

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Supercooled interfacial water in fine grained soils probed by dielectric spectroscopy

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Water as thermodynamic state parameter affects nearly all physical, chemical and biological processes on the earth. Recent Mars observations as well as laboratory investigations suggest that water is also a key factor of current physical and chemical processes on the martian surface, e.g. rheological phenomena. Therefore it is of particular interest to get information about the liquid like state of water on martian analog soils in the temperature range below 0 °C. In this context, a parallel plate capacitor has been developed to obtain isothermal dielectric spectra of fine grained soils in the frequency range from 10 Hz to 1.1 MHz at martian like temperatures down to -70 °C.

Two martian analogue soils have been investigated: a Ca-Bentonite (specific surface of 237 m² g⁻¹, up to 9.4 % w/w gravimetric water content) and JSC Mars 1, a volcanic ash (specific surface of 146 m² g⁻¹, up to 7.4 % w/w). Three soil-specific relaxation processes are observed in the investigated frequency-temperature range: two weak high frequency processes (bound or hydrated water as well as ice) and a strong low frequency process due to counter ion relaxation and the Maxwell–Wagner effect. To characterize the dielectric relaxation behavior, a generalized fractional dielectric relaxation model is applied assuming three active relaxation processes with relaxation time of the *i*/th process according to an Eyring equation. The real part of effective complex soil permittivity at 350 kHz was used to determine ice and liquid like water content by means of the Birchak or CRIM equation. There are evidence that Bentonite down to -70 °C has a liquid like water content of 1.17 monolayers and JSC Mars 1 a liquid like water content of 1.96 mono layers.

1 Introduction

Water is a key factor, especially in its liquid state, in nearly all physical, chemical and biological processes on the earth. In contrast, the Mars seems to be a dry desert planet at which all processes infected by water stopped before millions of years. However,

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Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measurements of the atmospheric humidity show a local distribution of possible precipitation of several μm (Smith, 2002). This available water as well as the observation of morning fog (Möhlmann et al., 2009) and ground frost (Viking Lander, 1979) clearly indicate the possibility of water sorption processes in the atmospheric layer near the planetary surface. Moreover, measurements of the total amount of water (chemically and physically bound, hydrated as well as ice) in certain surface areas suggest the possible occurrence of water in a range of up to ten per cent (Feldman, 2004). Recently observed rheological processes such as sedimentation and water percolation phenomena at dune slopes (Kereszturi et al., 2008, 2010) and a high oxidation state of material from the Martian surface (Möhlmann, 2004) give further indication of the existence of water. The outstanding role of few monolayers liquid-like water for the development of life is also shown in experimental investigations on terrestrial permafrost bacteria (Rivkina et al., 2000). This investigations show the possibility of metabolism with only a few amount of liquid water under extreme conditions. The mentioned works show that there is a lack of knowledge of the amount of water in the liquid state.

Against this background, Möhlmann (2008) developed a theoretical sandwich-model, for adsorption of water on mineral surfaces in soils. For an experimental verification and further refinement of the theoretical approach there is the need to determine the amount of liquid like water and ice in soil below 0°C . There are several techniques available for the characterization of the binding state of water in porous materials: nuclear magnetic resonance (NMR – Watanabe and Mizoguchi, 2002; Stillman et al., 2010; Watanabe et al., 2011), atomic force microscopy (AFM – Teschke et al., 2001), isothermal calorimetry (Anderson and Tiece, 1973) as well as broadband dielectric spectroscopy (BDS – Kaatze and Feldman, 2006). Especially the methods of broadband dielectric spectroscopy are sensitive to characterize structural and dynamical properties of water in porous materials (Kupfer et al., 2005). At high frequencies typically above 1 MHz, the effective complex permittivity can be physically related to the amount of fluid like water in the material based on mixture equations (Wagner et al., 2011). Therefore, different high frequency electromagnetic (HF-EM, radio- to microwave) field methods

