



Evaluation of ion separation coefficients by foam flotation using a carboxylate surfactant



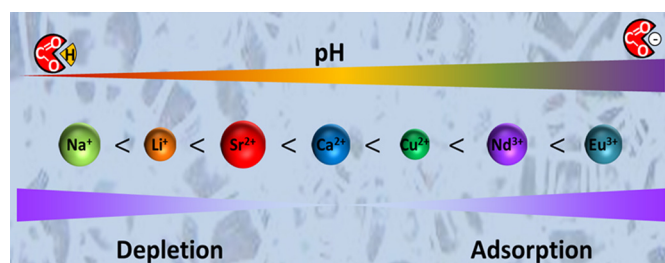
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HIGHLIGHTS

- Selectivity coefficients between ions have been evaluated from ion flotation results using a polyethoxy-carboxylate surfactant.
- Ion selectivity in the foam correlates with the ion selectivity at the micelle surface.
- A depletion effect of lithium ions from the foam was observed in the presence of neodymium (III) ions.

GRAPHICAL ABSTRACT



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ABSTRACT

Separation of metal cations of different charges, Na^+ , Li^+ , Ca^{2+} , Sr^{2+} , Cu^{2+} , Nd^{3+} and Eu^{3+} was investigated through ion foam flotation using a pH sensitive surfactant, nonaoxyethylene oleyl ether carboxylic acid. We propose here a method to evaluate ion selectivity coefficients using mass and volume balances. This method yields selectivity coefficients in agreement with those obtained with the classical slope method. The ion selectivity obtained by the flotation experiments was found to correlate well with the apparent charge of the surfactant micelles (zeta potential values) in the presence of different salts and is therefore not influenced by the surface curvature. Consequently the ion specificity order has been established according to the surfactant–ion affinity at the air–water and micelle–water interfaces as $\text{Na}^+ < \text{Li}^+ < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Cu}^{2+} < \text{Nd}^{3+} < \text{Eu}^{3+}$. It has been noticed that the selectivity coefficients between the different metal ions, obtained by ion flotation, differ from the ones predicted by using metal ion complexation constants of acetate, which is considered here as the non-surface active complexing part of the surfactant. This discrepancy was attributed to the surface complexation effects at the air–water interface in flotation experiments and at the micelle–water interface. For the separation of lithium and neodymium, a depletion phenomenon of lithium ions from the interface, hence from the foam, has been observed, i.e. once the flotation experiment was finished, the lithium concentration in the remaining foaming solution was indeed higher compared to the initial one. This phenomenon was explained by the strong adsorption of Nd^{3+} that leads Li^+ to be repelled from the foam.

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1. Introduction

Ion flotation was first described by *Sebba* in 1959 [1] and was used for the treatment of trace elements from aqueous phases. In

this process, an ionic surface-active agent (collector or surfactant) is used to concentrate and extract a non-surface active ion of the opposite charge (colligend) at the liquid/gas interface. Sparging gas through the aqueous phase enables the generation of a gas dispersion at the top of the solution. Small bubbles and low water content increase the interfacial area as well as the efficiency of the ion extraction process. When the collector/colligend couple has a solubility lower than 10^{-6} – 10^{-7} M and for concentrations

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below the critical micellar concentration (CMC), the gas dispersion is named “froth” [2] and is stabilized by *Langmuir* monolayers. In this type of process a solid residue is obtained once the froth is collapsed and collected. For concentrations above the CMC, bulk precipitates that are non-surface active are formed and reduce the efficiency of the flotation process. The term of “foam” [2] is used when the gas dispersion is stabilized by *Gibbs* monolayers. In ion foam flotation, a concentrated monophasic solution is then collected once the foam breaks down. There are two main advantages of foam flotation process over froth flotation for metal recycling from waste treatment: (i) the formation of a liquid effluent at the end of the process is easier to handle than a solid effluent which is produced in the case of foam stabilized by *Langmuir* monolayers and (ii) the flotation efficiency is not altered for concentrations above the CMC, and consequently solutions with higher feed concentrations can be treated. Foams formed by *Gibbs* monolayers are by far the less studied systems for multi-charged cations ion flotation [3–5]. Indeed most anionic surfactants generally form *Langmuir* films when the colligend is multicharged and precipitate when concentration is increased above the CMC e.g. calcium or magnesium soaps $(R-COO)_2Ca$ or $(R-COO)_2Mg$, with R representing an alkyl chain with typically at least seven carbon atoms [2,6,7]. The addition of chelating ligands (triethylenetetraamine) or macrocycles to the feed surfactant solution was proposed to create an interfacial film enriched in a particular metal cation and to change the ion selectivity [3,5]. We proposed lately an alternative to avoid the precipitation of anionic surfactant/multicharged cation couples by using a carboxylic surfactant that contains a non-ionic polyethoxylated part between its anionic polar head and its hydrophobic alkyl chains, the nonaoxyethylene oleylether carboxylic acid (trade-name AKYPO® RO 90 VG, herein “AKYPO®”, “surfactant” or “S”) [8].

