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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 nm^2 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

$$\mathrm{SiOH} + \mathrm{OH^-} \rightarrow \mathrm{SiO_2^-} + \mathrm{H_2O}.$$

The reaction

$$\mathrm{SiOH} + \mathrm{H_3O^+} \rightarrow \mathrm{SiOH_2^+} + \mathrm{H_2O}$$

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 $\Delta V_{\mathrm{OH^-}}$ the surface charge density was calculated according to eq. 1

$$\sigma_0 = F\,(\Gamma_{\mathrm{H_3O^+}} - \Gamma_{\mathrm{OH^-}}) = \frac{F}{S}\,(\Delta\, V_{\mathrm{H_3O^+}} \cdot C_{\mathrm{H_3O^+}} - \Delta\, V_{\mathrm{OH^-}} \cdot C_{\mathrm{OH^-}}) \qquad (1)$$

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F Faraday constant, Γ adsorbed amount (mol m^{-2}), S surface, $\Delta V_{H_3O^+}$, ΔV_{OH^-} volume difference of hydronium respectively hydroxyl ions between the pure electrolyte solution and the dispersion to obtain the same pH-value.

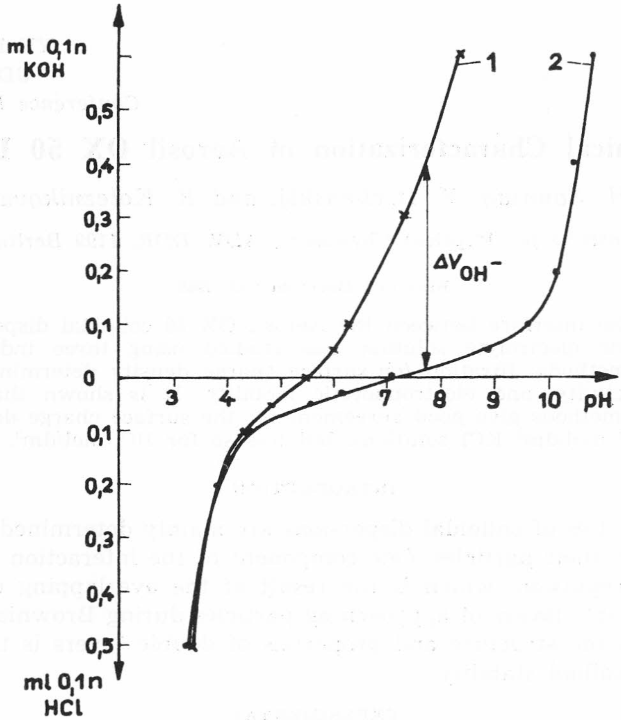

Figure 1. Titrations curves for the electrolyte solution (2) and a 2.5% aerosil OX 50 dispersion (1) in 10^{-3} normal K$^+$ solution.

The first reaction is dependent on the kind and concentration of counterions. 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 hydrochloride 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 jelley. 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

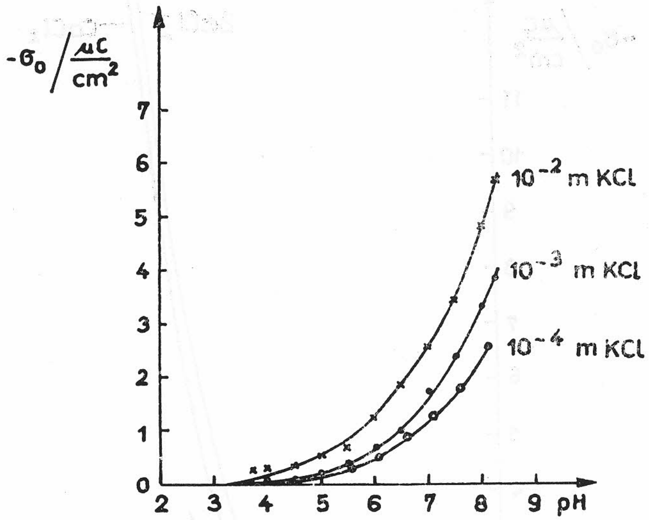

Figure 2. Surface charge density pH curves for 2.5% aerosil OX 50 dispersions at three different potassium chloride concentrations.