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

were used for the characterization of water in soils such as Time Domain Reflectometry (TDR), remote sensing methods or Ground Penetrating Radar (GPR – Hoekstra and Doyle, 1971; Delaney and Arcone, 1984; Seyfried and Murdock, 1996; Zhang et al., 2003; Yoshikawa and Overduin, 2005; Mironov et al., 2010). Especially HF-EM remote sensing techniques were used in planetary research, e.g. of Mars, such as satellite-based GPR (i.e. the MARSIS and SHARAD projects (Picardi et al., 2004; Seu et al., 2007)), in cryospheric applications (e.g. Eisen et al., 2003, 2006) as well as in studies of permafrost soils (e.g. Wollschläger et al., 2010). However, the relaxation of interfacial water in the radio- to microwave frequency range is empirically estimated (Mironov et al., 2010). Furthermore, the quantitative determination of ice-contents with HF-EM techniques in soils is limited due to the similar permittivity of ice ϵ_i with 3.18 (Bohleber et al., 2012) in comparison to other solid soil phases. In the low frequency range, the determination of the ice content is possible due to the relaxation frequency of ice in the kHz-range (Grimm et al., 2008). In addition to the ice-relaxation process further low frequency relaxation processes occur such as induced polarization, counter ion relaxation and Maxwell–Wagner effects (Calvet, 1975; Ishida et al., 2000, 2003; Rotenberg et al., 2005; Leroy et al., 2008; Stillman et al., 2010) which provides additional useful information of the porous material.

Grimm et al. (2008) systematically studied low-frequency electrical properties of polycrystalline saline ice and salt hydrates in the frequency range from 1 mHz to 1 MHz and temperature range from -90 to -3 °C. The authors observe a decrease in activation energy with increasing ion concentration and therefore a shift in the relaxation time to lower values or to corresponding higher frequencies with concentration. In the study of Bittelli et al. (2004) dielectric measurements on three fine grained soils in comparison to de-ionized polycrystalline ice in the frequency range from 100 Hz to 200 kHz and temperature range from -30 to 5 °C were investigated. The results of the ice measurements are in good agreement with the results from the study of Auty and Cole (1952). Two relaxation processes were discussed: a low frequency Maxwell–Wagner-Process as well as a relaxation process due to ice and liquid like water. Maeno et al. (1992)

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



separated ice and water relaxation based on the effective electrical conductivity at a frequency of 100 kHz. In recent broadband investigations by Stillman et al. (2010) on four soils (sand, glass powder, JSC Mars 1 and a Ca-Bentonite) at least five relaxation processes were discussed. The appropriate amount of interface water was estimated with NMR-measurements. However, the authors did not differentiate between adsorbed and hydrated water. Furthermore, a three phase mixture equation of the Lichtenecker and Rother type (cf. Wagner et al., 2011) is used to estimate the ice content in case of the sand based on the quasi static effective permittivity of the soil.

In this study, dielectric spectroscopy was carried out in the frequency range from 10 Hz to 1.1 MHz and temperature range from -70 to 20°C for a systematic characterisation of the state of water under martian conditions. Two mars analogous soil were investigated: a clay soil (Ca-bentonite) and a volcanic ash (JSC-Mars 1). The dielectric relaxation behaviour was investigated based on a generalized fractional relaxation model assuming thermally activated processes. The real part of effective complex soil permittivity at 350 kHz was used to separate ice and liquid like water content by means of a power-law mixture equation. The experimental results were used to analyse the theoretical sandwich-model of water on mineral surfaces according to Möhlmann (2008).

2 Theoretical background

2.1 The sandwich-model of water on mineral surfaces

In porous media like soils two processes of ice melting (Dash et al., 2006) are responsible for the freezing point depression of interfacial water at the temperature T_S below the bulk freezing point of free water T_m (273.15 K): (i) the premelting of ice governed by van der Waals forces and (ii) the premelting of ice as a results of local curvatures and the pore geometry (cf. Gibbs–Thomson effect, Möhlmann, 2008). For this unfrozen water in the following the term “interfacial water” is used.

