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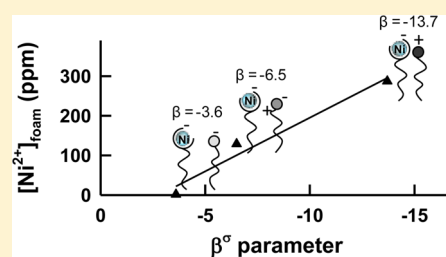
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Headgroup Interactions and Ion Flotation Efficiency in Mixtures of a Chelating Surfactant, Different Foaming Agents, and Divalent Metal Ions

Ida Svanedal,* Susanne Boija, Magnus Norgren,* and Håkan Edlund*

Fibre Science and Communication Network (FSCN), Mid Sweden University, SE-851 70 Sundsvall, Sweden

ABSTRACT: The correlation between interaction parameters and ion flotation efficiency in mixtures of chelating surfactant metal complexes and different foaming agents was investigated. We have recently shown that chelating surfactant 2-dodecyldiethylenetriaminepentaacetic acid (4-C₁₂-DTPA) forms strong coordination complexes with divalent metal ions, and this can be utilized in ion flotation. Interaction parameters for mixed micelles and mixed monolayer formation for Mg²⁺ and Ni²⁺ complexes with the chelating surfactant 4-C₁₂-DTPA and different foaming agents were calculated by Rubingh's regular solution theory. Parameters for the calculations were extracted from surface tension measurements and NMR diffusometry. The effects of metal ion coordination on the interactions between 4-C₁₂-DTPA and the foaming agents could be linked to a previously established difference in coordination chemistry between the examined metal ions. As can be expected from mixtures of amphoteric surfactants, the interactions were strongly pH-dependent. Strong correlation was found between interaction parameter β^σ for mixed monolayer formation and the phase-transfer efficiency of Ni²⁺ complexes with 4-C₁₂-DTPA during flotation in a customized flotation cell. In a mixture of Cu²⁺ and Zn²⁺, the significant difference in conditional stability constants (log *K*) between the metal complexes was utilized to selectively recover the metal complex with the highest log *K* (Cu²⁺) by ion flotation. Flotation experiments in an excess concentration of metal ions confirmed the coordination of more than one metal ion to the headgroup of 4-C₁₂-DTPA.



1. INTRODUCTION

Mixing two or more surfactants often result in synergistic effects, the most commonly investigated being synergism in surface tension reduction and in mixed micelle formation.^{1–3} These types of synergism are the results of interactions between the surfactants, which can be measured by calculating interaction parameters for mixed monolayer formation at interfaces, β^σ , and mixed micelle formation in solutions, β^M , using the regular solution approach.^{4,5} This is a robust description of the nonideal mixing behavior of surfactants, although the approximation is limited by the assumption of zero excess entropy of mixing.^{6,7} The β parameters reflect the nature of the interactions in the mixture compared to the self-interactions of the individual surfactants. The synergistic effects of mixing surfactants can be utilized in many practical applications, including foam flotation. In previous reports on this subject, synergism in surface tension reduction and/or mixed micelle formation in relation to foaming properties has been studied.^{8–11} In this article, a slightly different approach is adopted, where we investigate the correlation between interaction parameters and ion flotation efficiency in mixtures of chelating surfactant metal complexes and different foaming agents.

The binding of divalent or trivalent metal ions to the headgroup of chelating surfactants differs from that of conventional surfactants due to the formation of coordination complexes of high stability. These counterions are therefore very tightly bound to the chelating surfactant and are not

exchanged regularly as counterions normally are. Chelating surfactants can therefore be used as magnetic resonance imaging contrast agents.^{12,13} The strong coordination of metal ions is also utilized when chelating surfactants are used for the recovery of metal ions from aqueous solutions by, for example, foam flotation.¹⁴ In such an application, a foaming agent may be necessary in order to achieve sufficient foaming. The interactions between the two surfactants would play an important role in the efficiency of the process, especially the interactions at the air–water interface, described by β^σ . Ion flotation of the systems is thus a way of studying the effects of the interactions. DTPA (diethylenetriaminepentaacetic acid)-based chelating surfactant 2-dodecyldiethylenetriaminepentaacetic acid (4-C₁₂-DTPA) has been successfully used for the recovery of Cu²⁺ and Mn²⁺ ions by foam flotation in mixtures with a foaming agent.^{15–17} Because of their amphoteric nature,¹⁸ the metal complexes of 4-C₁₂-DTPA interact with ionic surfactants by accepting or donating protons to the aqueous solution in order to increase the attractive interaction.^{19,20}

We have previously described the solution behavior of chelating surfactant 4-C₁₂-DTPA²¹ as well as its interactions, in the absence of metal ions, with different ionic surfactants in mixed micellar systems.¹⁹ The main purpose of the present

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study is to investigate the correlation between headgroup interactions and ion flotation efficiency in mixtures of 4- C_{12} -DTPA metal complexes and foaming agents. We start by examining the interactions at the air–water interface and in mixed micelles of two 4- C_{12} -DTPA metal complexes and differently charged foaming agents. We have recently shown that there is a difference between the coordination of the two studied metal ions, Mg^{2+} and Ni^{2+} ,²² which is likely to affect the interactions with the different foaming agents. The surfactants all have the same hydrocarbon chain length, and the effects can therefore be attributed to the headgroups.²³ By measuring the pH as a function of concentration, we study the exchange of protons between the metal complex and the aqueous solution upon the formation of micelles, which is connected to the interactions in the mixed micelles. We examine the ion flotation efficiency of 4- C_{12} -DTPA in mixtures with different foaming agents and investigate the correlation to the interactions in mixed monolayer formation. Furthermore, we investigate the effect of the difference in conditional stability constants between Cu^{2+} and Zn^{2+} complexes with 4- C_{12} -DTPA upon the selective flotation of metal ions.

