

Communication

The Effects of Ethanol Concentration and of Ionic Strength on the Zeta Potential of Titania in the Presence of Sodium Octadecyl Sulfate

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Abstract: Sodium octadecyl sulfate ($C_{18}H_{37}SO_4Na$) induces a negative zeta potential of metal oxides at very low surfactant concentrations as compared with shorter-chained sodium alkyl sulfates. The problem of low solubility of sodium octadecyl sulfate in water was solved by the addition of the surfactant to dispersions as ethanolic stock solution, but then the presence of ethanol in dispersions was inevitable. We demonstrate that the concentration of ethanol (up to 5% by mass) in a dispersion containing titania (TiO_2) and sodium octadecyl sulfate has an insignificant effect on the zeta potential of particles. We further demonstrate that the shifts in the IEP of titania induced by the presence of sodium octadecyl sulfate are independent of the NaCl concentration. The results obtained in this study can be generalized for 1-1 salts other than NaCl, for metal oxides other than titania, for organic co-solvents other than ethanol, and for sparingly soluble ionic surfactants other than sodium octadecyl sulfate.

Keywords: isoelectric point; anionic surfactant; anatase; mixed solvent; electrophoretic mobility; pH-dependent surface charging; solubility

1. Introduction

Ionic surfactants induce substantial shifts in the isoelectric point (IEP) of solid particles even at very low concentrations, and long-chained surfactants are more efficient in this respect than their shorter-chained analogs [1,2]. Anionic surfactants shift the IEP to low pH, and cationic surfactants shift the IEP to high pH, and at sufficiently high surfactant concentration, the zeta potentials are negative over the entire pH range for anionic surfactants [3,4], and positive over the entire pH range for cationic surfactants [5,6]. On top of the shifts in the IEP induced by surfactants alone, dispersions containing surfactants and other compounds, e.g., polymers [7,8], sugars [9–11], and mixtures of various surfactants [12] have been extensively studied. The shifts in the IEP observed in such dispersions are not necessarily simple sums of the effects of particular solutes, but they may show unexpected synergistic or competitive effects. Such effects are due to the interactions between the solutes in bulk solution and on the surface. As this work appears in a Special Issue, we emphasize that Professor Emil Chibowski published a substantial number of papers devoted to the adsorption of surfactants from solution [13–15], although his work is not directly related to this study.

The low solubility of long-chained surfactants in water is a problem which reduces their applications, and most published studies have been carried out with water-soluble surfactants. We showed, in our recent paper [16], that dilute aqueous solutions of surfactants which are sparingly soluble in water can be conveniently prepared from their stock solutions in water-miscible organic solvents. In particular, sodium octadecyl sulfate shows sufficient solubility in ethanol to prepare its aqueous

solutions (up to saturation and even supersaturated) by dilution of ethanolic stock solution. We used sodium octadecyl sulfate to shift the IEP of alumina, titania and hematite to low pH and to induce negative zeta potential of these oxides over the entire pH range. Since we added the surfactant to the dispersions as ethanolic solution, we have to consider if ethanol (which was inevitably present in the dispersion) could have affected the adsorption behavior of the surfactant, and consequently the zeta potential of oxide particles. We originally assumed that in view of the low concentration of ethanol (less than 1% by mass in most dispersions, ethanol concentration was variable and proportional to the concentration of surfactant) and thus negligible effect of ethanol on the physical properties of the mixed solvent, the effect of the organic co-solvent on the adsorption of sodium octadecyl sulfate is also negligible. It is also very unlikely that an amount of ethanol as low as a fraction of 1% would substantially affect the solubility of sodium octadecyl sulfate in water. Moreover, there is direct experimental evidence that ethanol (up to 30%) does not affect the zeta potential of oxide particles when the ionic strength is not too high (below 0.1 M) [17]. Yet, a negligible effect of alcohol on the zeta potential in metal oxide dispersions containing sodium octadecyl sulfate needs a direct experimental evidence, and this is the goal of the present study. In order to prove that ethanol indeed does not affect the zeta potentials in the above systems, we compare the results obtained in dispersions containing less than 1% of ethanol [16] with similar dispersions except containing 5% ethanol. If the difference in the zeta potential between dispersions containing <1% on the one hand and 5% ethanol on the other is negligible, then we can safely assume that also the difference between dispersions containing 0 and up to 5% ethanol is negligible. The concentration of ethanol (5% by mass) used in this study was arbitrarily selected as a compromise between two opposite requirements. The concentration must be higher by at least a factor of two than the highest concentration used in our previous study (only comparison of results obtained at substantially different concentrations of ethanol can potentially produce significantly different zeta potentials). On the other hand, high concentrations of ethanol cause a number of difficulties, e.g., with definition and measurements of pH, with incomplete dissociation of the electrolyte, etc. These problems were discussed in detail in our previous studies [18].