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Based on the theory of Hamaker (1937), Möhlmann (2008) developed a sandwich-model that describes the interaction of van der Waals forces of two plan parallel surfaces (soil, ice) and the interfacial water between In combination with the Gibbs–Duhem relationship (Eq. 1), the model allows to predict the thickness of a liquid like water film in soils as a function of temperature below T_m .

$$L = \left(\frac{H \cdot T_m \cdot v^{-3}}{6 \cdot \pi \cdot (T_m - T_S) \cdot \rho_I \cdot q_m} \right)^{1/3} \quad (1)$$

Herein are L – number of monolayers, T_S – actual freezing point temperature [K], ρ_I – ice density [916.7 kg m^{-3}], q_m – enthalpy of fusion of ice [$333\,427 \text{ J kg}^{-1}$] (values cf. Chaplin, 2012), H – Hamaker-constant [J] and v – the diameter of an monolayer of water ($3.5 \times 10^{-10} \text{ m}$ – cf. Möhlmann, 2008).

In this paper, the sandwich-model is used to compare its predictions with the measured values from the capacitor measurement system (Sect. 3.1). Due to the small investigated number of in maximum 1.96 monolayers water, only the freezing point depression by van der Waals forces was considered.

2.2 Dielectric soil properties

Based on Maxwell's equations of electrodynamics broadband electromagnetic transfer functions of a soil sample can be defined in terms of complex relative effective permittivity

$$\varepsilon_{r,\text{eff}}^*(\omega, T, \rho, \dots) = \frac{\varepsilon_{\text{eff}}^*(\omega, T, \rho, \dots)}{\varepsilon_0} \quad (2)$$

or effective conductivity

$$\sigma_{\text{eff}}^*(\omega, T, \rho, \dots) = j\omega\varepsilon_{\text{eff}}^*(\omega, T, \rho, \dots) \quad (3)$$

and complex relative effective magnetic permeability

$$\mu_{r,\text{eff}}^*(\omega, T, p, \dots) = \frac{\mu_{\text{eff}}^*(\omega, T, p, \dots)}{\mu_0} \quad (4)$$

with absolute complex permittivity $\varepsilon_{\text{eff}}^*$ or magnetic permeability μ_{eff}^* , imaginary unit $j = \sqrt{-1}$, angular frequency $\omega = 2\pi f$ as well as permittivity ε_0 and magnetic permeability μ_0 of free space. The transfer functions depend on frequency ω as well as on the thermodynamic state parameters such as temperature T , pressure p , and water content w (cf. Wagner et al., 2011). In this study the magnetic permeability was not evaluated. In case of the clay soil the assumption is justified that magnetic effects can be neglected and relative magnetic permeability is equal to 1. The martian analog JSC Mars 1 contains magnetite phases. However, low-frequency measurements by Stillman and Olhoeft (2008) show, that the real part of the relative magnetic permeability is less than 1.008.

In order to parameterise the relaxation behaviour in dependence of the thermodynamic state parameters a generalized broadband transfer function (generalized dielectric response – GDR) is suggested by Wagner et al. (2007):

$$\varepsilon_{r,\text{eff}}^*(\omega) - \varepsilon_\infty = \sum_{i=1}^N \frac{\Delta\varepsilon_i}{(j\omega\tau_i)^{\alpha_i} + (j\omega\tau_i)^{\beta_i}} - j \frac{\sigma_{\text{DC}}}{\omega\varepsilon_0} \quad (5)$$

with high frequency limit of permittivity ε_∞ , relaxation strength $\Delta\varepsilon_i$, relaxation time τ_i , stretching exponents $0 \leq \alpha_i, \beta_i \leq 1$ of the i th process and direct current electrical conductivity σ_{DC} . The relaxation time τ_i was assumed to depend on absolute temperature T and pressure p according to the Eyring-equation:

$$\tau_i(T, p) = \kappa_i \frac{h}{k_B T} \exp\left(\frac{E_{a,i}(T, p)}{RT}\right) \quad (6)$$

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Herein, h denotes Planck constant, k_B Boltzmann constant, $\kappa_i \approx 1$ the transmission coefficient, R gas constant, activation energy

$$E_{a,i}(T, \rho) = \Delta G_i(T, \rho) + T \Delta S_i(T, \rho), \quad (7)$$

free enthalpy of activation or Gibbs energy $\Delta G_i(T, \rho)$ and entropy of activation $T \Delta S_i(T, \rho)$ of the i th process (Wagner et al., 2007; Wagner and Scheuermann, 2009).