2. EXPERIMENTAL SECTION

2.1. Materials. Chelating surfactant 2-dodecyl-diethylenetriamine-pentaacetic acid (4- C_{12} -DTPA) was delivered by Syntagon AB. The synthesis and analyses have been reported earlier.^{21,24} Water for the preparation of samples was of Milli-Q grade. Magnesium chloride, nickel chloride, copper chloride, zinc chloride, dodecyltrimethylammonium chloride (DoTAC), sodium dodecyl sulfate (SDS), and dimethyldodecylamine-*N*-oxide (DDAO) were of analytical grade and used without further purification. In the preparation of samples for metal analysis, Fluka TraceSELECT >69% HNO_3 was used.

2.2. Sample Preparation for pH Measurements, Surface Tension, and NMR Diffusometry. Concentrated stock solutions of 1:1 metal complexes with 4- C_{12} -DTPA, the foaming agents, and their mixtures were prepared at different pH values by appropriate amounts of the respective metal chloride and/or surfactant(s) and sodium hydroxide or hydrochloric acid in water. The labeling of solutions as pH 5 or 7 refers to the pH of the adjusted concentrated stock solutions. Samples for pH (using a Mettler Inlab micro pH electrode), surface tension, and NMR diffusometry measurements were prepared by diluting the concentrated stock solutions with pH-adjusted water.

2.3. Surface Tension Measurements. The surface tension was measured with a Krüss K6 tensiometer and a platinum du Noüy ring at a temperature of approximately 22 °C. The surface tension was measured once right after sample preparation, and then the sample was left for 5 min before it was measured four times consecutively. The mean values are reported.

2.4. NMR Diffusometry. The NMR diffusometry measurements were carried out using the stimulated echo pulsed field gradient (STE-PFG) NMR sequence. This technique is well established, and a detailed description can be found elsewhere.^{25–27} The experiments were performed on a Bruker Avance DPX 250 MHz NMR spectrometer equipped with a Bruker self-diffusion probe capable of providing magnetic field strengths of up to 1200 G/cm. The temperature was kept at 22 °C. The attenuation of the echo signal was fitted using eq 1 to extract self-diffusion coefficient D

$$I = I_0 e^{\{-D(2\pi\gamma G\delta)^2(\Delta - \frac{\delta}{3}) \times 10^4\}} \quad (1)$$

where I denotes the observed echo intensity, I_0 is the echo intensity in the absence of field gradient pulses, γ is the magnetogyric ratio, G is the field gradient strength, δ is the duration of the gradient pulse, and Δ is the time between the leading edges of the gradient pulses. In all experiments, δ was set to 1.5 ms and Δ was set to 40 ms while gradient G was varied linearly. For the water self-diffusion measurements, we used a repetition time of 10 000 ms, a gradient starting value of 5 G/cm, and an end value of 75 G/cm, and 21 data points were measured,

while for the surfactant measurements we used a repetition time of 3000 ms, a gradient starting value of 75 G/cm to suppress the water signal as much as possible without compromising the surfactant signals, an end value adjusted to the expected self-diffusion coefficient for the surfactant, and at least 31 data points.

2.5. Ion Flotation. Ion flotation was performed at room temperature in an earlier-described customized flotation cell consisting of a Plexiglass cylinder and a sintered glass frit mounted at the bottom of the cell.^{15,16} A nitrogen flow of approximately 0.5 L/min through the frit, to induce bubbles, was applied. Different flotation strategies were used for the two different flotation studies performed. In the investigation of the β parameter's influence on the phase transfer of the chelating surfactant– Ni^{2+} complex from the bulk solution to the foam fraction, due to the specific foaming agent added (SDS, DDAO, or DoTAC), the initial Ni^{2+} concentration in the bulk solution was about 1 ppm. Samples of 4- C_{12} -DTPA, nickel chloride, and one of the three foaming agents in a molar ratio of 1.2:1:10 were prepared at a volume of 1.0 L. The flotations were performed gently to allow for drainage of the formed foam in the flotation cell before 1.7 g of the initially formed foam was collected. The foam fraction was defined as the mass ratio of the collected foam to the remaining bulk liquor. The metal ion content in the foam samples, as well as in the remaining bulk solution, was determined as described in section 2.6. In the study of the conditional stability constant's relation to the ion selectivity during flotation, DDAO was chosen as the foaming agent, and molar ratios between the chelating surfactant and DDAO were 1.2:10 in single metal ion flotation experiments (Cu^{2+} , Zn^{2+}) and 1:10 for investigations of the competition between copper and zinc, respectively. To be able to follow the depletion of metal ions in the cell during the flotation process, samples were taken from the bulk solution at different times during the flotation and analyzed as described in section 2.6. The flotations were terminated after approximately 1 h, when the foam formation in the cell diminished.