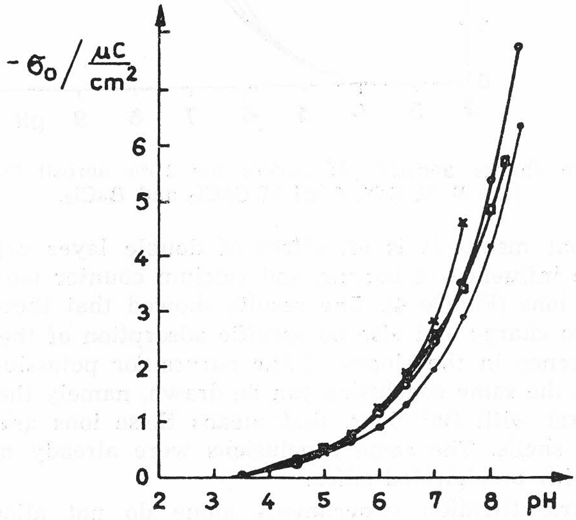

Figure 3. Surface charge density pH curves for 2.5% aerosil OX 50 dispersions in 10^{-2} M alkaline chloride solutions ● LiCl ○ KCl × RbCl (coulometrically) □ KCl potentiometrically.

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 comparisson 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

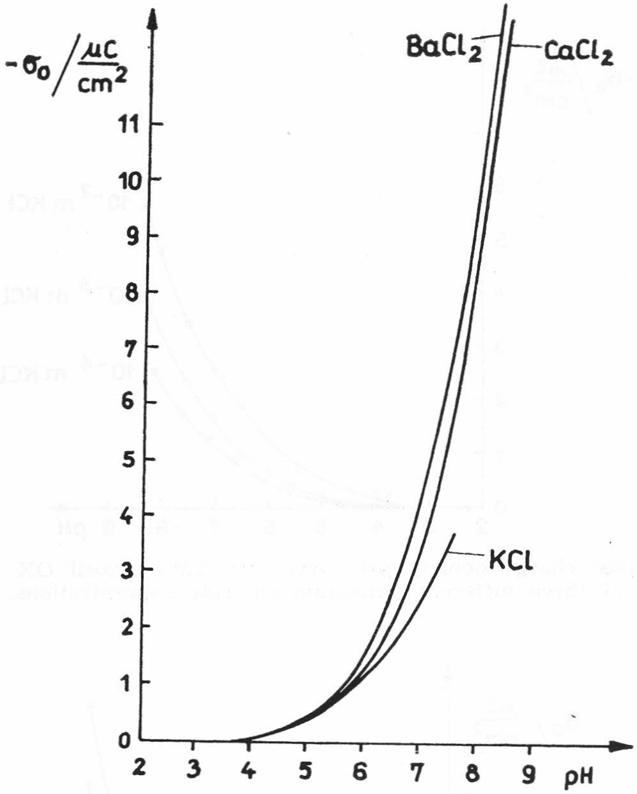

Figure 4. Surface charge density pH curves for 2.5% aerosil OX 50 dispersions in 0.01 M KCl, 0.005 M $CaCl_2$ and $BaCl_2$.

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 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.[2]

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[3] that above pH 8 there was a small specific adsorption of Ca^{2+} and 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[4] that the difference between the thermodynamic potential (ψ_0) and Stern potential is negligible, if the surface charge is formed by adsorption of ions. The Stern potential ψ_δ is related to surface charge density by the following equation

$$\sigma_o = \frac{\varepsilon_1 \varepsilon_0 \varkappa k_B T}{2 \pi e z_i} \left(sh \frac{\tilde{\psi}_\delta}{2} + \frac{2}{\varkappa a} + th \frac{\tilde{\psi}_\delta}{4} \right) \tag{2}$$

ε_1 dielectric constant, ε_o influence constant, $\varkappa^{-1}$ Debye parameter. The dimensionless potential is defined $\tilde{\psi} = z_i e\psi/kT$.