Five % ethanol solution has higher viscosity and lower dielectric constant than water, and these quantities affect the calculation of the zeta potential from electrophoretic mobility, but the physical constants for water-ethanol mixtures are easily available from the literature [19]. Moreover, we studied the effect of the ionic strength on the zeta potential in metal oxide dispersions containing sodium octadecyl sulfate. Published literature [3] and our previous experiments showed that the increase in NaCl concentration from 10^{-3} to 10^{-2} M had a rather insignificant effect on the shifts in the IEP caused by SDS.

The range of the ionic strengths discussed in this paper and in other similar studies is limited by the following factors:

- With very low ionic strengths (10^{-4} M or less), the available pH range is limited. For example, with the ionic strength of 10^{-4} M, a pH below 4 is not available, because at pH < 4 the acid added to adjust the pH produces an ionic strength higher than 10^{-4} M. In other words, a very low ionic strength is difficult to adjust and control.
- With very high ionic strengths (10^{-1} M or more) the dispersions are unstable against coagulation, especially near the IEP, while electrophoretic measurements require a relatively stable dispersion. Moreover, the zeta potentials at high ionic strengths are low in absolute value, and the signal-to-noise ratio is poor. This problem can be solved by using the electroacoustic technique [20] instead of electrophoresis, but this is a separate topic unrelated to the present work.

We may generalize the above findings with SDS for other sodium alkyl sulfates, but again, direct experimental proof would be much desired. For example, NaCl, even at low concentrations, can affect the solubility of sodium octadecyl sulfate, and thus, indirectly, its adsorption. In order to directly answer the question about the possible effect of the ionic strength we compare the zeta potentials of titania in the presence of sodium octadecyl sulfate obtained in 10^{-3} and 10^{-2} M NaCl at otherwise the

same conditions. Titanium dioxide is not only a perfect model system in the studies of pH-dependent surface charging (low solubility, point of zero charge PZC in the center of the pH-scale), but it also has wide applications, e.g., as the component of paints, cosmetics, paper whitener, and even food additive, thus the results showed in this study may be directly applied in practice.

2. Materials and Methods

A series of 1:10,000 *w/w* dispersions of P25 (Evonik, Essen, Germany), which is TiO_2 , chiefly anatase, was prepared by mixing titania powder with ethanolic solution of sodium octadecyl sulfate, 98% (Acros, Geel, Belgium), 96% ethanol (Stanlab, Lublin, Poland), 0.1 M NaCl (POCh, Lublin, Poland) and water (Hydrolab, Straszyn, Poland) in different proportions to obtain desired concentrations of the surfactant, of ethanol, and of NaCl. The dispersions were adjusted to different pH using NaOH and HCl solutions. The dispersions were stored in plastic test tubes and used shortly after preparation.

The electrophoretic mobility was studied with a Malvern ZetaSizer Nano ZS (Malvern, Malvern, England) at 25 °C, and the Smoluchowski equation was used to calculate the zeta potential. The viscosity and dielectric constant of 5% ethanol were taken directly or interpolated from the literature data. More detailed description of the experimental procedures can be found elsewhere [16].

3. Results and Discussion

The zeta potential vs. pH curves of titania obtained at a few selected concentrations of sodium octadecyl sulfate in 10^{-3} and 10^{-2} M NaCl in 5% *w/w* ethanol are presented in Figures 1 and 2, respectively. We must emphasize that all surfactant concentrations reported in this paper are total (rather than equilibrium) concentrations. The sets of electrokinetic curves obtained at different surfactant concentrations shown in Figures 1 and 2 are very similar, and they are also similar to analogous results from our previous study [16], obtained at a lower concentration of ethanol (variable, up to 0.7% *w/w*). They show the following common behavior, which is independent of alcohol concentration and of the ionic strength:

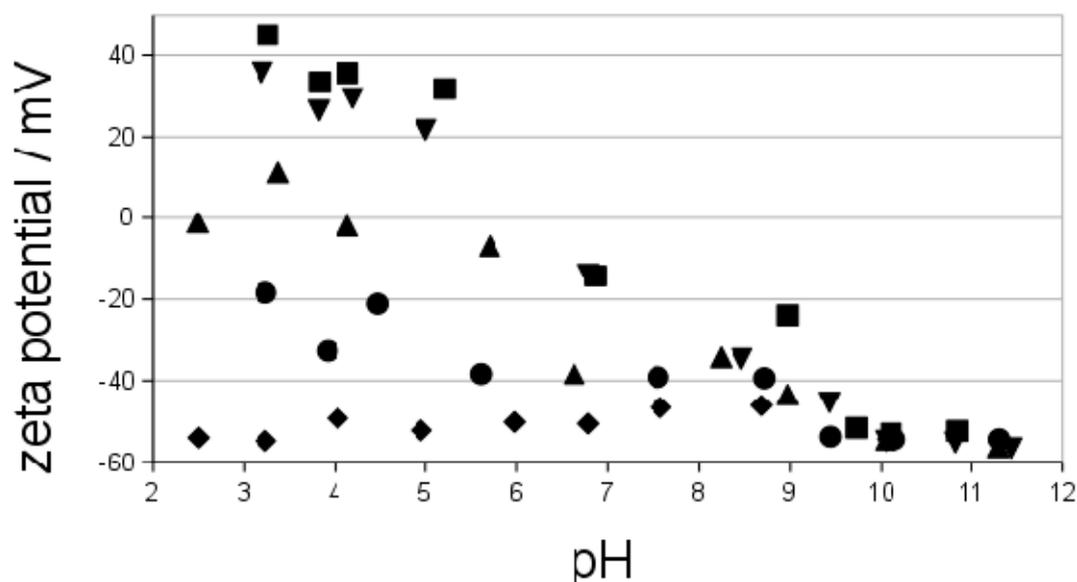


Figure 1. The zeta potentials of titania in 10^{-3} M NaCl at various concentrations of sodium octadecyl sulfate in 5% ethanol. ■ 0, ▼ 1.1×10^{-6} , ▲ 5.4×10^{-6} , ● 1.1×10^{-5} , ◆ 2.1×10^{-5} M sodium octadecyl sulfate.

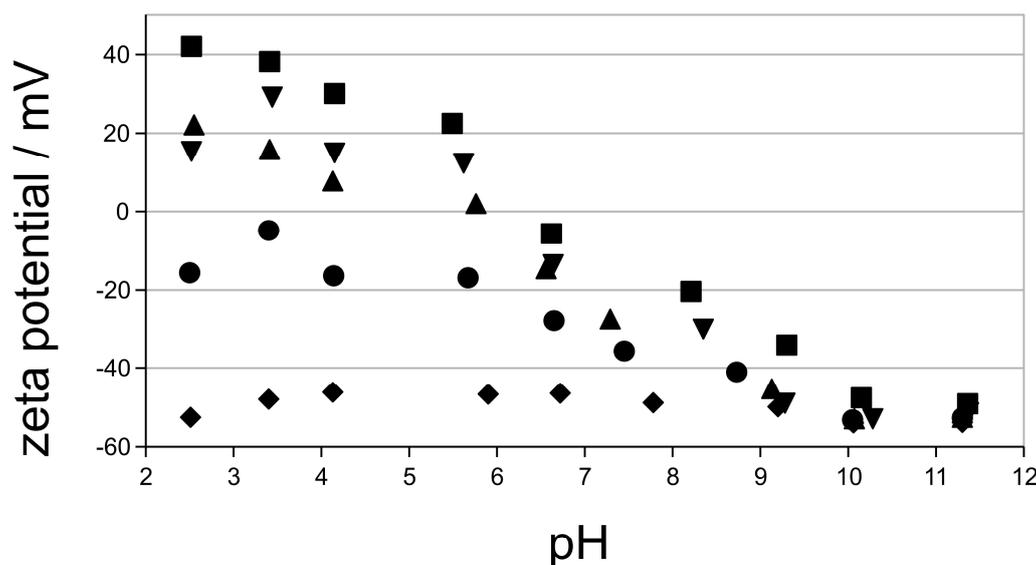


Figure 2. The zeta potentials of titania in 10^{-2} M NaCl at various concentrations of sodium octadecyl sulfate in 5% ethanol. ■ 0, ▼ 3.2×10^{-6} , ▲ 5.4×10^{-6} , ● 1.1×10^{-5} , ◆ 2.1×10^{-5} M sodium octadecyl sulfate.