2.6. Metal Analysis. The metal analyses were performed by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7700 series ICP-MS. The ICP-MS metal standards used were diluted with 2% HNO_3 . To yield proper concentrations for the preparation of linear calibration curves, samples of 10 mL were acidified with 200 μ L of >69% HNO_3 .

3. RESULTS AND DISCUSSION

3.1. Interaction Parameters in Mixtures of Metal Complexes and Foaming Agents. Interaction parameter β^σ for mixed adsorption at the air–water interface was calculated from surface tension data using eqs 2 and 3.⁵ Equation 2 is solved numerically for X_1 , the mole fraction of surfactant 1 in the mixed monolayer, which is then substituted into eq 3 to calculate β^σ

$$\frac{X_1^2 \ln\left(\frac{\alpha C_{12}}{X_1 C_1^0}\right)}{(1 - X_1)^2 \ln\left[\frac{(1 - \alpha)C_{12}}{(1 - X_1)C_2^0}\right]} = 1 \quad (2)$$

$$\beta^\sigma = \frac{\ln\left(\frac{\alpha C_{12}}{X_1 C_1^0}\right)}{(1 - X_1)^2} \quad (3)$$

where α is the mole fraction of surfactant 1 in the mixed solution (on a surfactant-only basis) and C_1^0 , C_2^0 , and C_{12} are the solution-phase molar concentrations of surfactants 1 and 2 and their mixture at α , respectively, required to produce a given surface tension value (Figure 1).

Interaction parameter β^M for mixed micelle formation was calculated from the critical micelle concentrations (cmc's) of individual surfactants 1 and 2 (cmc_1 and cmc_2) and their mixture (cmc_{12}) at the mole fraction α of surfactant 1 in the

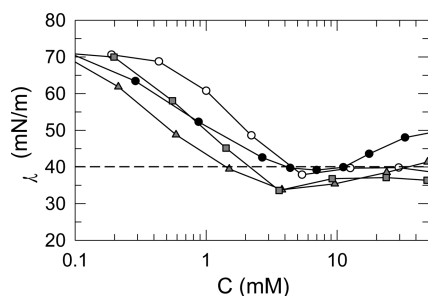


Figure 1. Surface tension vs concentration for Ni^{2+} -4- C_{12} -DTPA (●), SDS (○), and their mixtures at $\alpha_{\text{Ni}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.75$ (▲) and $\alpha_{\text{Ni}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.25$ (■) at pH 5. C_1^0 , C_2^0 , and C_{12} were obtained at $\gamma = 40$ mN/m.

mixed solution (on a surfactant-only basis).⁴ Equation 4 is solved numerically for X_1^M , the mole fraction of surfactant 1 in the micelles, which is then substituted into eq 5 to calculate β^M .

$$\frac{(X_1^M)^2 \ln\left(\frac{\alpha \text{cmc}_{12}}{X_1^M \text{cmc}_1}\right)}{(1 - X_1^M)^2 \ln\left[\frac{(1 - \alpha) \text{cmc}_{12}}{(1 - X_1^M) \text{cmc}_2}\right]} = 1 \quad (4)$$

$$\beta^M = \frac{\ln\left(\frac{\alpha \text{cmc}_{12}}{X_1^M \text{cmc}_1}\right)}{(1 - X_1^M)^2} \quad (5)$$

The cmc's were determined by NMR diffusometry (Figure 2) if not otherwise stated.

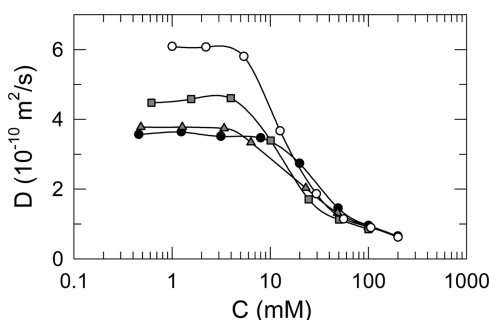


Figure 2. Self-diffusion coefficient vs concentration for Mg^{2+} -4- C_{12} -DTPA (●), SDS (○), and their mixtures at $\alpha_{\text{Mg}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.75$ (▲) and $\alpha_{\text{Mg}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.25$ (■) at pH 7.

The interaction parameters reflect the nature of the interactions in the mixed system relative to the self-interactions for the two individual surfactants. The value of β is proportional to the excess free energy of mixing, and the stronger the attractions and/or the weaker the repulsions in the mixture relative to the self-interactions for the individual surfactants, the more negative the β parameter. Since surfactants with the same hydrophobic chain length were studied here, the effects are related to interactions between headgroups.