Porous mineral materials consist mainly of four phases: solid particles (various mineral phases), pore air, pore fluid as well as a solid particle – pore fluid interface (Fig. 1). In principle the fractions of these phases vary both in space (due to composition and density) and time (due to changes of water content, porosity, pore water chemistry and temperature).

The electromagnetic properties of the solid particles can be assumed to be frequency independent in the considered temperature-pressure-frequency range. Real relative permittivity ε_G of inorganic dielectric mineral materials varies from 2 to 15 (cf. Schoen, 1996; Campbell, 2002; Olhoeft, 1974; Behari, 2005; Robinson, 2003, 2004a,b). However, the available datasets are restricted to limited frequency and temperature ranges and appropriate external measurement conditions were mostly not provided. Hence, the results obtained by different groups vary considerably. This suggests further systematic investigations with broadband electromagnetic techniques under controlled boundary conditions.

The pore fluid as well as the interface fluid can be considered as an aqueous solution with a temperature-pressure-frequency dependent relative complex permittivity $\varepsilon_W^*(\omega, T, \rho)$ according to the modified Debye model (Kaatze, 2007a) as a special case of the GDR according to Eq. (5) with $N = 1$, $\alpha_i = 0$ and $\beta_i = 1$:

$$\varepsilon_W^*(\omega, T, \rho) - \varepsilon_\infty(T, \rho) = \frac{\varepsilon_S(T, \rho) - \varepsilon_\infty(T, \rho)}{1 + j \cdot \omega \cdot \tau(T, \rho)} - j \cdot \frac{\sigma_{DC}(T, \rho)}{\omega \cdot \varepsilon_0} \quad (8)$$

with static permittivity $\varepsilon_S(T, \rho)$. Under atmospheric conditions the dielectric relaxation time of water $\tau(T)$ depends on temperature T according to the Eyring-equation (6)

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and 1.0 (Dirksen and Dasberg, 1993). In this study the CRIM or Birchak approach with $a = 0.5$ is used. Moreover, the electromagnetic properties of the interface water phase in soils are poorly understood and therefore are difficult to quantify (cf. Wagner and Scheuermann, 2009). In practical applications the interface water phase is therefore neglected or crudely approximated (Schwartz et al., 2009). The mostly negative surface charge of the mineral surface (silicates) in contact with an aqueous electrolyte solution results in the formation of a boundary layer (electrical double layer, EDL). In principle, the interface layer consists of the surface charge of the mineral and an equivalent number of so-called counter-ions in the free electrolyte (Merriam, 2007). Tieleman and Berendsen (1996) stated that water molecules are ordered at the mineral surface according to two principles: (i) they effectively compensate for the local dipolar charge distribution of the surface molecules, and (ii) they reorient themselves due to the geometric constraints of the surface. Furthermore, Teschke et al. (2001) points out that the water molecules closest to the mineral surface orient themselves under optimization of their inter-water hydrogen bonds. This suggests there exists a more aligned molecular distribution in the interface region between mineral surface and bulk water than in the bulk and consequently, a layer with a lower effective permittivity than in the bulk. Teschke et al. (2001) suggested an expression purposed by Podgornik et al. (1987) based on Hamaker theory for the dependence of the static dielectric permittivity at atmospheric conditions as a function of the distance from a mica particle surface:

$$\varepsilon_S(d, T) = \frac{\varepsilon_{S,f}(T)}{1 + \left(\frac{\varepsilon_{S,f}(T)}{\varepsilon_{S,p}(T)} - 1 \right) \cdot \exp\left(-\frac{2d}{\lambda}\right)} \quad (11)$$

with static free water permittivity $\varepsilon_{S,f}(T)$, static permittivity at the particle surface $\varepsilon_{S,p}(T)$, distance from the surface d and correlation length λ .

