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Influence of metal ions on the aggregation of anionic surfactants. Studies on the interactions between environmental pollutants in aqueous solutions

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ABSTRACT

Surfactants, which are environmental pollutants, are also used in processes dedicated to the removal of heavy metals from contaminated environment. Thus, to clarify surfactant/heavy metals effects occurring in water and soil and to successfully use amphiphiles for metal elimination, the information on the interactions between surfactants and metal ions are highly required. In this work the influence of Cd^{2+} and Zn^{2+} on the aggregation of anionic surfactants: sodium dodecyl sulfate (SDS) and Sarkosyl was investigated. The experiments involved electrical conductance and pH measurements as well as the flame atomic absorption spectrometry (FAAS) studies. The results evidenced that both studied metal ions form aggregates of different stability with SDS and Sarkosyl at the concentrations below critical micelle concentration and they are able to bind also to the negatively charged micelles. SDS was found to be more effective than Sarkosyl in binding metal ions, however, both surfactants manifested stronger binding capacity to Cd^{2+} as compared to Zn^{2+}. It was also summarized that the ability of SDS and Sarkosyl to bind metal ions changes in the following order: $Pb^{2+} > Cd^{2+} > Zn^{2+}$. The foregoing findings were discussed in the relation to the differences in the values of the hydrated ionic radii and the enthalpies of hydration of the studied metal ions.

1. Introduction

Human activities lead to the emission of a large fraction of heavy metals to the environment and a lot of efforts is put to remove these highly hazardous contaminants from water and soil. The toxicity of heavy metals is related to the fact that they are not biodegradable and may accumulate in the food chain becoming harmful to plants, animals and humans. In fact, some of heavy metals e.g. magnesium, copper, zinc or manganese, are classified as essential nutrients and they are vital for various biochemical processes occurring in cells, however, at given doses also these metals are toxic [1–3]. The technologies used for elimination of heavy metals from the environment are based on a whole range of physicochemical and interfacial processes including precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation or flotation [1,4–5]. However, the practical use of particular technique is determined by several factors including not only the effectiveness of a given method (limited for example by the concentration of pollutants, the presence of co-pollutants or physicochemical conditions) but also its cost or environmental risk [1,4]. Therefore, the investigations aimed at optimizing the methods of metal removal to make them the most efficient, cheap and environmentally friendly, are continuously performed [6,7]. To the methods dedicated to the removal of metals as well as other pollutants belong also those, in which the surface active agents (surfactants) are used (e.g. soil washing [8], micellar-enhanced ultrafiltration (MEUF) [9–12], Cloud-Point extraction (CPE) [13,14] or flotation [15]). These compounds, having amphiphilic structure, are able to adsorb at the interfaces and modify their properties as well as, at a given concentration (called critical micelle concentration, CMC), to aggregate and form micelles [16]. The above mentioned properties determine the use of surfactants in remediation processes. Namely, the ability of these compounds to accumulate at the interfaces enhances desorption and mobility of pollutants, while the micellization and the capacity to include the contaminants in the aggregates (solubilisation) makes the pollutants, trapped in the micelles interior, much easier to the removal and further separation [17,18]. The assistance of surfactants in the elimination of metal ions is based on the formation of associates between dissociated surfactant in its monomeric form or on solubilisation process. Namely, at the concentrations below CMC the ionic surfactants may bind metal ions via electrostatic forces and this complexation (sometimes followed by precipitation) may result in immobilization of metal ions and improve their separation. Above CMC ionic pollutants may bind to the micelles formed from ionic surfactants or the pollution may be solubilized in the micelle

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core formed from ionic or nonionic surface active agent [18,19]. The surface activity and resulting interfacial and aggregation properties of surfactants is of much significance in the removal of pollutants from the environment, however, it should be mentioned that the same properties are responsible also for their harmful effect on abiotic part of the environment as well as their toxicity to the living organisms [17,20–24]. Because of this, it is highly important to use these substances effectively, economically and with reduced environmental risk. The foregoing arguments motivate also the investigations on optimization of the remediation processes utilizing the surface active agents. The basic and indispensable element of these studies are the experiments providing a fundamental knowledge on the nature, strength and mechanism(s) of interactions between surfactants and pollutants at various conditions. Such kind of investigations are also systematically done for anionic surfactant: sodium dodecyl sulfate (SDS) and (mainly) trivalent metal ions systems [25–30]. The information provided by these investigations concern the effect of metal ions on the aggregation of SDS molecules at the concentrations below and above CMC and are important from the point of view of the application of anionic surfactants as the agents for the removal of metal ions from contaminated water and soil or as the additives supporting these processes. Recently similar experiments were done for different anionic surfactants: sodium dodecyl sulfate (SDS), *N*-Lauroylsarcosine sodium salt (Sarkosyl) and Sodium dodecylbenzenesulfonate (SDBS) to compare their interactions with and the capacity to bind lead(II) ions [31]. It was found that all the studied surfactants form insoluble complexes of different stability with lead(II) ions below CMC and that metal ions bind in the highest extend to the micelles formed from SDS while their binding to SDBS micelles is the least effective. In the continuation of these studies, to verify the relationship between the kind of divalent metal ions and their effect on surfactant properties, in this work the influence of zinc and cadmium ions on two anionic surfactants: SDS and Sarkosyl was investigated by means of electrical conductance and pH measurements as well as the flame atomic absorption spectrometry (FAAS) experiments. The aim of these experiments was to compare the effect of the studied metal ions on the aggregation of the surface active agents in a wide range of concentrations and to evaluate the ability of these two surfactants to bind metal ions in the solutions. The collected results were analyzed in reference to the data published previously for lead(II) ions and the conclusions concerning the factors affecting the binding of particular metal ions to anionic surfactants and their micelles were provided.