As shown in Figure 3, there are two types of donor atoms in the headgroup of 4- C_{12} -DTPA. The carboxylate oxygen atoms, giving rise to negative charges when they are dissociated, and the tertiary amine nitrogen atoms, generating positive charges in their protonated form, cause a rather complex titrating behavior with overlapping pK_a -values.²¹ In the absence of metal ions, all donor atoms are titrating and the headgroup charge

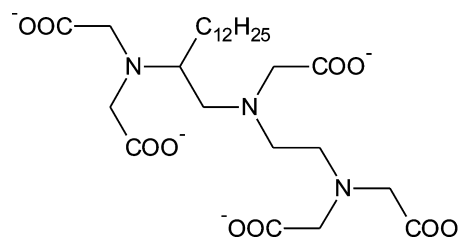


Figure 3. Molecular structure of 4- C_{12} -DTPA at high pH, with eight possible donor atoms that can coordinate metal ions, i.e., the five carboxylate oxygen atoms and the three nitrogen atoms.

varies with pH, in theory from +3 at low pH to −5 at high pH. At the two investigated pH levels (pH 5 and 7) 4- C_{12} -DTPA is zwitterionic with a negative net charge. There is flexibility in the configuration of the headgroup as well as in the allocation of protons within the headgroup, which is affected by the interactions between neighboring surfactants in adsorbed monolayers and micelles. The coordination of a metal ion markedly changes the headgroup of the chelating surfactant. The negative net charge is reduced by the coordination of the positively charged metal ion, there is less flexibility in the headgroup, and the number of dissociation states is reduced.

The titrating groups of 4- C_{12} -DTPA complicate the description of the systems,¹⁹ even though the number of dissociation states is markedly reduced by the coordination of a metal ion. At any intermediate pH level, there will be a distribution of differently charged species, and the complexity of the system depends on the number of overlapping pK_a values. This picture becomes even more complex as micelles start to form, since the high charge density at the micellar surface affects the dissociation of surfactants in micelles.²¹ A solution of a 4- C_{12} -DTPA metal complex is thus already a mixed system, where the different components and mixing ratio depend on the pH. Therefore, when treating mixtures of a 4- C_{12} -DTPA metal complex and a foaming agent as a binary mixture, the following limitations are assumed: (i) the metal complex of 4- C_{12} -DTPA is defined as the distribution of differently charged species at a specific pH, (ii) the dissociation of the metal complex in the mixed micelles will be affected by the presence of the foaming agent, and thus the mixed micelles may consist of a distribution of species that differs from the distribution in micelles of the metal complex alone, and (iii) the interaction parameter is dominated by the strongest interactions in the systems, and the calculated β parameter primarily describes these interactions.

In the derivation of the equations for calculating the interaction parameters,^{4,5} electrical effects are ignored. The ionic strength should therefore be kept constant by adding a swamping electrolyte when dealing with ionic surfactants in order to obtain interaction parameters that correctly describe the system over all mixing ratios.²⁸ In surfactant mixtures containing the chelating surfactant, a variation in the ionic strength with the mixing ratio is expected due to the numerous functional groups, and a slight dependence on the mixing ratio was also observed for the interaction parameters. The mixtures were examined in several different mixing ratios, and the mean values are reported in Table 1. A relatively high background electrolyte would have been necessary to maintain a constant ionic strength in these experiments due to the numerous titrating groups of the chelating surfactant, but this would have reduced the synergistic effects in mixtures of metal complexes and foaming agents pursued in foam flotation. It is therefore of

Table 1. Average Calculated β Parameters for the Mixtures

	SDS pH 5		SDS pH 7		DDAO pH 5		DoTAC pH 5	
	β^M	β^S	β^M	β^S	β^{Ma}	β^S	β^M	β^S
4-C ₁₂ -DTPA	-3.1 ^b	n/a ^c	-3.6 ^b	n/a ^c	-11.6	-8.6	-9.3 ^b	n/a ^c
Mg ²⁺ -4-C ₁₂ -DTPA	-4.2	-6.1	-3.6	-1.8	n/a ^c	n/a ^c	-8.2	-8.9
Ni ²⁺ -4-C ₁₂ -DTPA	-3.5	-3.6	-4.6	-1.2	-7.2	-6.5	-11.3	-13.7

^aDetermined from surface tension measurements. ^bFrom ref 19. ^cNot determined.

great interest to examine these systems without added electrolyte in order to achieve maximum synergism.