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

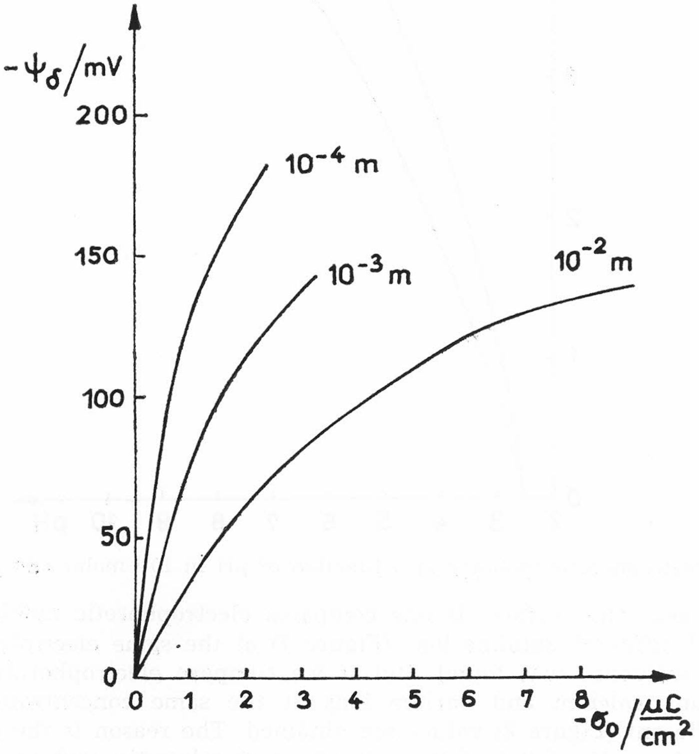

Figure 5. Stern potential surface charge density curves at different KCl concentrations calculated according to eq. 2.

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 aggreement with the Gouy-Stern-theory namely then higher the concentration of the electrolyte then higher the counterion con-

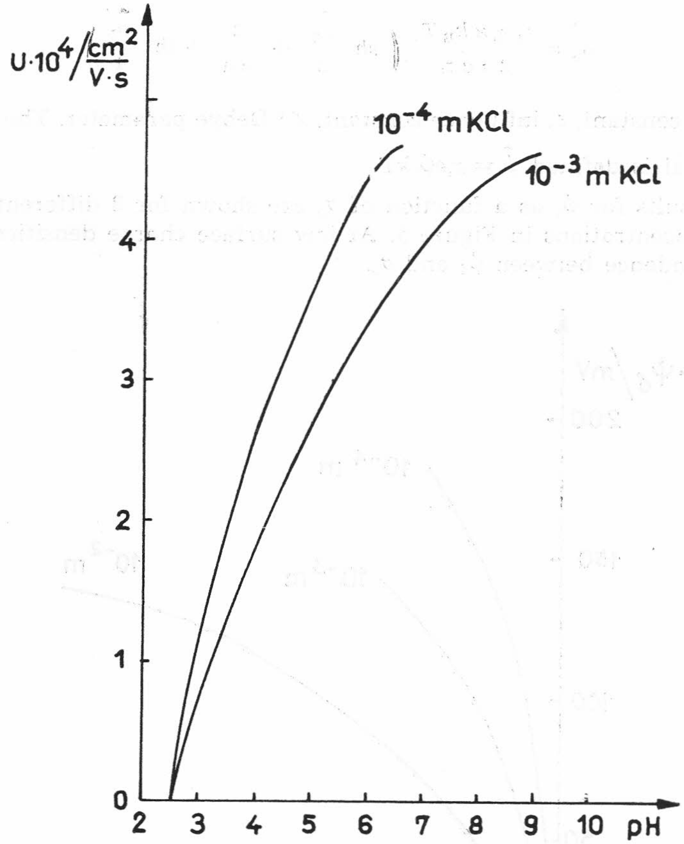

Figure 6. Electrophoretic mobility as a function of pH in 10^{-4} molar and 10^{-3} M KCl.

centration 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 $K^+ < Ca^{2+} < Ba^{2+}$. From electrophoretic mobility the ζ — potential was calculated using Wiersema-Loeb-Overbeek-theory.[6] The ζ-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 ζ-potential are higher then calculated Stern potentials from surface charge density at low σ_o. 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[7] later by Henry[8] and Booth.[9] The influence of the polarisation of the

