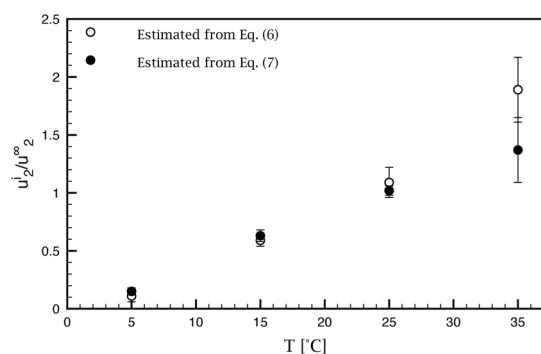# Low-frequency electric conductivity of aqueous kaolinite suspensions III: Temperature effects

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The electrical conductivity of aqueous kaolinite suspensions was studied as a function of both temperature and KCl concentration and interpreted in terms of surface conductance and electrokinetic potentials. The surface conductivity in the inner part of the double layer shows a temperature behaviour, which differs significantly from that of the diffuse part. While the latter is characterized by a temperature-independent activation energy, the ionic transport in the inner double layer appears to be influenced by additional, temperature-dependent processes at temperatures below 15 °C. Possible mechanisms for this observation are discussed and it is shown that an increase of temperature leads to more pronounced ionic transport in the double layer, which is then dominated by the diffuse portion. Finally, we estimate the counterion mobility in the inner part of the double layer and find these quantities to display a different temperature dependence than the corresponding bulk mobilities.

1. Introduction

The understanding of electric double layers and the theoretical description of electrokinetic phenomena have matured in the last decades. One of the main steps forward was the recognition of surface conductance and its incorporation into electrokinetic theories, because ζ-potentials calculated without considering this quantity can be substantially in error. Rutgers [1], for instance, realized that the apparent radius-dependence of electrokinetic potentials in cylindrical capillaries, derived from streaming potentials, can be corrected for when surface conductance is taken into account. Another hint towards the existence of surface conductance, which was observed very early [2,1], are spurious maxima in ζ vs. log c curves, where c is the concentration of the supporting electrolyte. These maxima can usually be

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removed when surface conductance is properly taken into account. For a summary of these observations the reader is referred to, e.g. [3–5].

After the first treatment of surface conductivity by Bikerman [6] in the 1930s, experiments made at that time showed that his treatment could not explain all experimental observations and often under-estimated the experimental values of surface conductivity. It became then clear that an additional contribution to the surface conductivity originates in the inner part of the electric double layer. The total surface conductivity (K^σ) is nowadays commonly regarded as a sum of a diffuse layer contribution K^{σ^d} and a contribution from the inner double layer K^{σ^i} [7]. With this improved model of the double layer many more experimental results can now be described in a consistent manner (see [3–5] for a summary of the developments). Due to the recognition that the inner part of the double layer often contains mobile counterions, current theoretical and experimental efforts are centered around describing the dynamics of this part of the double layer and determining the ionic mobilities of counterions in the double layer. By now a solid body of experimental work exists on the surface conductivity in the inner part of the double layer and the associated counterion mobility. This work, however, is mostly restricted to room temperature and comparatively little is known about these quantities as a function of temperature.

The temperature dependence of double layer parameters in general is of interest in a number of fields such as microfluidics [8], mineral processing [9], geophysics [10–13] and reservoir engineering [14]. As a consequence of this widespread interest it is not too surprising that the interpretation of experimental quantities is carried out at varying levels of sophistication. Often surface conductance is not taken into account at all [8,9,15,16,14,17], which begs the question if the temperature dependence of electrokinetic potentials can be correctly obtained at all. For porous materials surface conductivity is often assessed via formation factors, e.g. [11,13], which are determined at a certain reference temperature and subsequently used for calculations at different temperatures. Because these quantities might be temperature dependent themselves, there is some uncertainty whether the temperature coefficients of the surface conductivity – and therefore electrokinetic potentials – can be correctly determined.

Several publications [18–22] confirm that the surface conductivity is usually temperature dependent. Far less information is available on the separate temperature dependencies of the diffuse- and non-diffuse contribution of the surface conductivity. Such information is, however, vital for a more detailed understanding of the ionic transport within the respective parts of the double layer.

In this article we will present temperature dependent conductivity measurements on aqueous kaolinite suspensions, which are interpreted in terms of surface conductivity and its contributions as well as electrokinetic potentials. It will be shown that the temperature dependence of the diffuse layer surface conductivity is distinctly different from the one in the inner part of the double layer. This highlights that different transport mechanisms operate in the respective parts of the double layer.