Due to the low water content of the materials only interface water was considered in this study. Hence, under atmospheric conditions Eq. (9) was used in three phase form

with air, solid particles and interface water:

$$\varepsilon_{r,\text{eff}}^{*0.5}(\Theta_W, n, \omega, T) = \Theta_W \cdot \varepsilon_W^{*0.5}(\omega, T) + \Theta_G \cdot \varepsilon_G^{0.5} + \Theta_A \cdot \varepsilon_A^{0.5} \quad (12)$$

with unknown permittivity ε_G of the solid phase, the permittivity of air $\varepsilon_A = 1$, complex permittivity of water ε_W^* , the volume fraction of the solid phase $\Theta_G = 1 - n$ and volumetric air content $\Theta_A = 1 - \Theta_W - \Theta_G$. ε_G was estimated based on empirical equations according to Olhoeft (1974), Campbell (2002) or Dobson et al. (1985) as well as from the mineralogical composition according to Robinson (2004a) with data from Schoen (1996) for the single mineral phases. Moreover, ε_G was determined from the permittivity of the dried material with:

$$\varepsilon_G = \left(\frac{\varepsilon_{r,\text{eff}}^{*0.5} - \Theta_A - \Theta_W \cdot \varepsilon_W^{0.5}}{\Theta_G} \right)^2 \quad (13)$$

3 Experimental procedure

3.1 Experimental set-up

The developed gas sealed parallel plate capacitor consists of circular capacitor plates with guard ring electrode (Lorek, 2008). Due to the resulting parallel electric field (Rost, 1978) and a well-defined air gap between investigated soils and upper electrode, permittivity measurements on fine grained powdered materials are possible (Fig. 2; Agilent, 2000). The measurements were performed in a wide temperature regime from -70 to 25°C .

At 25°C the gold-coated polished brass plates have a distance of 1.26 mm. The resulting fractions are for the air gap $d_1 = 0.45$ mm and for the soil $d_2 = 0.81$ mm. The lower plate has a diameter of 90 mm and is located in a cavity with a diameter d_3 of 91 mm. The distance between this plate and the upper brim of the cavity is the soil

height d_2 . The upper plate has a diameter d_{KP} of 77.56 mm. The volume for the soil sample inside the capacitor θ_{Soil} is 5.268 cm^3 .

The housing material is a hydrophobic polycarbonate (Makrolon), a material with permanent mechanical load capacity down to -50°C (PVDF, 2003). The housing has integrated gas in- and outlets and is gas sealed by silicon rubber zero rings. These are at least cold-resist down to -60°C (RALICKS, 2012).

The absolute value $|\varepsilon_{r,eff}^*|$ of the complex relative effective permittivity $\varepsilon_{r,eff}^*$ is determined for a capacitor with circular plates and the in serial connected capacities C_{Gas} and C_{Soil} based on (see definitions in Fig. 2):

$$|\varepsilon_{r,eff}^*| = \frac{d_2 \cdot C \cdot \varepsilon_G}{\varepsilon_A \cdot \varepsilon_0 \cdot \frac{\pi}{4} \cdot d_{KP}^2 - d_1 \cdot C} \quad (14)$$

with capacitance C of the plate capacitor. $\varepsilon'_{r,eff}$ and $\varepsilon''_{r,eff}$, the real and imaginary part of $\varepsilon_{r,eff}^*$, respectively, are given with measured loss factor $\tan \delta_{eff}$ (cf. Lorek, 2008):

$$\varepsilon'_{r,eff} = |\varepsilon_{r,eff}^*| \cdot (\tan \delta_{eff}^2 + 1)^{-0.5}, \quad (15)$$

$$\varepsilon''_{r,eff} = |\varepsilon_{r,eff}^*| \cdot \tan \delta_{eff} (\tan \delta_{eff}^2 + 1)^{-0.5}. \quad (16)$$

Figure 3 shows the entire experimental setup. For defined temperatures, the capacitor was placed in a thermal-test chamber (KWP 240, Weiss GmbH) at defined temperature. For the Measurement at 62 different frequencies between 10 Hz and 1.1 MHz, a LCR-bridge (PSM 1700 PsimetriQ, Newtons4th Ltd (UK)) was used. To set the investigated soil on a defined value of moisture, a gas flow of 15 L h^{-1} with an absolute humidity of ca. 0.00193 g m^{-3} at 25°C was applied through the air gap (Fig. 2). The humidity was determined by an Easidew-dewpoint-transmitter (Michell Instruments GmbH). Reaching the required soil moisture and vice versa the corresponding capacity, the gas in- and outlets of the capacitor were closed.

