
PROBING ION DYNAMICS IN A CLAY-WATER SYSTEM WITH DIELECTRIC SPECTROSCOPY

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abstract

Dielectric spectroscopy characterization of clay-water mixtures is presented and the obtained spectra are analysed. A theoretical model for ion dynamics is proposed in which motion of ions in pore space electrolyte is interrupted by trapping events at the mineral surfaces. The typical time scales for these processes are given in terms of the physical properties of the material. It is shown that the microscopic motion of the ions in a complex environment of clay-water system can be described with fractional dynamics leading to subdiffusive behavior.

keywords

dielectric spectroscopy, porous media, conductivity, fractional dynamics

1 INTRODUCTION

Characterization of complex heterogeneous materials such as clay minerals turns out to be a complicated issue experimentally as well as theoretically [1, 2]. One of the reasons for the difficulties is the time scale of the ion dynamic processes which are mostly diffusion governed. The most suitable techniques to probe ion dynamics on these intermediate time scales are NMR and dielectric spectroscopy.

Numerous studies have already demonstrated and analysed the anomalous properties of transport in natural porous media caused by its heterogeneous nature [3]. On the other hand, certain anomalous features of transport were also recently discovered studying random walks [4] and dc electrical conductance [5] on complex networks.

The main consequence of anomalous diffusion of contaminants in geological formations surrounding a potentially contaminated site is the time dependence of the diffusion coefficient [6]. The microscopic properties of diffusion transport of ions in clayey soils [7] present important issues in migration studies of contaminants in moist soil, for soil remediation problems and engineering of natural nuclear waste repository barriers. The effective diffusion constant is sometimes considered [8], while the dependence of the diffusion coefficient on the distance from the clay-water interface was studied by [9] showing as much as a ten times increase in the diffusion coefficient near the interface with respect to its value in the bulk.

With respect to transport through natural porous media (such as soil or rock) the anomalous features stem from the motion of particles owing to the flow of water in saturated soils and the interaction with the solid matrix. The most important property of the porous media has been identified as its surface conductivity [10] and the structure of the electric double layer (EDL) in general. Within the dynamic Stern layer assumption (where counterions in the Stern layer express a

certain mobility), the surface conductivity depends on the contributions from the Stern and the diffusive layer. Recently, a model was proposed for surface electrochemical properties of clay minerals, in which the surface conductivity of the clay was computed based on the dynamic Stern assumption, with the argumentation that the surface conductivity is frequency dependent [11]. However, the analysis of the results of electrical and dielectrical characterization of porous media turns out to be a very complicated issue, specifically in the low frequency region, due to the observed dispersion of the conductivity and the electrode polarization effect [1, 12]. Among the numerous homogenization methods, the Differential Effective Medium (DEM) schemes [13, 14] and the Moment Method (MoM) [15] have shown to be powerful tools for modelling the relationships between microstructural features and electromagnetic parameters (dielectric permittivity and electrical conductivity).

In this paper we present the analysis of a low frequency part of the conductivity spectra of kaolinite clay samples prepared at different water contents approximately covering the range between plastic and liquid limits. We show that the measured spectra exhibit an anomalous part in the low frequency region displayed as a power-law frequency dependence before reaching the plateau. We also show that the conductivity dispersion curves for samples with different water contents follow the same master curve signalling the universality as frequently observed in disordered matter [16]. An attempt to explain experimentally observed features is here presented with a model of ion motion in pore space electrolyte interrupted by trapping events at the mineral surface. The typical time scales for these processes are given in terms of the physical properties of the material. The specific features of measured dielectric spectra can be well described by introducing harmonic restoring potential into the ion equation of motion.

2 EXPERIMENTAL DATA

Electrical characteristics of the clay-water system were measured using a low frequency impedance analyser at room temperature. The admittance of the sample placed in the measuring cell between two planparallel electrodes (area $S=5.5 \text{ cm}^2$, distance $L=4.5 - 5 \text{ mm}$) was determined from the linear response of the sample to the small oscillating bias on the electrodes of the magnitude of 10 mV. The real (conductance) and imaginary parts (capacitance) of the admittance were measured in the frequency interval of 100 Hz to 100 MHz.