We briefly review the interactions in mixed micellar systems of 4-C₁₂-DTPA with DoTAC and SDS, respectively.¹⁹ Amphoteric 4-C₁₂-DTPA interacts with cationic DoTAC by donating protons to the aqueous solution in order to increase the number of negative charges and thereby increase the attractive interactions. In mixtures with the anionic SDS, on the other hand, 4-C₁₂-DTPA accepts protons from the aqueous solution to increase the number of positive charges. Due to the negative net charge of 4-C₁₂-DTPA at the investigated pH levels, the interactions were found to be stronger with DoTAC than with SDS. As seen in Table 1, this was the case also for the Mg²⁺ and Ni²⁺ complexes with 4-C₁₂-DTPA. The influence of metal ion coordination on the magnitude of β^M for the mixture with DoTAC was, however, different for the two investigated metal ions. The coordination of Ni²⁺ increases the magnitude of the β^M parameter, whereas the coordination of Mg²⁺ decreases the magnitude of the β^M parameter. The difference correlates to a difference in coordination between the two ions.²² Mg²⁺ is coordinated preferably by the carboxylate oxygen atoms, thereby reducing the number of negatively charged groups. This reduces the attractive interactions with the cationic DoTAC, as seen from the smaller β^M value. Ni²⁺ is coordinated strongly by both types of donor atoms. The coordination of Ni²⁺ consequently reduces the number of amine groups available for protonation, and thereby the number of positive charges in the headgroup. This increases the attractive interactions with the cationic DoTAC, hence the increased magnitude of the β^M value. The strong attractive interaction in the Ni²⁺-4-C₁₂-DTPA/DoTAC system was evident from the formation of precipitate at equal mixing of the surfactants or a higher mole fraction of DoTAC. Generally, β^S values are more negative than β^M values, i.e., interactions in mixed monolayers are stronger than interactions in mixed micelles.²⁹ This was observed for both metal complexes with DoTAC, and the consequences of the difference in coordination chemistry of the metal ions are even more pronounced for the β^S values than for the β^M .

Both metal ions increase the magnitude of the β^M values in mixtures with anionic SDS at pH 5 since the net negative charge of 4-C₁₂-DTPA is reduced by the coordination of the positively charged metal ion, but now the interaction is strongest with the Mg²⁺ complex. Again, the difference correlates with the difference in the coordination chemistry of the two metal ions. Since Mg²⁺ ions are coordinated preferably by the carboxylate oxygen atoms, the number of negatively charged groups is more effectively reduced by the coordination of Mg²⁺ ions than by the coordination of Ni²⁺ ions. At pH 7, on the other hand, β^M is not significantly affected by either of the metal ions, even though the cmc values in the mixtures with

SDS are indeed reduced by the coordination of the metal ions. This can be explained by the reduced self-repulsions of 4-C₁₂-DTPA due to metal ion coordination, i.e., lower cmc's of the metal complexes compared to that of pure 4-C₁₂-DTPA. For both metal complexes, the reduced repulsions in the mixtures with SDS are balanced by the reduced self-repulsions of the metal complexes. In mixtures with SDS, both metal complexes show more negative β^S than β^M values at pH 5 but not at pH 7. Nevertheless, the Mg²⁺ complex shows stronger interactions than the Ni²⁺ complex also in mixed monolayers at both pH values examined, correlating to the difference in coordination chemistry discussed above. As seen from the effects of pH on the β^S values in the mixtures with SDS, pH has a significant effect on the interactions in mixtures of amphoteric surfactants.

The Ni²⁺ complex was also examined in mixtures with pH-responsive DDAO, which is cationic at low pH and zwitterionic at high pH. The pK_a value of DDAO monomers is 4.78.³⁰ For pure 4-C₁₂-DTPA at pH 5, the interactions with DDAO are even stronger than with DoTAC. We previously studied this mixture at pH 7, where significantly weaker interactions were observed ($\beta^M = -6.2$).¹⁹ The stronger interaction at pH 5 is a natural consequence of the increased protonation of both surfactants at lower pH, leading to reduced repulsions in the mixed micelles, which further illustrates the significant effect of pH on the interaction parameters. The coordination of Ni²⁺ ions reduces the interaction with DDAO. Precipitate was, however, also formed in this system at equal molar mixing or excess DDAO. In mixtures of two titrating surfactants, it may be more difficult to predict the effects of metal ion coordination on the interaction parameters. A possible reason for the weaker interactions may lie in the reduced electrostatic interactions between DDAO and 4-C₁₂-DTPA as a consequence of the coordination of Ni²⁺ ions.

The composition of mixed micelles at cmc vs the composition in the solution is shown in Figure 4a,b for mixtures of Mg²⁺-4-C₁₂-DTPA and Ni²⁺-4-C₁₂-DTPA, respectively. The maximum synergism and minimum cmc are found

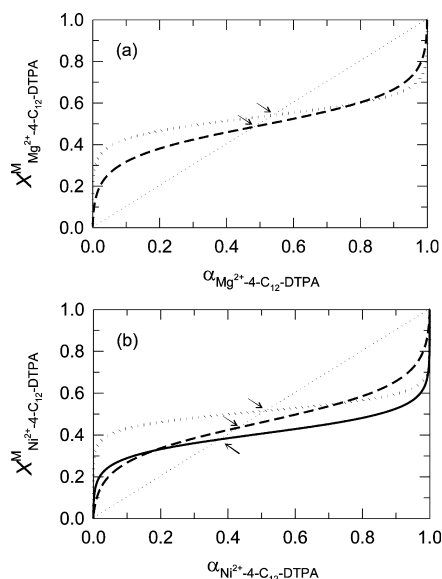


Figure 4. Mole fraction in micelles at cmc vs mole fraction in solution for mixtures of Mg²⁺-4-C₁₂-DTPA (a) and Ni²⁺-4-C₁₂-DTPA (b) with DoTAC (···), SDS (---), and DDAO (—) at pH 5. The different optimum compositions for the mixtures are indicated by the arrows.