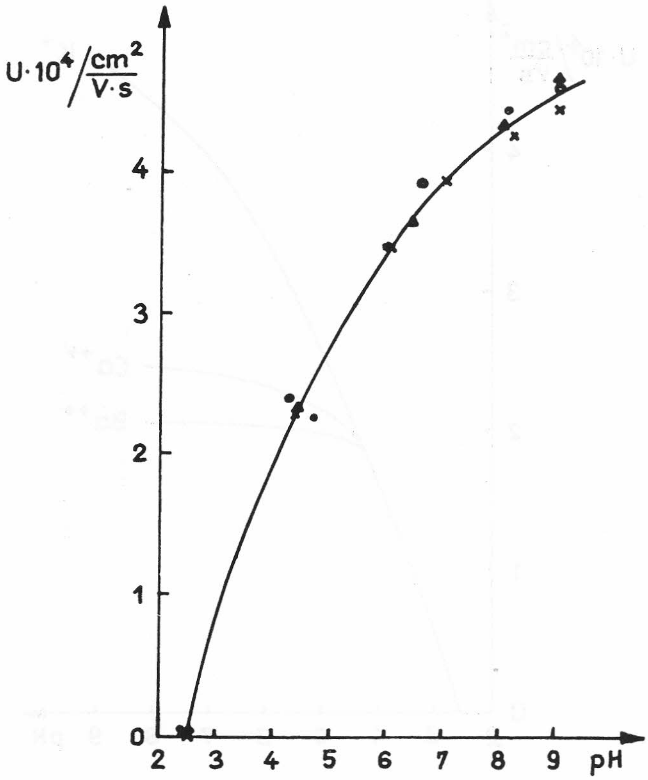

Figure 7. Electrophoretic mobility as a function of pH in 10^{-3} normal solutions of different alkaline ions.

double layer on the electric conductivity of colloidal dispersions for $\varkappa a \gg 1$ was first developed by Duchin and Schilov.[10] According to Duchin the following relation is valid between the specific conductivity of the dispersion ($\overline{k}$), the specific conductivity of the dispersion medium (k), the volume fraction p of the dispersed phase and the parameter R_{el}, which characterizes the surface conductivity (k^σ) and the polarization of the double layer:

$$\frac{\overline{k}}{k} = 1 - \frac{3}{2} p \left(1 - \frac{3 R_{el}}{1 + 2 R_{el}} \right) \tag{3}$$

$$R_{el} = \frac{k^\sigma}{k a} = \frac{\overline{1}}{\varkappa a} \left[4 (1 + 3 m) \sin h^2 \left(\frac{\breve{\zeta}}{4} \right) + 2 (\cos h \left(\frac{\breve{\psi}_\delta}{2} \right) - \cos h \left(\frac{\breve{\zeta}}{2} \right) \right] \tag{4}$$

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

k_B Boltzmann constant, T temperature, ε dielectric constant, ε_o influence constant, e elementary charge, η viscosity, D diffusion coefficient.