The clay sample used was source clay Kaolin KGa-1b purchased from The Clay Minerals Society with mineral kaolinite as the primary constituent, containing also small amounts of metals (Ca, K, Na, Mg). The plastic and liquid limits of the sample were at 25.9 % and 40.1 % water content, respectively. The specific surface of the clay sample was $10 \text{ m}^2/\text{g}$ and its solid specific gravity 2.6.

The frequency dependence of the conductance and capacitance was first determined for a dry sample, and then for wet samples, with gravimetric water content ranging from 32 % to 56 %. Wet samples were obtained with the addition of distilled water to the clay.

3 RESULTS AND DISCUSSION

The values for real and imaginary parts of frequency dependent conductivity were obtained with recalculating the measured conductance and capacitance. The frequency dependence of the complex conductivity for the samples with different water contents can be well described with the following expression whose physical basis is described below:

$$\sigma(\omega) = \frac{\sigma_0}{1 + i\omega\tau_1 + (i\omega\tau_2)^{-\alpha}} \quad (1)$$

where σ_0 , τ_1 , τ_2 and α are constants determined from substituting the expressions given by Eq. (1).

The results for conductivity as a function of frequency are presented in Fig. 1 for the real part of the expression given by Eq. (1) and in Fig. 2 for the imaginary part. The results for the samples with 36 % and 56 % water content are only shown. All the samples show qualitatively similar behaviour. The values obtained for the calculated curves shown in Fig. 1 and Fig. 2 are given in Table 1.

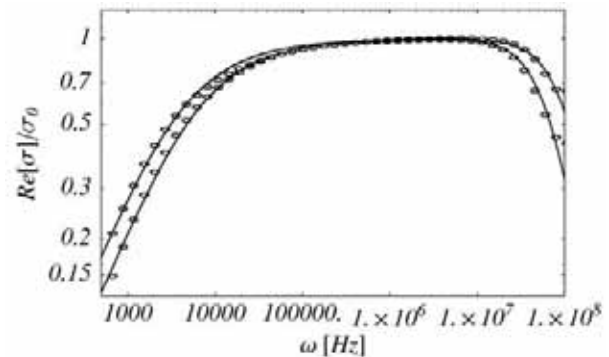


Figure 1. Measured (open dots) and calculated (solid lines) real part of frequency dependent conductivity of kaolinite clay samples at 36 % (lower curve) and 56 % (upper curve) water contents.

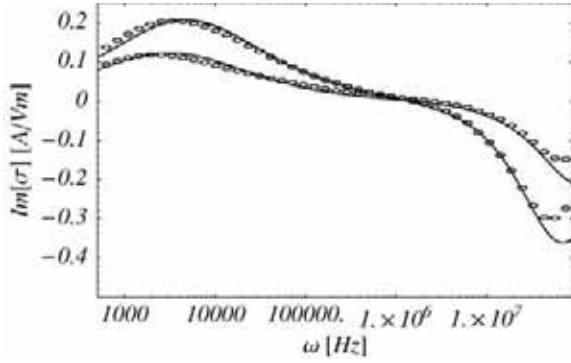


Figure 2. Measured (open dots) and calculated (solid lines) imaginary part of frequency dependent conductivity of kaolin-clay samples at 36 % (lower curve) and 56 % (upper curve) water contents.

Table 1. Values of the parameters used to calculate the real and imaginary parts of the conductivity shown in Fig. 1 and Fig. 2.

