Electrochemical Characterization of Aerosil OX 50 Dispersions*

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The interface between the Aerosil OX 50 colloidal dispersion and the electrolyte solution was studied using three independent methods: titration for surface charge density determination, conductivity, and electrophoretic mobility. It is shown that all three methods give good agreement for the surface charge density in 10^{-2} mol/dm^3 KCl solutions, but less so for 10^{-3} mol/dm^3.

INTRODUCTION

The properties of colloidal dispersions are mainly determined by the interaction between their particles. One component of the interaction is the electric double layer repulsion, which is the result of the overlapping of the diffuse part of the double layers of approaching particles during Brownian encounters. Knowledge on the structure and properties of double layers is therefore very important in colloid stability.

EXPERIMENTAL

We investigated aerosil OX 50 dispersions of 2.5 respectively 5 weight percent. OX 50 was first dried at 420 K for two hours and then dispersed either by ultrasonication (45 minutes) or using an ultraturrax. The electrochemical properties of the aerosil particles are determined by the silanol groups. On the average there are 5 silanol groups at 1 nm² at the surface. The number of silanols dissociated, that means the surface charge density, depends on the pH of the solution according to the reaction

\[ \text{SiOH} + \text{OH}^- \rightarrow \text{SiO}_2^- + \text{H}_2\text{O} \]

The reaction

\[ \text{SiOH} + \text{H}_2\text{O}^+ \rightarrow \text{SiOH}_2^+ + \text{H}_2\text{O} \]

was not observed in aerosil OX 50 dispersions.

RESULTS AND DISCUSSION

A typical titration curve is shown in Figure 1; curve 1 for the dispersion and curve 2 for the solution. From \( \Delta V_{\text{OH}^-} \) the surface charge density was calculated according to eq. 1

\[ \sigma_o = F \left( \Gamma_{\text{H}_2\text{O}^+} - \Gamma_{\text{OH}^-} \right) = \frac{F}{S} \left( \Delta V_{\text{H}_2\text{O}^+} \cdot C_{\text{H}_2\text{O}^+} - \Delta V_{\text{OH}^-} \cdot C_{\text{OH}^-} \right) \]  

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\( F \) Faraday constant, \( I \) adsorbed amount (mol m\(^{-2}\)), \( S \) surface, \( \Delta V_{H^+} \), \( \Delta V_{OH^-} \) volume difference of hydronium respectively hydroxyl ions between the pure electrolyte solution and the dispersion to obtain the same pH-value.

Figure 1. Titrations curves for the electrolyte solution (2) and a 2.5\% aerosil OX 50 dispersion (1) in \( 10^{-3} \) normal K\(^+\) solution.

The first reaction is dependent on the kind and concentration of countereions. In Figure 2 this is shown for 3 different potassium chloride concentrations. Then higher the potassium chloride concentration, then higher the surface charge density. From this, it follows, that the surface charge density may not be varied simply by alkaline addition. On the other hand the experiments have shown that chloride ions are not adsorbed at the silica interface. So the pH was varied by adding hydrochloric acid to aerosil dispersions of constant alkali concentration. With this method surface charge density measurements can be performed only with soluble hydroxides. For unsoluble hydroxides a described coulometric method was used.\(^1\) The hydroxyl ions were produced electrochemically at a platinized platinum electrode. In experiments in which hydrogen can influence on the surface charge of the dispersed particles a palladium cathod was used in which the gaseous hydrogen is absorbed. The anode was made from silver, and the silver ions are settled as silver chloride in an agar-agar jelly. A porous filter prohibited agar-agar molecules to diffuse into the electrolyt solution. A stirrer, a glass electrode and a calomel electrode are placed within the cell. Argon flows through the cell during the experiment to avoid adsorption of carbon dioxide. Two celles
Figure 2. Surface charge density pH curves for 2.5% aerosil OX 50 dispersions at three different potassium chloride concentrations.