- IEP at pH 6.5 in the absence of surfactant and at very low surfactant concentrations, which is consistent with IEP of P25 and of other titanias reported in the literature [21].
- Substantial shift in the IEP at 5.4×10^{-6} M sodium octadecyl sulfate, but still positive zeta potentials in the acidic range.
- Negative zeta potentials over the entire pH-range at 1.1×10^{-5} M sodium octadecyl sulfate, but the zeta potentials are more negative (about -50 mV) at $\text{pH} > 7$, and less negative (about -20 mV) at $\text{pH} < 4$.
- Negative and pH-independent zeta potentials of about -50 mV over the entire pH-range at 2.1×10^{-5} M sodium octadecyl sulfate.

The above numerical values of surfactant concentrations refer to specific solid-to-liquid ratio (1:10,000 in our study) and they will be different if we change this ratio. Normalization of “critical” surfactant concentrations to amount of surfactant per unit of specific surface area (rather than to concentration in solution) in comparison of results obtained at various solid-to-liquid ratios has been considered [3,6], but even the normalized “critical” concentrations are not entirely consistent.

The results from our previous study (low concentration of ethanol) [16] and from the present study (5% ethanol), Figure 1 (10^{-3} M NaCl) and Figure 2 (10^{-2} M NaCl), are compared in Figure 3. In order to avoid overcrowding of data points, we plot the zeta potential at constant pH (3 or 4) as the function of surfactant concentration at various concentrations of NaCl and of ethanol. The similarity of zeta potentials in nearly alcohol-free dispersions (squares) on the one hand, and in dispersions in 5% ethanol (circles) on the other, suggests that, at least over the concentration range of 0–5%, ethanol does not affect the zeta potential in dispersions of titania containing sodium octadecyl sulfate.

The zeta potential vs. pH curves of titania obtained at different concentrations of sodium octadecyl sulfate in 10^{-3} M NaCl in 5% *w/w* ethanol (circles) are very similar to analogous results obtained with 10^{-2} M NaCl (triangles). This result shows that NaCl does not affect the shifts in the IEP and the sign reversal of the zeta potential from positive to negative in the acidic range induced by sodium octadecyl sulfate.

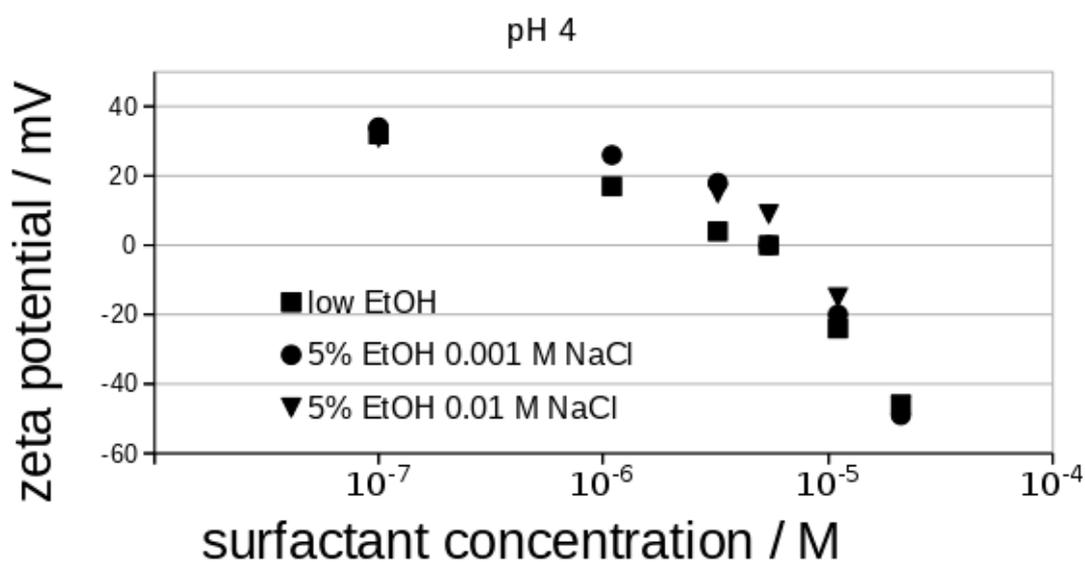
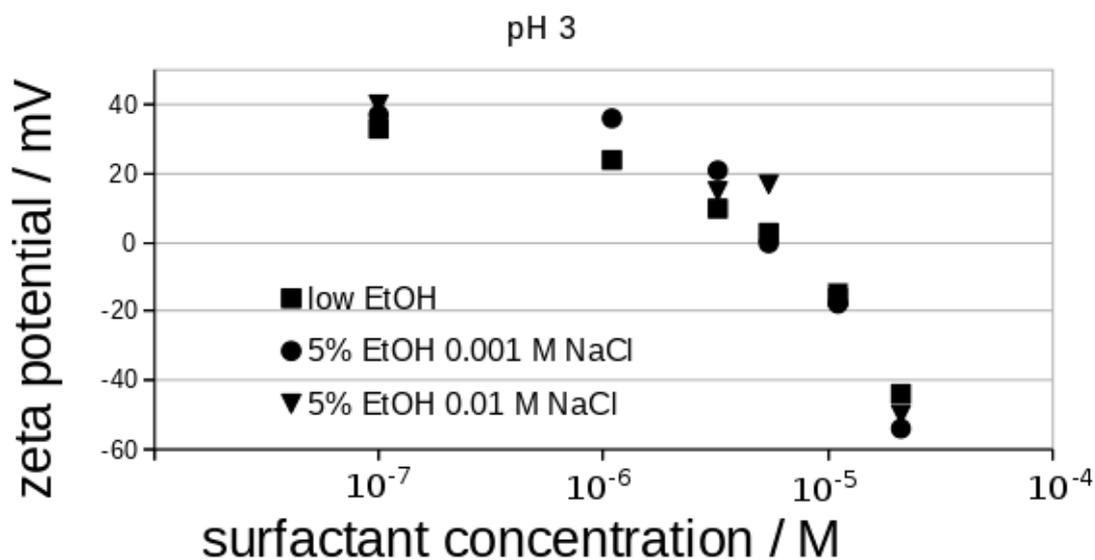