Parameters	Water content	
	36%	56%
σ_0 [A/Vm]	0,43	0,725
τ_1 [s]	$0,9 \cdot 10^{-8}$	$1,45 \cdot 10^{-8}$
τ_2 [s]	$3,2 \cdot 10^{-4}$	$2,1 \cdot 10^{-4}$
α	0,67	0,67

Let us now discuss the physical basis of the Eq. (1) describing the dynamic response of the ions in a clay-water system. In general the ion current can be given by:

$$j(t) = qn_{ion}v(t) \quad (2)$$

where q is the elementary charge, n_{ion} is the ion concentration and $v(t)$ is the ion velocity. Without loss of generality, a simple one-particle one-dimension picture is used here. The ions in the clay-water system move in a complex environment consisting of pore space filled with pore electrolyte. During the motion they also interact with the clay mineral surfaces which are charged. Ions moving in the pore space experience drag force which is proportional to ion velocity:

$$F_d = -m\gamma v \quad (3)$$

Here m is the mass of the ion, and γ is the drag force coefficient. To describe the electrode-pore electrolyte interface an additional harmonic force is introduced acting on the ion in the double layer near the electrode [1]:

$$F_h = -\frac{q^2 n_{ion}}{\epsilon_s \epsilon_0} x \quad (4)$$

Here, the static dielectric constant is the low frequency limit of the real part of the dielectric function $\epsilon_s = \epsilon'(\omega \rightarrow 0)$. The equation of motion for the ion in the external field $E(t)$ is:

$$\frac{dv(t)}{dt} + \gamma v(t) + \omega_0^2 x(t) = \frac{q}{m} E(t) \quad (5)$$

where the characteristic frequency is defined as:

$$\omega_0^2 = \frac{q^2 n_{ion}}{\epsilon_s \epsilon_0 m} \quad (6)$$

The physical mechanism of the ion dynamics near the mineral particle surface consists of the successive trapping and releasing of the particle. After each such event (at the pore/clay particle surface) the particles undergo the Brownian motion in the pore space electrolyte. The time scale for this motion between trapping events is $\tau_r = 1/\gamma$, while τ_t is set for the intrinsic time scale for the trapping event. We can estimate the characteristic trapping time by considering the linear dimension of the clay particle a (i.e. radius) and thermal velocity of the particle $v_{th} = \sqrt{kT/m}$, where T is the temperature and k is the Boltzmann constant:

$$\tau_t = \frac{a}{v_{th}} \quad (7)$$

The characteristic time for the motion in the pore space depends on the mean free path of the ion and its thermal velocity. For an unsaturated clay-water system we can estimate the mean free path with the average distance between the two adjacent clay particles:

$$\tau_r = \frac{\langle l \rangle}{v_{th}} \approx \frac{1}{a^2 n_{clay} v_{th}} \quad (8)$$

In this simplified picture the relation between the characteristic times of ion dynamics can be written as:

$$\tau_r = p\tau_t, \quad (9)$$

where the details of the clay structure, relative orientation of clay particles and the topology is simply collected within a single parameter p , usually of order one.

It was shown [17, 18] that the stochastic motion of the particle experiencing trapping events lead to a memory relation between the mean position and the mean velocity of the particle expressed with a fractional derivative of velocity:

$$\phi \frac{dx(t)}{dt} = {}_{-\infty} D_t^{1-\alpha} v(t) \quad (10)$$

where $\phi = \tau_i^\alpha / \tau_r$. The Fourier transform of the velocity leads to:

$$v(\omega) = \phi (i\omega)^\alpha x(\omega) \quad (11)$$

After the Fourier transformation of the equation of motion (10) and using $j(\omega) = \sigma(\omega)E(\omega)$ the frequency dependent conductivity is:

$$\sigma(\omega) = \frac{\sigma_0}{1 + (\omega_0 \tau_r)^2 (i\omega \tau_t)^{-\alpha} + i\omega \tau_r} \quad (12)$$

where

$$\sigma_0 = \frac{q^2 n_{ion} \tau_r}{m} = \varepsilon_s \varepsilon_0 \omega_0^2 \tau_r \quad (13)$$