Figure 3. Surface charge density pH curves for 2.5% aerosil OX 50 dispersions in $10^{-2}$ M alkaline chloride solutions: • LiCl, ○ KCl, × RbCl (coulometrically) and □ KCl potentiometrically.

were used in series one contained the dispersion the other only the electrolyte solution. The results are shown Figure 3. for lithium (•), potassium (○) and rubidium chloride (×). For comparison the curve for potassium chloride obtained by titration (□) is included in Figure 3. This lyotropic row is explained by adsorption of hydrated cations and the decrease of hydration from lithium
to rubidium, that means it is an effect of double layer capacity. We also investigated the influence of barium and calcium counter ions in comparison with potassium ions (Figure 4). The results showed that there is no shift of the point of zero charge and also no specific adsorption of these kind of ions. From the difference in the slopes of the curves for potassium, calcium and barium chloride the same conclusion can be drawn, namely the surface charge density is highest with $\text{Ba}^{2+}$ ions, that means these ions are adsorbed with their hydration shells. The same conclusions were already made by Tadros and Lyklema with precipitated silica.\textsuperscript{8}

Potentiometric titration experiments alone do not allow the decision whether there is specific adsorption of earth alkaline ions or not. This was possible by measuring electric light scattering in the low frequence region. It was shown\textsuperscript{3} that above pH 8 there was a small specific adsorption of $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ at the aerosil surface. According to the Gouy-Chapman theory there exists a relation between surface charge density and surface potential. On the other hand it was shown by Martynov\textsuperscript{4} that the difference between the thermodynamic potential ($\psi_o$) and Stern potential is negligible, if the surface charge is formed by adsorption of ions. The Stern potential $\psi_s$ is related to surface charge density by the following equation

![Figure 4. Surface charge density pH curves for 2.5% aerosil OX 50 dispersions in 0.01 M KCl, 0.005 M CaCl$_2$ and BaCl$_2$.](image-url)
AEROSIL OX 50

(2)

\[ \sigma_0 = \frac{\varepsilon_1 \varepsilon_0}{2\pi e z_1} \left( \frac{\varepsilon_0}{2} \right) + \frac{2}{\pi a} + \frac{\psi_t}{4} \]

\( \varepsilon_1 \) dielectric constant, \( \varepsilon_0 \) influence constant, \( x^{-1} \) Debye parameter. The dimensionless potential is defined \( \tilde{\psi} = \frac{z_1 \psi}{e k T} \).

The results for \( \psi_t \) as a function of \( \sigma_0 \) are shown for 3 different potassium chloride concentrations in Figure 5. At low surface charge densities there is a linear dependence between \( \psi_t \) and \( \sigma_0 \).

![Figure 5. Stern potential surface charge density curves at different KCl concentrations calculated according to eq. 2.](image)

**Electrophoretic Mobility**

The electrophoretic mobility of aerosil particles cannot be measured by single particle electrophoresis due to the low particle radii. We used mass transport electrophoresis. The method was described.\(^5\)

The electrophoretic mobility was found to be dependent on the surface charge density and on the concentration of the indifferent ions too. With increasing electrolyte concentration the electrophoretic mobility became lower (Figure 6) this is in agreement with the Gouy-Stern-theory namely then higher the concentration of the electrolyte then higher the counterion con-
Figure 6. Electrophoretic mobility as a function of pH in $10^{-4}$ molar and $10^{-3}$ M KCl.

...concentration near the surface. If one compares electrophoretic mobility in the presence of different alkaline ions (Figure 7) at the same electrolyte concentration no influence was found. But if we compare electrophoretic mobility of potassium, calcium and barium ions at the same concentration of $10^{-3}$ normal different (Figure 8) values are obtained. The reason is the increase of adsorption from $\text{K}^+ < \text{Ca}^{2+} < \text{Ba}^{2+}$. From electrophoretic mobility the $\zeta$ potential was calculated using Wiersema-Loeb-Overbeek-theory. The $\zeta$-potential-surface charge density curve is compared with the Stern potential-surface charge density curve, calculated with eq. 2 from surface charge density (Figure 9). Unexpectedly the experimental values of the $\zeta$-potential are higher than calculated Stern potentials from surface charge density at low $\sigma_0$. In $10^{-2}$ molar KCl solutions both curves are identical.