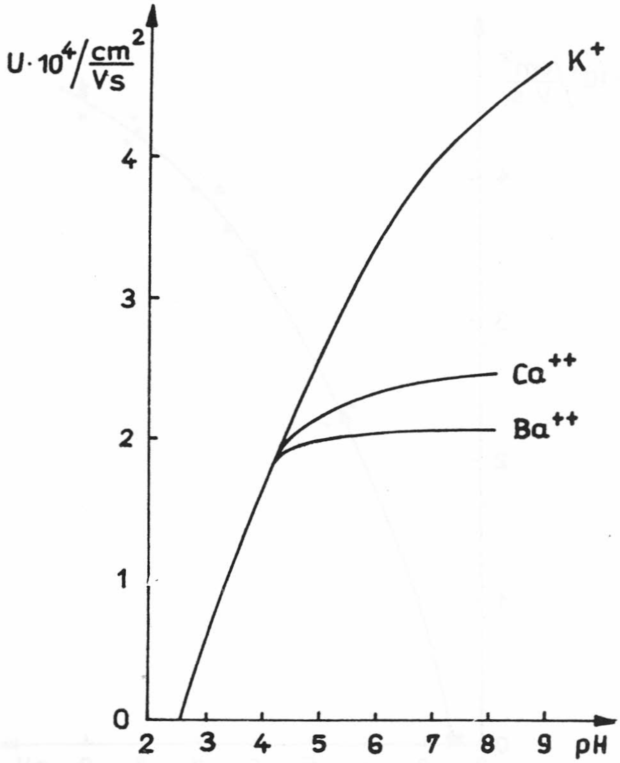

Figure 8. Electrophoretic mobility in 10^{-3} M KCl, 5×10^{-4} M $CaCl_2$ and $BaCl_2$ at different pH.

If R_{el} 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 $\overline{k}$, 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 $\overline{k}/k$ 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 $k/k = 1 — 3/2\ p$.

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

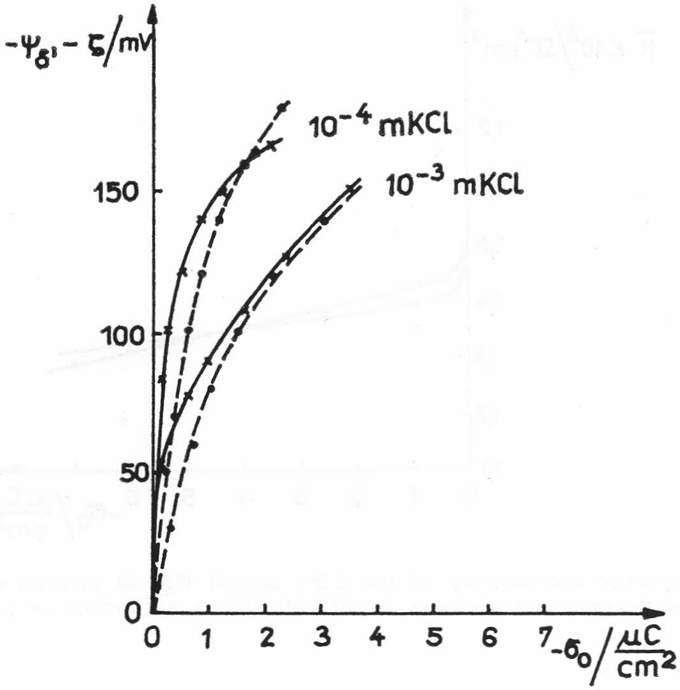

Figure 9. Comparison of the Zeta- (×) and the Stern- (●) potential calculated from σ_o (eq. 2).

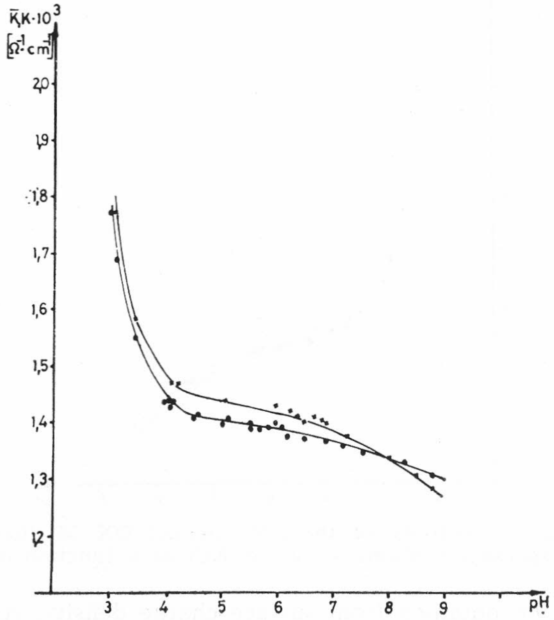

Figure 10. Specific conductivity of the 2.5% aerosil OX 50 dispersion ● and of the dispersion medium X in 10^{-2} M KCl as function of σ_o.