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Next, the chamber temperature was first isothermally decreased in 5 K and 10 K steps to the lowest temperature of -70°C and then isothermally increased using the same step sizes. For every step the temperature was stabilized for 5 h. On this, capacitor and test material had time to reach thermal equilibrium, confirmed by stable capacity values. Measurement of gas temperature was performed with a Pt100 temperature sensor after the gas stream has passed the capacitor.

After the experiment, the soil was completely removed to identify the gravimetric water content (Sect. 3.3). The measurements with the clay soil were carried out at three water contents: 1.53 monolayers (9.4 % w/w), 1.17 monolayers (7.2 % w/w) and 0.7 monolayers (4.3 % w/w). The experiments with JSC Mars 1 samples were done with 1.96 monolayers (8.7 % w/w), 1.71 monolayers (7.6 % w/w) and 1.37 monolayers (6.1 % w/w).

3.2 Investigated soils

3.2.1 Swelling clay soil

The clay soil is based on a commercial available Ca-Bentonite (Edasil, Agrimont GmbH). This Bentonite mainly contains Ca-dioctahedral smectites, i.e. Montmorillonite, which are swelling clay minerals. Surface areas consisting of similar swelling clay minerals were detected on Mars (Poulet et al., 2005). Because of their formation history these areas are preferred as possible habitats of former or current life on Mars (Chevrier and Mathe, 2007). Table 1 shows measured and published values for the used powdered Ca-Bentonite.

The high Montmorillonite content leads to a relatively large surface with $74\text{ m}^2\text{ g}^{-1}$ (BET surface area with N_2) (Jänchen et al., 2009b). Studies on Montmorillonite using the BET method with water in place of nitrogen have shown an surface enlargement to $217\text{ m}^2\text{ g}^{-1}$ (Jänchen et al., 2009a). These finding was confirmed by the measured specific surface areas of the investigated clay soil.

3.2.2 Volcanic ash

JSC Mars 1 is a volcanic ash from Mauna Kea (Hawaii) and defined as mars analog material (Allen et al., 1998). The natural grain sizes 800–1000 μm were too large for the capacitor. Therefore, the soil was crushed and fractionated to certain sizes. To determine differences to the original material (Table 2) the fractions were analyzed individually.

3.3 Sample preparation

At constant temperature and humidity, multiple samples from the clay and JSC Mars 1 have been prepared. The prepared samples have an equivalent dry density ρ_D and thus comparable soil surface areas S . The gravimetric water content θ_G was determined by drying the sample for 24 h at 105 °C in air atmosphere (Wernecke, 2003; Scheffer and Schachtschabel, 1989). All measurements described in this paper were done on samples prepared according to this procedure.

The average weight of the clay samples in the capacitor was 4.185 ± 0.01 g with a gravimetric water content of about 9.27 % w/w . From this it results a dry soil content m_G of 3.83 ± 0.01 g clay and a surface area S of 908 ± 2 m^2 (with a specific surface area S_{sp} of 237 $\text{m}^2 \text{g}^{-1}$, c.f. Table 1). The weight of a monomolecular water layer is 2.6×10^{-4} g m^{-2} (Hauffe and Morrison, 1974) which corresponds to a gravimetric water content per monolayer of 6.16 % w/w .

Each sample was completely connected to the lower capacitor plate, spread evenly and pressure less smoothed to avoid fluctuations in density and thickness. After the experiment, the capacitor has been opened; the material promptly placed into a covered sample dish, and the weight was determined. The resulting difference due to the adsorption of water from surrounding air while extracting and weighing the samples was less than 3 % of the measured gravimetric water content.