at the point where the solution composition equals the optimum composition in the mixed micelles, i.e., where the curves in the figure cross the diagonal. The optimum composition depends on the difference between the cmc's of the individual components. The smaller this difference, the closer to 0.5 is the optimum composition, as seen in the Mg^{2+} -4- C_{12} -DTPA/SDS mixture in Figure 4a where the cmc of the Mg^{2+} complex is 10 mM and the cmc of SDS is 9 mM. When the cmc values differ, the optimum composition is shifted toward increased mole fractions of the surfactant with the lowest cmc, which is most pronounced when the Ni^{2+} complex with cmc 14 mM is mixed with DDAO with cmc 2.5 mM shown in Figure 4b. When comparing Figure 4a,b, it is clear that the optimum compositions in the mixtures are positioned at a lower mole fraction of Ni^{2+} -4- C_{12} -DTPA compared to that of Mg^{2+} -4- C_{12} -DTPA due to the higher cmc of Ni^{2+} -4- C_{12} -DTPA. The β^{M} parameter is visible in the slope of the linear part of the curve; the stronger the attraction between the two surfactants, the stronger the tendency of the system to strive toward the optimum composition in micelles over the whole solution composition. As shown in Table 1, both metal complexes show the most negative β^{M} parameter in mixtures with DoTAC, and this is seen also in Figure 4.

The pK_{a} values of the metal complexes with 4- C_{12} -DTPA are governed by the electrostatic interactions between the titrating groups within the complex. Upon the formation of mixed micelles, the interaction between the surfactants affects the protonation of the metal complexes. Just like the pure chelating surfactant, the metal complexes are amphoteric and interact with different ionic surfactants by accepting or donating protons to the aqueous solution in order to adjust its electrical charge and increase the attractive interactions in the micelles. Measuring the pH of the surrounding solution as a function of concentration thus gives information on whether the repulsions between positive or negative charges dominate the mixed micelles. The pH behavior of the mixtures of Ni^{2+} -4- C_{12} -DTPA with SDS and DoTAC, respectively, are shown in Figure 5.

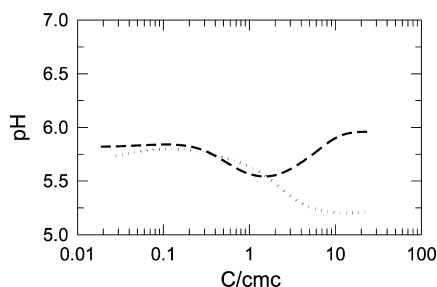


Figure 5. pH vs concentration/cmc for mixtures of Ni^{2+} -4- C_{12} -DTPA with SDS (---) and DoTAC (···).

Protons are absorbed by the complex in the mixture with SDS due to repulsion between negative charges, while in the mixture with DoTAC, protons are released from the complex to the aqueous solution as a result of repulsion between positive charges.

3.2. Interaction Parameter's Influence on the Phase Transfer of Metal Chelates During Ion Flotation. During metal ion flotation, besides the foamability of surfactant–water mixtures that relates to the hydrophilic–hydrophobic balance and the critical packing parameter, outspoken synergetic interactions in mixed surfactant systems could be expected to affect the surfactant phase distribution between the formed

foam and the bulk solution and accordingly the metal ion distribution. To our knowledge, no attempts have been presented in the literature within the scope to outline this properly. Thus, in order to investigate possible relationships between the interaction parameters β^{O} for the chelating surfactant–foaming agent presented in Table 1, different mixtures of 4- C_{12} -DTPA and the foaming agent in a 1 ppm Ni^{2+} solution at a molar ratio of 1.2:10:1 were gently flotated to allow for good water drainage of the formed foam. The initial 1.7 g of the foam was collected, and the metal content was determined. The results from the experiments are presented in Table 2.

Table 2. Ni^{2+} Bulk Depletion and Phase Transfer to Initially Formed Foam During Ion Flotation Using Different 4- C_{12} -DTPA Foaming Agent Mixtures

foaming agent	$[\text{Ni}^{2+}]_{\text{initial}}$ (ppm)	foam fraction ^a (ppt)	$[\text{Ni}^{2+}]_{\text{foam}}$ (ppm)	Ni^{2+} bulk depletion (%)
SDS	1.08	1.7	1.50	0.25
DDAO	0.99	1.7	129	22
DoTAC	1.03	1.7	287	47

^aMass ratio of collected foam and remaining bulk liquor.

From the results shown in Table 2 it is evident that the choice of foaming agent plays a significant role in the transfer of the Ni^{2+} -chelating surfactant complex from the bulk to the foam phase during ion flotation. In the case of the SDS-chelating surfactant mixture, more or less no depletion of the bulk phase and subsequently no enrichment of Ni^{2+} in the foam fraction can be observed, whereas the DoTAC-4- C_{12} -DTPA system transfers almost half of the total Ni^{2+} content from the bulk to the foam collected at a very low foam fraction, below 2 ppt of the original liquor's mass.