Conductivity Experiments

The specific conductivity of colloidal dispersions depends on the specific conductivity of the dispersion medium, and of the dispersed phase and on the surface conductivity. The last term was first considered by von Smoluchowski later by Henry and Booth. The influence of the polarisation of the
Figure 7. Electrophoretic mobility as a function of pH in $10^{-3}$ normal solutions of different alkaline ions.

double layer on the electric conductivity of colloidal dispersions for $\kappa a \gg 1$ was first developed by Duchin and Schilov. According to Duchin the following relation is valid between the specific conductivity of the dispersion ($\bar{k}$), the specific conductivity of the dispersion medium ($k$), the volume fraction $p$ of the dispersed phase and the parameter $R_{cl}$, which characterizes the surface conductivity ($k^s$) and the polarization of the double layer:

$$\bar{k} = \frac{1}{k} \left( 1 - \frac{3}{2} p \left( 1 - \frac{3 R_{cl}}{1 + 2 R_{cl}} \right) \right)$$

$$R_{cl} = \frac{k^s}{k a} = \frac{1}{\kappa a} \left[ 4 \left( 1 + 3 m \right) \sin^2 \left( \frac{\zeta}{4} \right) + 2 \left( \cos h \left( \frac{\psi_b}{2} \right) - \cos h \left( \frac{\zeta}{2} \right) \right) \right]$$

$$m = \frac{k_B^2 T^2 \varepsilon \varepsilon_0}{e^2 6 \pi \eta D}$$

$k_B$ Boltzmann constant, $T$ temperature, $\varepsilon$ dielectric constant, $\varepsilon_0$ influence constant, $e$ elementary charge, $\eta$ viscosity, $D$ diffusion coefficient.
If $R_d$ increases and becomes 1 the term in brackets in eq. 3 becomes zero. Under such condition dispersion and dispersion medium have the same conductivity (isoconductivity). In Figure 10 the conductivity of the dispersion (●) and centrifugate (×) is shown in $10^{-2}$ M KCl as a function of pH and in Figure 11 as a function of surface charge density. In Figure 12 the conductivity is shown in $10^{-3}$ M KCl (● dispersion, + centrifugate) as a function of pH. One can see that with increasing surface charge density $k$, becomes higher than $k$ (enhanced conductivity). The position of the point of isoconductivity depends on the electrolyte concentration and moves to higher pH values with increasing electrolyte concentration.

In Figure 13 the ratio $k/k$ is shown as a function of the volume fraction $p$ for different electrolyte concentrations. All the straight lines cut the ordinate at the point of isoconductivity. The drawn line corresponds to the equation $k/k = 1 - 3/2p$.

The experimental result that with higher electrolyte concentrations the curves are lower than the theoretical curve may be caused by formation of aggregates. If we now compare the calculated Stern potentials in $10^{-2}$ and
Figure 9. Comparison of the Zeta- (X) and the Stern- (●) potential calculated from $\alpha_0$ (eq. 2).

Figure 10. Specific conductivity of the 2.5% aerosil OX 50 dispersion ● and of the dispersion medium X in $10^{-2}$ M KCl as function of $\alpha_0$. 
Figure 11. Specific conductivity of the 2.5% aerosil OX 50 dispersion (●) and of the dispersion medium (×) in $10^{-3}$ M KCl as a function of pH.

Figure 12. Specific conductivity of the 2.5% aerosil OX 50 dispersion (●) and of the dispersion medium (×) in $10^{-3}$ M KCl as a function of pH.

$10^{-3}$ M KCl solution obtained from surface charge density, zeta potential and conductivity the following results are obtained:
Figure 13. Relative conductivity $k/k$ as a function of the volume fraction in different KCl solutions $\square 5 \times 10^{-2}\text{ M}$, $\triangle 1.5 \times 10^{-4}\text{ M}$, $\nabla 5 \times 10^{-4}\text{ M}$, $\bigcirc 10^{-3}\text{ M}$, $+ 10^{-2}\text{ M}$. The drawn line corresponds to eq. 5.

The agreement between these values in the $10^{-2}\text{ molar solution}$ is rather good, but in $10^{-3}\text{ molar solution}$ the calculation from conductivity according to Duchin-Schilov gives too low value. May be the limiting condition for the D-S-Theory ($x a \gg 1$) is no more valid (for $10^{-3}\text{ M} x a \sim 2.6$).

REFERENCES


SAŽETAK

Elektrokemijska karakterizacija Aerosil OX 50 disperzija

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Primijenjene su tri neovisne metode na određivanje polarizacije u električkom dvosloju na granici faza Aerosil OX 50/otopina elektrolita. Pokazano je da sve tri metode — vodljivost, titracija za određivanje površinske gustoće naboja i elektroforetska pokretljivost — daju vrlo sukladne rezultate za KCl koncentraciju $10^{-2}\text{ mol/dm}^3$, ali i značajno veća neslaganja za koncentraciju $10^{-3}\text{ mol/dm}^3$. Razlog je tome što za nižu koncentraciju nije ispunjen uvjet $x a \gg 1$.