2. Material and methods

2.1. Experimental

The surfactants: sodium dodecyl sulfate (SDS, ≥99.9%) and *N*-Lauroylsarcosine sodium salt (Sarkosyl, ≥97%) and inorganic salts: Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 98%) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%) were purchased from Sigma Aldrich and used as received. The investigated compounds were weighted out on the analytical balance (Mettler Toledo, the accuracy: ±0.01 mg) and then dissolved in UltrapureMilli-Q water (water has the surface tension of 72.6 mN/m and resistivity of 18MΩcm at 20.0 ± 0.1 °C). The solutions of desirable concentrations were obtained by dilution of the respective stock solutions.

2.2. Methods

Electrical conductance of the solutions was measured at the temperature of 23 ± 1 °C with Elmetron CPC – 505 multifunction meter (pH/conductivity/salinity meter). The cell constant was calibrated with KCl aqueous solutions. The conductivity of water at the same conditions was also measured. The electrical conductance was measured for a series of solutions differing in the concentration of the respective surfactant and various concentrations of particular metal ions ($C_{\text{metal ions}} =$ 0; 0.001; 0.01; 0.1; 0.5 and 1 mM). The measurements were initialized immediately after the preparation of the solutions. The conductivity was recorded after reaching a stable value, that is, when the fluctuations were lower than 0.5 μS/cm within 1 min. The electrical conductivity for each solution was obtained from at least two independent measurements. The solutions specific conductance presented as a function of the surfactant concentration was calculated from experimentally obtained values (κ_{exp}) corrected for the value obtained for water κ_{water}: $\kappa = \kappa_{\text{exp}} - \kappa_{\text{water}}$.

The pH values of fresh selected solutions were measured by using a laboratory pH meter (Elmetron, Poland) equipped with a combined glass/reference electrode (Ag/AgCl), which was calibrated before experiments.

Moreover, the selected solutions of particular surfactants at the concentrations covering the range below and above CMC value and containing 0.01 mM of Cd^{2+} or Zn^{2+} ions as well as their mixture were filtered through PVDF membrane (0.22 μm syringe filter, EuroClone S. p. A, Italy) and then the concentration of metal ions in filtrate was determined with the flame atomic absorption spectrometry (FAAS) using a Perkin Elmer apparatus AAnalyst 300. For each sample the measurements were repeated at least three times and the average value as well as the relative standard deviations of each sample were calculated.

2.3. The analysis of the electrical conductivity data

Based on the specific conductance vs. surfactant concentration plots the aggregation parameters for the studied surfactants were obtained from the intersection of the linear curves fitted to the experimental data below and above particular break points (to each part of the plot 1000 points were fitted; it was illustrated in Fig. 2). However, at lower concentrations of metal ions in the system the alterations in the slope of the curves below CMC were not observed or they were very vague. Although in these cases the second derivative method was additionally applied (namely, the approach based on the fact that the aggregation parameters manifest as minima and maxima in the $\partial^2\kappa / \partial C^2$ vs C plots) for some of the studied systems the determination of the aggregation parameters was impossible. At higher metal ions level the results obtained from the application of the second derivative method and those collected from the intersection of the curves fitted to the experimental data were comparable.

Moreover, the degree of counterion binding to the micelles was calculated based on the equation: $\beta = 1 - S_2/S_1$, where S_1 and S_2 are the slopes of the lines fitted to pre-micellar and post-micellar region in the specific conductance vs. surfactant concentration plots [32].

3. Results

3.1. Electrical conductivity data

In Fig. 1 the specific conductance (κ) vs. surfactant concentration (C) plots for aqueous solutions of SDS and Sarkosyl at various concentrations of Cd^{2+} or Zn^{2+} are shown. As it can be seen in Fig. 1 for all the studied surfactant systems the specific conductivity increases with the concentration of the surfactant in the solution as well as for a given surfactant, with the concentration of metal ions. This is the consequence of the increase of the content of the charge carriers in the solution (that is the ions of dissociated surfactant molecules and metal ions). However, κ values do not increase monotonically, but the regions of different slops in the $\kappa = f(C)$ plots can be noticed. This is due to the changes in the concentration of charge carriers in the solution. Namely, for sole surfactant solutions two region of different slopes can be seen in the plot. First of them is attributed to the situation when the surfactant is presented in the form of monomers (pre-micellar region), while the second one, of smaller conductivity changes, reflects the concentration region when micelles are formed in the solution and the level of free charge carriers