2. Materials and methods

The detailed preparation and characterization of the K-kaolinite sample is documented elsewhere [23]. Apart from kaolinite the sample contains quartz (0.01 g/g) and illite/muscovite (0.18 g/g). The sample was repeatedly exposed to > 3 M KCl solutions, followed by subsequent washing with deionized water in order to obtain homoionic material.

Electrical conductivities have been measured with a WTW LF-3000 meter and a Campsec-K25 four-electrode cell. The detailed description of the measurement equipment can be found in [23]. The cell constant has been calibrated at each experimental temperature (5–35 °C in 10 °C steps) in 0.01 mol/kg KCl solutions [24]. The cell constant decreased slightly with decreasing temperature, which is in accordance with the
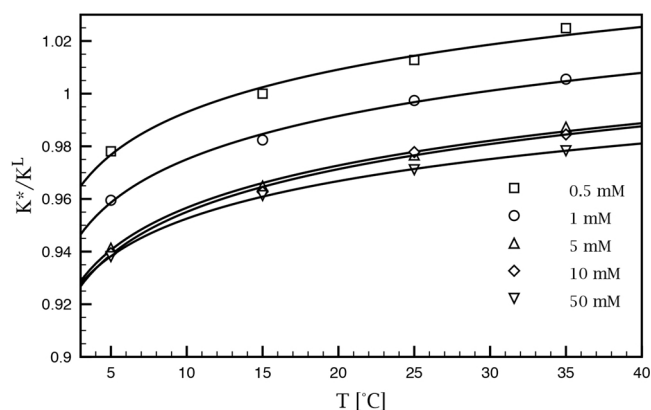

Fig. 1. Ratio of suspension conductivity (K^*) to the conductivity of the equilibrium electrolyte solution (K^L) as a function of temperature. The volume fraction is 0.011 in each case.

thermal expansion of the carbon electrodes. In order to assure the absence of electrode polarization, KCl solutions of lower concentration were measured at 5 and 25 °C. Reference conductivities for these measurements have been obtained by interpolation of Barthel's equations [25] and show an agreement within 1–3 µS/cm with the cell constants determined at higher concentration. This signifies that electrode polarization is not an issue within the studied concentration range.

All solutions and suspensions have been tempered to ± 0.1 °C of the desired temperature in a double-walled glass vessel, which was connected to a recirculating water bath with heating and cooling capacity. Suspensions have been prepared by immersing an appropriate amount of sample (volume fraction $\phi = 0.011$) into an electrolyte solution of the desired concentration. The conductivity of this suspension was first measured at 25 °C. After the particles had settled, the conductivity of the equilibrium electrolyte solution was measured and the temperature was changed. After the temperature series was completed the electrolyte concentration was adjusted by addition of solid KCl.

This procedure requires that no temperature-induced changes occur during the experiment. In preliminary experiments the temperature reversibility was tested by measuring the 25 °C point at the beginning, after the suspension was cooled to 5 °C and after it was heated to 35 °C. No discernible hysteresis was observed.

3. Results and interpretation

The ratio of suspension conductivity K^* to solution conductivity K^L increases logarithmically with increasing temperature (Fig. 1).

Isoconductive points points ($K^*/K^L = 1$) are observed for temperatures > 5 °C. Extrapolating the 5 °C data to $K^*/K^L = 1$ shows that the isoconductive point increases exponentially from 0.3 mol/m³ at 5 °C to 1.3 mol/m³ at 35 °C. This experimental data is analyzed with the aid of O'Brien and Ward's theory [26]. This theory is valid for the static conductivity of dilute suspensions of randomly oriented spheroids with radii of curvature larger than an inverse Debye length.[1] For a two-species electrolytes the relevant equation is [26]:

$$\frac{K^*}{K^L} = 1 - \phi\left[f^0(0) + 2f^1(0)\right] - \frac{\phi D_2 z_2^2 n_2^\infty}{\Sigma_{j=1}^N D_j z_j^2 n_j^\infty}$$
$$[f^0(Du_2) - f^0(0) + 2\{f^1(Du_2) - f^1(0)\}] \tag{1}$$

Here ϕ is the volume fraction, z the charge, D the diffusion coefficient

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[1] The characteristic length scale of this system is $l \approx 0.147$ µm, which provides at the lowest concentration and temperature $\kappa l = 11$, increasing to $\kappa l = 109$ at 50 mM and 35 °C.