This surfactant was used in a previous work to generate foam under continuous bubbling during several hours [8]. It was shown that, this pH sensitive surfactant interacts strongly with a multicharged ion, namely neodymium, without precipitating, and so it can be considered a good collector for ion foam flotation. The present study investigates this surfactant for the separation of metal cations with different charges in ion foam flotation.

The thermodynamics of ion exchange in the ion flotation process has been previously described by Morgan et al. [9] and a calculation of selectivity coefficients based on ion-exchange equilibrium at the anionic surfactant film was proposed. For metal cations of same charges, n , this equilibrium was described as follows:



where X^{n+} and Y^{n+} are the ions in competition, and (aq) and (ads) denote aqueous and adsorbed species respectively.

For this ion-exchange equilibrium, the selectivity coefficient is expressed:

$$K_X^Y = \frac{\Gamma_{X^{n+}} C_{Y^{n+}}}{C_{X^{n+}} \Gamma_{Y^{n+}}} \quad (2)$$

where Γ is the surface excess and $C_{X^{n+}}$ and $C_{Y^{n+}}$ are bulk concentrations of the metallic ions X^{n+} and Y^{n+} respectively.

It was shown that the selectivity coefficient can be obtained [10–13] by measuring the equilibrium concentrations of the competing ions during the flotation process and using the following theoretical relationship [9,10]:

$$\ln C_{X^{n+}} = K_X^Y \ln C_{Y^{n+}} + C \quad (3)$$

where C is a constant depending on the initial solution conditions. K_X^Y corresponds then to the slope of the $\ln C_{X^{n+}}$ vs. $\ln C_{Y^{n+}}$ plot, and will be referred to herein as $K_X^{Y, slope}$.

This method for the calculation of ion selectivity coefficients was used in many works previously [5,9–17]. Below, $K_X^{Y, slope}$ will be calculated only from final and initial concentrations in the residual solution and not from the ion concentration in the foaming solution along the flotation process, as usually performed by Warr et al., due to volume and semi-batch conditions. This method will induced higher uncertainties in the determination of the selectivity coefficients due to a poor statistic in the linear regression determination.

In the present work we propose another method to calculate the selectivity coefficient of AKYPO® for dissimilar ions, mono, di and tricharged, based on recovery rate of extraction. Selectivity coefficients were discussed in regards to micelles zeta potential and foam film thickness measurements [8].

2. Experimentals

2.1. Materials

AKYPO® RO 90 VG (nonaoxyethylene oleylether carboxylic acid, $R-O-(CH_2CH_2O)_n-CH_2COOH$, $R=C_{16}/C_{18}$, $n=9$) from Kao Chemicals was used as received (surfactant content 89.0%, $M_w = 722 \text{ g mol}^{-1}$). The water content (9.4%) of the surfactant was determined by the Karl Fischer analysis method (Coulometer Metrohm KF 764) with a detection range from 10 μg to 10 mg water per measurement. The surfactant concentration in the solutions was checked by a total organic carbon analyser (TOC-VCSH, Shimadzu). A solution of potassium phthalate was used as the calibration standard. The apparent pK_a value, estimated at 5.4 ± 0.2 , was determined by pH titration at the concentration used to perform the ion foam flotation experiment (0.5 mM). Therefore, this value corresponds to the apparent average pK_a of the surfactant carboxylate function in the micellar state and not in the monomeric state [8,18].

Different metal cations were examined in ion foam flotation and zeta potential experiments. For monocharged cations, sodium nitrate (Strem Chemicals, 99% purity), lithium nitrate (Sigma, 99% purity) and cesium nitrate (Aldrich, 99% purity) were used. For dicharged ions, calcium nitrate (Sigma–Aldrich, 99% purity), strontium nitrate (Sigma–Aldrich, 99% purity) and copper nitrate (Strem Chemicals, 99.5% purity) were used. For tricharged cations, neodymium nitrate (Sigma–Aldrich, 99.9% purity) and europium nitrate (Rectapur 99% purity) were used.

The pH was adjusted by adding either sodium hydroxide solution prepared from sodium hydroxide (Strem Chemicals, >97% purity) or nitric acid solution (Fluka, >69% purity).

2.2. Ion foam flotation

Flotation solutions were prepared by dissolving the industrial surfactant AKYPO® to reach a concentration of 0.5 mM and two different nitrate salts in purified water (Milli-Q water 18 M Ω Millipore). Concentration of metal cations and pH for each solution are listed in Tables 1 and 2.

Flotation experiments were performed by pouring 80 mL of flotation solutions into the column shown in Fig. 1 (28 mm inner diameter and 250 mm high, cooled with water at 21 °C). Nitrogen gas was injected with a flow-rate of 5 mL min⁻¹ through a sintered glass with 16–40 μm pores at the bottom of the glass column. The foam was retrieved in a 1 L glass balloon at a height of 210 mm, with the foam column above the solution being 80 mm high above the solution. Experiments were stopped when the solution stopped foaming (around 6 h after beginning of the experiment). Samples were withdrawn at the beginning of the flotation in the initial solution and at the end in the residual solution. Each experiment was repeated at least three times.

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