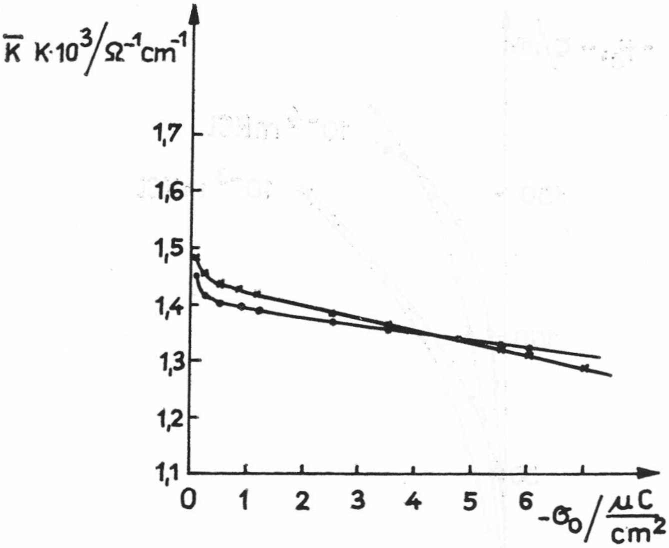

Figure 11. Specific conductivity of the 2.5% aerosil OX 50 dispersion ● and of the dispersion medium × in 10^{-3} M KCl as a function of pH.

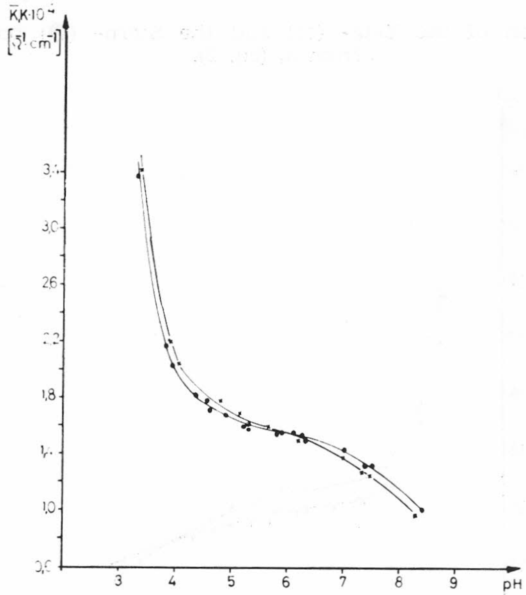

Figure 12. Specific conductivity of the 2.5% aerosil OX 50 dispersion ● and of the dispersion medium × 10^{-3} M KCl as a function of pH.

10^{-3} M KCl solution obtained from surface charge density, zeta potential and conductivity the following results are obtained:

KCl (mol/dm^{-3})	Ψ_δ/σ_o (mV)	Ψ_δ/ζ (mV)	$\Psi_\delta/k/k$ (mV)
10^{-2}	105	114	108
10^{-3}	70	75	55

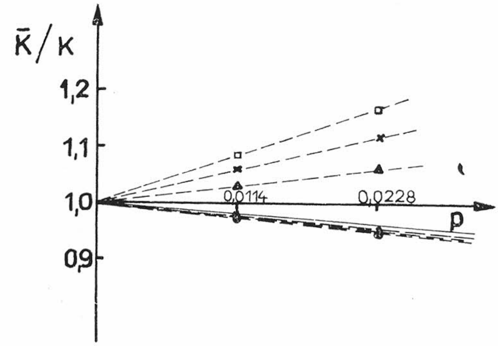

Figure 13. Relative conductivity k/k as a function of the volume fraction in different KCl solutions □ 5×10^{-5} M, × 10^{-4} M, △ 1.5×10^{-4} M, ▽ 5×10^{-4} M, ○ 10^{-3} M, + 10^{-2} M. The drawn line corresponds to eq. 5.

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

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SAŽETAK

Elektrokemijska karakterizacija Aerosil OX 50 disperzija

H. Sonntag, V. Itschenskij i R. Koleznikova

Primijenjene su tri neovisne metode na određivanje polarizacije u električkom dvosloju na granici fazâ 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 koncentracije 10^{-2} mol/dm^3, ali i značajno veća neslaganja za koncentraciju 10^{-2} mol/^{3}. Razlog je tome što za nižu koncentraciju nije ispunjen uvjet $\varkappa a \gg 1$.