 min.

Extraction efficiency was further investigated under different sulfuric acid concentrations. Figure 3 shows a correlation between acid concentration levels and higher extraction efficiency; maximum extraction efficiency is reached at 3.0 *M*. At this point, greater amounts of the reagent no longer affect efficiency. Therefore, 3.0 *M* sulfuric acid became the concentration of choice.

The influence of nitrite concentration on the bromine reduction in the receiving phase was studied with the other optimum reagents concentration. The results are shown in Table 1, that show the maximum transfer occurred at a concentration of 0.10 *M*. The final concentration of 0.3 *M* nitric acid (optimal stoichiometric excess) was used for all experiments.

The oxidizing ability of nitrite within pH levels of 3–8 in the presence and absence of buffer in the receiving solution were studied. Results show that transfer efficiency is independent of pH. However, the transfer efficiency in the receiving phase decreased with a pH below 2.0. Therefore, a buffer was not used in the nitrite solution in the receiving phase. No considerable effects on the extraction efficiency were found for bromide concentrations (source phase) ranging form 0.02 to 0.10 *M*. The bromide transfer from the source solution to the liquid membrane and from the membrane to the receiving solution behaves in accordance to first-order kinetics, as no additional carrier is used for the extraction.

Table 1. Effect of Sodium Nitrite Concentration on the Bromide Transport

Concentration of Sodium Nitrate × 10^2(mol/L)	Percentage Transported into Receiving Phase	Percentage Remaining into Source Phase
0.0	1.1	7.1
1	30.9	7.2
3	59.5	5.0
5	82.6	7.3
10	92.1	4.5
15	92.5	3.8
20	92.4	4.1
30	91.5	3.5

Conditions: source phase, 5.0 mL solution containing 8.0×10^{-2} *M* potassium bromide, 3.0 *M* sulfuric acid, and 0.25 *M* sodium dichromate; membrane phase, 30 mL of chloroform; receiving phase, 10 mL of sodium nitrite solution; time of transport, 70 min.

The increase in stirring time and its influence on transfer efficiency was tested using a 0.08 *M* bromide concentration (Fig. 4). The results show that after 70 min about 92.0% of the bromide was transferred through the liquid membrane, whereas after 120 min, 97.3% of the bromide was transferred.

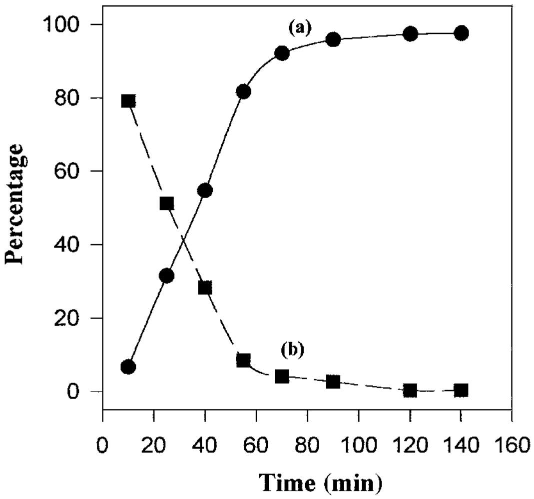


Figure 4. Dependence of transfer efficiency vs. time; a) in the receiving phase and b) in the source phase. Conditions: NO_2^-, 0.30 *M* in the receiving phase, H_2SO_4, 3.0 *M* and 0.25 *M* $Cr_2O_7^{2-}$ in the source phase, and 30 mL of chloroform as a membrane phase.

Table 2. Effect of Some of Ions on the Bromide Transport

Ion (Concentration)	Percentage Transported into Receiving Phase	Percentage Remaining in Source Phase
$Br^-(4.0 \times 10^{-2} M)$	91.1	3.3
$Cl^-(0.4\ M)$	0.0	99.5
$I^-(0.4\ M)$	0.15	—
$Br^-(4.0 \times 10^{-2}\ M)$ and $I^-(0.4\ M)$	92.1	3.8
	0.25	—
$Br^-(4.0 \times 10^{-2}\ M)$ and $Cl^-(0.4\ M)$	92.7	2.7
	0.0	99.7
$Br^-(4.0 \times 10^{-2}\ M)$ and Mg^{2+}, Ca^{2+},	91.3	2.9
K^+, Na^+ $(4.0 \times 10^{-2}\ M)^a$	0.0	100
$Br^-(4.0 \times 10^{-2} M)$ and PO_4^{3-}	90.6	3.5
$(4.0 \times 10^{-2}\ M)^a$	0.0	99.8

Conditions: source phase, 5.0 mL solution containing 4.0×10^{-2} M potassium bromide, 0.25 M sodium dichromate, and 3.0 M sulfuric acid; receiving phase, 10.0 mL of 0.30 M sodium nitrite; membrane phase, 30 mL of chloroform; time of transport, 70 min.

[a] Concentration of each of the ions was added to the source solution.

Selectivity of the extraction method was evaluated after adding a variety of ions to the standard bromide solution within the source phase. The following cations, Mg^{2+}, Ca^{2+}, and K^+, and Na^+ and anions, SO_4^{2-}, PO_4^{3-}, I^-, and Cl^- were tested. The results are shown in Table 2. Chloride ion cannot be oxidized by dichromate in the source phase, and iodine ion cannot be reduced by nitrite in the receiving phase and thus are not transferred into the receiving phase. Anions, PO_4^{3-} and SO_4^{2-} do not react with dichromate, therefore these ions do not produce neutral extractable species to extract that would interfere with bromide transfer.

Water from the Persian Gulf was used to carry out a practical application of the proposed bromide extraction method. The phenol red standard method (12) was used to compare the results obtained from both methods. The amount of seawater bromide ions found using the standard method (12) was 69.8 ± 2.8 μg/mL ($n = 5$) and 66.4 ± 2.5 μg/mL ($n = 5$) using the new extraction method. This concludes good compatibility and applicability of the proposed extraction method for bromide as a practical analytical tool.

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