In Figure 6, the interaction parameter, β^{O} , of the different foaming agent–chelating surfactant mixtures from Table 1 is

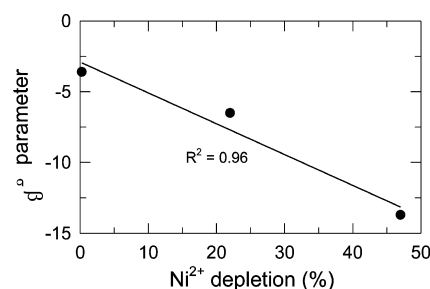


Figure 6. Interaction parameter in different foaming agent–4- C_{12} -DTPA mixtures as a function of metal ion bulk depletion during the ion flotation of Ni^{2+} solutions.

plotted vs the Ni^{2+} bulk depletion obtained from Table 2. The outcome shows a surprisingly good linear correlation. This clearly implies that the magnitude of the interaction parameter is important for the efficiency of ion flotation in mixed surfactant systems.

3.3. Ion Flotation Selectivity and Efficiency in Relation to Conditional Stability Constants. Since chelating surfactant 4- C_{12} -DTPA has eight possible donor atoms that can coordinate to metal ions, the strength of interaction, usually depicted by the conditional stability constant, K , is dependent on the specific metal ion's physical properties and the solution conditions.^{19,21,22} Interactions with metal ions of valency higher

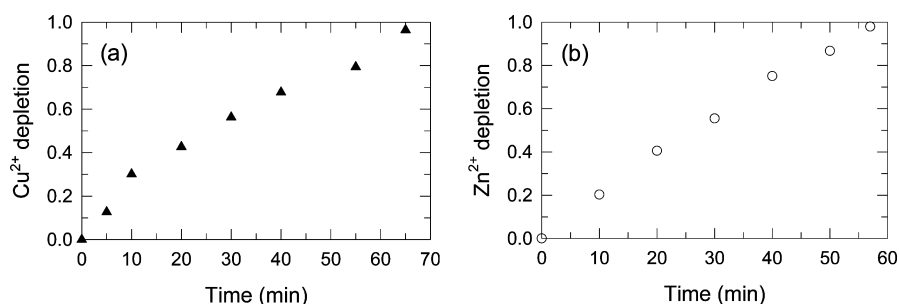


Figure 7. Bulk depletion of metal ions vs time during ion flotation at pH 5 and room temperature. The molar mixing ratio of 4- C_{12} -DTPA, DDAO, and the specific metal ion was 1.2:10:1. (a) Cu^{2+} ; (b) Zn^{2+} .

than 1 often render conditional stability constants of numerical magnitudes that, due to practical reasons, are represented by their logarithmic values when reported. In the case of a chelating surfactant, these differences in strength open up possibilities to separate specific metal ions selectively in mixtures. In a recent investigation, we showed that logarithmic conditional stability constants of five different 4- C_{12} -DTPA–divalent metal ion complexes are very close to the values of similar metal complexes formed by DTPA.²² For instance, for copper and zinc ions, the conditional stability constants with 4- C_{12} -DTPA determined at room temperature and pH 5 were $\log K_{Cu} = 11.9$ and $\log K_{Zn} = 9.9$, respectively.

In Figure 7, ion flotations of 1 ppm solutions of (a) copper and (b) zinc using DDAO as a foaming agent are shown. It can be noticed that the depletion of the bulk phase vs time is very similar in both cases, and any deviation noticed is due to small variations over time in the flow of nitrogen that is injected to generate foaming. The metal ion end-concentrations in the bulk solution were 0.03 and 0.02 ppm for the copper and zinc flotations, respectively, which indicate a good removal of the metal chelates formed. The accumulated foam fractions were 3% of the initial solution weights.

Figure 8 shows results from ion flotations of mixed metal ion solutions comprising Cu^{2+} and Zn^{2+} . Under the solution

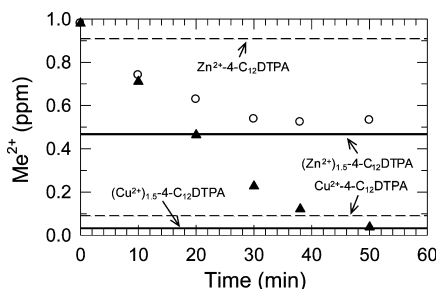


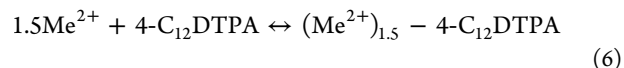
Figure 8. Ion flotation of Cu^{2+} (▲) and Zn^{2+} (○) complexes vs time. The molar mixing ratio of 4- C_{12} -DTPA, DDAO, Cu^{2+} , and Zn^{2+} was 1:10:1:1. The dashed lines represent calculated concentrations of uncomplexed metal ions, assuming equimolar reaction stoichiometry with the chelating surfactant. The full lines are calculated concentrations of uncomplexed metal ions when each 4- C_{12} -DTPA is assumed to be able to bind 1.5 metal ions.

conditions of the experiment, the difference in $\log K$ between the two metal chelates formed is 2 units. If the reaction stoichiometry between the two metal ions and the chelating agent is 1:1:1, then this stresses that when the chelating agent is added, the metal chelate with the highest $\log K$, which in this case is Cu^{2+} -4- C_{12} -DTPA, theoretically should be present in a

concentration ratio of 10:1 with respect to the zinc chelate at equilibrium. In Figure 8, the uncomplexed metal ion concentrations that would be expected to support this are indicated by the dashed lines.