Figure 3. The zeta potentials of titania at pH 3 (a) and 4 (b) interpolated from the results shown in Figures 1 and 2 at various concentrations of NaCl and of ethanol.

We only performed experiments in a carefully selected model system: for one metal oxide (titania), one salt (NaCl), one ionic surfactant (sodium octadecyl sulfate) and one organic co-solvent (ethanol). The results presented in this study corroborate the expectations, and they can probably be generalized. Due to the similarity of surface-charging behavior of different metal oxides in solutions of different 1-1 electrolytes, we suppose that insensitivity of electrokinetic curves presented in Figure 3 to the concentration of ethanol (at least up to 5%) and to the concentration of NaCl (at least up to 10^{-2} M) can be generalized for other metal oxides (hematite, alumina, zirconia), and for other 1-1 salts (KCl, KNO_3 , NaClO_4). We further speculate that our present results are also valid for other polar organic co-solvents

(acetone, acetonitrile), and even for other long-chained ionic surfactants. In other words, our study further confirms that the shifts in the IEP of metal oxides induced by ionic surfactants and rather insensitive to the nature and concentration (at least up to 10^{-2} M) of 1-1 salt present in the dispersion irrespective of the nature of the metal oxide, of organic co-solvent, and of the surfactant. Our results suggest that also addition of water-miscible organic co-solvent (at least up to 5% *w/w*) does not affect the shifts in the IEP of metal oxides induced by ionic surfactants. The later conclusion is new, and we have not found similar experimental studies in the literature. Many electrokinetic studies have been carried out with solutions of surfactants in anhydrous or nearly anhydrous organic solvents [22,23], but this is a completely different topic unrelated to the present work.

The reversal of sign of the zeta potential of quartz to positive at pH 6.5–6.9 induced by long chained amine acetates (up to C18) was studied in [24]. Unlike in the present study, the cationic surfactants studied in [24] have sufficient solubility in water to reverse the sign of the zeta potential of quartz within the solubility limit. The IEPs reported in [24] are not comparable with the IEPs presented in Figure 3 of this study, because quartz has a low specific surface area.

Our previous study [2] showed two types of sets of zeta potential vs. pH curves obtained at moderate anionic surfactant concentrations. A maximum in zeta potential vs. pH curves at pH near the pristine IEP of the powder was observed in shorter-chained surfactants, but not in their longer-chained analogs. Most examples in [2] were sodium alkyl sulfates. One of the referees of this papers turned our attention to [25], where a sharp maximum in the zeta potential of alumina at pH 6.9 in the presence of sodium dodecyl sulfonate was reported. Unlike most studies cited in Reference [2], in which the zeta potential was studied at constant total surfactant concentration, the graph in Reference [25] was obtained at a constant residual surfactant concentration.

Author Contributions: M.K.: conceptualization, writing; E.M.: experiment. All authors have read and agreed to the published version of the manuscript.

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