By rewriting the derived expression for the conductivity (13) we can obtain the forms of Eq. (1). Here the notations $\tau_2 = \tau_t (\omega_0 \tau_r)^{-2/\alpha}$, and $\tau_1 = \tau_r$ were introduced. τ_2 is the effective low frequency relaxation time as detected in the dielectric spectra, determining the peak of the imaginary component of conductivity $\sigma_2^* = \text{Im}[\sigma(\omega = 1/\tau_2)]$. The value of the static dielectric constant can thus be estimated as:

$$\varepsilon_s = \sigma_2^* \tau_2 / \varepsilon_0 \quad (14)$$

Since τ_1 and τ_2 are usually several orders of magnitude apart (see Table 1) we also have:

$$\varepsilon_s = \frac{\sigma_0 \tau_2 \sin(\pi\alpha/2)}{2\varepsilon_0 (1 + \cos(\pi\alpha/2))} \quad (15)$$

All the parameters of the model are (Eqs. (13)-(15)) expressed in this way with two free parameters p and α , while all other quantities are material dependent (ion density, temperature, clay particle radius (i.e. specific surface), ion mass). Further investigation into the properties of the ion-surface interaction is necessary to determine the exact values of the remaining parameters.

In the low frequency limit, the frequency dependence of the conductivity follows the power-law behaviour:

$\sigma \propto \omega^\alpha$. The properties of the diffusive motion of the ions near the clay particle-water interface are contained in the frequency dependent diffusion constant $D(\omega)$ to which the conductivity is connected via the generalized Einstein relation [19]:

$$\sigma(\omega) = \frac{q^2 n_{ion}}{kT} D(\omega) \quad (16)$$

Recently Revil and Linde [20] have studied the transport of ions and water in charged, deformable porous media, and showed that the relationship between the diffusion coefficient and conductivity was much more complex than the one given in Eq. (16). Since the focus here is on the motion of ions near the clay particle – water interface we consider Eq. (16) as an operational model in which the couplings to other transport mechanisms (such as chemico-osmotic effect) are neglected [21].

The frequency dependent diffusion coefficient is given by [19]:

$$D(\omega) = -\frac{1}{6} \omega^2 \int_0^\infty e^{-i\omega t} \langle x^2 \rangle dt, \quad (17)$$

where $\langle x^2 \rangle$ is the mean-square displacement of the ion. Normal diffusion is characterized by the mean-square displacement that is linear in time $\langle x^2 \rangle \propto t$, while anomalously diffusing particles display the mean-square displacement of the $\langle x^2 \rangle \propto t^\beta$, where $\beta \neq 1$. For $\beta = 1 - \alpha$ in Eqs. (3) and (4) we obtain the expression for the low frequency limit of the ion conductivity in the clay-water mixture $\sigma \propto \omega^\alpha$. The ion surface diffusion transport is therefore subdiffusive, and could be characterized with the time-dependent diffusion coefficient $D(t) \propto t^{-\alpha}$. This indicates that the experimentally observed dielectric properties result from anomalous ion transport in a clay-water system characterized with the time-dependent diffusion coefficient often observed in complex systems [22, 23]. Recently Dudko et al. have considered the time-dependent diffusion coefficient in periodic porous materials and showed that the diffusion coefficient decreases with time from its value in a free solvent to its effective value which is much smaller [24].

4 CONCLUSIONS

The conductivity spectra as obtained by dielectric spectroscopy measurements of the clay-water mixtures at different water content levels are analysed. It is shown that the origin for the anomalous conductivity dispersion can be attributed to the motion of the ions near the clay particle-water interface. The ion dynamics is described with the Brownian motion interrupted with trapping events at clay surfaces. The transport of the ions near the clay particle surface is found to be subdiffusive with the effective time-dependent diffusion constant.

We have shown that the analysis of the low-frequency part of the dielectric spectra can yield an important insight into certain properties of the diffusion processes of ions in porous media. With respect to contaminant transport it contributes to better understanding and prediction of the long time migration of contaminants in complex environments.

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