As can be seen, there are relatively large deviations between experiments and the applied theory. However, assuming an equimolar stoichiometry for the metal complexation reaction might not be correct.³¹ According to our recent studies, 4- C_{12} -DTPA is shown to sequester more than one metal ion per molecule; mixtures of 1:1 and 2:1 complexes between Cu^{2+} and 4- C_{12} -DTPA could be detected by UV–visible spectroscopy measurements at pH 5.²²

At the end of the flotation, the bulk concentration of Cu^{2+} and Zn^{2+} in Figure 8 indicates a total depletion of metal ions of approximately 1.5 ppm. This corresponds to a reaction stoichiometry of 1.5:1 between metal ions and the chelating agent, as illustrated in eq 6



which gives the following coupled equilibrium equation for the competitive complexation between Cu^{2+} and Zn^{2+} and 4- C_{12} -DTPA

$$\frac{K_{Cu}}{K_{Zn}} = \frac{[(Cu^{2+})_{1.5}4-C_{12}DTPA][Zn^{2+}]^{1.5}}{[(Zn^{2+})_{1.5}4-C_{12}DTPA][Cu^{2+}]^{1.5}} \quad (7)$$

where K_{Cu} and K_{Zn} are the conditional stability constants of the two metal complexes formed. To test this hypothesis against the experimental outcome, eq 7 was solved numerically, and the resulting uncomplexed metal ion concentrations are indicated by the full lines in Figure 8. The latter approach clearly gives a much better compliance with the experimentally obtained data, and it is reasonable to assume that eq 6 describes the complexation reactions in the system fairly well. To confirm this further, 4- C_{12} -DTPA was added to a solution of Cu^{2+} , Zn^{2+} , and DDAO in a molar mixing ratio of 1:2:1:10 and floated. In Figure 9, the results are shown together with calculated uncomplexed metal ion concentrations (full lines) using eq 7. From the experimental results, we can notice a minor deviation from the targeted zinc ion concentration that obviously should have been 1 ppm. Still, the calculated uncomplexed metal ion concentrations satisfy the experiments extremely well, and eq 6 is thus a very good description of the complexation reactions between 4- C_{12} -DTPA and Cu^{2+} and Zn^{2+} .

4. CONCLUSIONS

The strength of the interactions between the studied metal complexes with 4- C_{12} -DTPA and different foaming agents

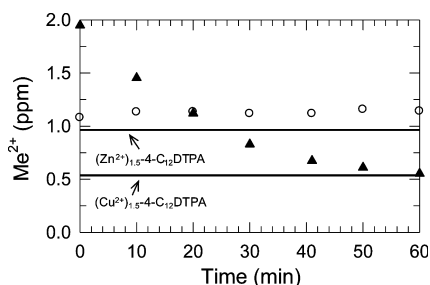


Figure 9. Ion flotation of Cu^{2+} (▲) and Zn^{2+} (○) complexes vs time. The molar mixing ratio of 4- C_{12} -DTPA, DDAO, Cu^{2+} , and Zn^{2+} was 1:10:2:1. The full lines are calculated concentrations of uncomplexed metal ions when each 4- C_{12} -DTPA is assumed to be able to bind 1.5 metal ions.

correlates to the headgroup charges if the components in the mixtures. Because of the negative net charge of the metal complexes at the specific pH levels, the interactions were strongest in mixtures with cationic DoTAC, followed by zwitterionic DDAO, and weakest with anionic SDS. The coordination of Mg^{2+} and Ni^{2+} did, however, affect the interactions with the foaming agents slightly differently, which correlates to the previously established difference in the coordination chemistry between the two metal ions leading to a slight difference in the relative numbers of positive and negative charges in the headgroup.²² As can be expected from mixtures of amphoteric surfactants, the interactions are strongly pH-dependent, and control of the pH is important for controlling the interactions.

A strong correlation was found between the surfactant interactions in mixed monolayers, as calculated by β^{σ} parameters, and the phase-transfer efficiency in mixtures of the Ni^{2+} complex of chelating surfactant 4- C_{12} -DTPA and different foaming agents during ion flotation. This clearly implies that the magnitude of the interaction parameter is important for the efficiency of ion flotation in mixed surfactant systems. In a mixture of metal ions, a significant difference in $\log K$ between the metal complexes could be utilized to selectively recover the metal complex with the highest conditional stability constant by ion flotation. Flotation experiments in an excess concentration of metal ions confirmed the coordination of more than one metal ion to the headgroup of 4- C_{12} -DTPA.²²

AUTHOR INFORMATION

Corresponding Authors

*E-mail: ida.svanedal@miun.se.

*E-mail: magnus.norgren@miun.se.

*E-mail: hakan.edlund@miun.se.

Notes

The authors declare no competing financial interest.

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