For JSC Mars 1 the fraction with grain sizes of 32–63 μm (Sect. 3.2) was optimal for the homogeneous distribution in the capacitor. This fraction has compared to the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



original soil a larger specific surface area. Due to the assumption of more fine dust in the first few millimeters of the Martian surface the use of this fraction is reasonable.

The average weight of JSC Mars 1 samples was 4.252 ± 0.05 g. The negligible difference of 3.3% in the gravimetric water content can be explained with the absorption of water from the ambient humidity during extraction and weighing. The samples had a gravimetric water content of about 9.81% *w/w*. This leads to a m_G value of 3.872 ± 0.05 g and a S value of 662 ± 28 m². One monolayer of water corresponds to a gravimetric water content of 4.45% *w/w*.

4 Experimental results

Figure 4a (left) shows $\epsilon'_{r,\text{eff}}$ (Eq. 15) and $\epsilon''_{r,\text{eff}}$ (Eq. 16) of the soils at the highest investigated water content in a temperature range -70 to 20 °C. A direct indication for freezing is not observable especially in case of the volcanic ash. In $\epsilon''_{r,\text{eff}}$ an additional relaxation peak is expected for freezing in the frequency range < 10 kHz and below 0 °C (Ulaby et al., 1986; cf. Lorek, 2008). However, in case of the clay soil there exists a strong relaxation peak even at 20 °C which shifts with decreasing temperature to lower frequencies.

In Fig. 4a (right) the dataset is represented in addition as complex electric modulus (Jonscher, 1983) to separate different relaxation mechanisms.

$$M^* = \frac{1}{\epsilon^*_{r,\text{eff}}} = \frac{1}{\epsilon'_{r,\text{eff}} - j\epsilon''_{r,\text{eff}}} = \frac{\epsilon'_{r,\text{eff}}}{\epsilon'^2_{r,\text{eff}} - \epsilon''^2_{r,\text{eff}}} + j \frac{\epsilon''_{r,\text{eff}}}{\epsilon'^2_{r,\text{eff}} - \epsilon''^2_{r,\text{eff}}}. \quad (17)$$

The dielectric relaxation behavior was analyzed with three different methods: (i) based on the temperature dependence of characteristic frequencies such as the maximum frequency in the imaginary part of the complex effective permittivity, (ii) based on inverse modeling technique by means of fitting the frequency dependency of the complex

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



permittivity at each measured temperature, and (iii) a simultaneous fit of the frequency and temperature dependence.

With the approach in (i) it was assumed, that the temperature dependence of a characteristic frequency f_r is related to the relaxation time $f_r = (2 \cdot \pi \cdot \tau)^{-1}$. Then, the appropriate activation energy was determined with an Arrhenius-approach in Eyring-equation (6):

$$\tau_i(T) = \tau_{0,i} \cdot \exp\left(\frac{E_{A,i}}{R \cdot T}\right) \quad (18)$$

Using this approach, apparent activation energy $E_{A,i} = \Delta G_i$ is assumed to be constant. Appropriate pre-factor is then given by $\tau_{0,i} = \frac{h}{k_B \cdot T} \cdot \exp\left(\frac{\Delta S_i}{R}\right)$. Here the temperature independence of ΔG_i and ΔS_i is further implied. In a representation of the logarithm of appropriate characteristic frequencies as a function of reciprocal temperature $x = T^{-1}$ Eq. (18) can be modeled with a linear equation $\log(f_r) = A + B \cdot x$ which was fitted to the measurements. The offset A is related to the pre-factor $A = \ln(\tau_0)$ and the slope to the apparent activation energy $B = E_A \cdot R^{-1}$.

Approach (i) is not applied to the volcanic ash due to the weak dispersion. In Fig. 5 the results in case of the clay soil are represented for the β and γ process. In Fig. 6 the resultant master curve representation of the dataset in the temperature range from -20 to 19°C for the γ process is given. From this representation of the data it becomes clear, that the low frequency γ process can not be modeled with a simple Debye-equation. Here a Cole–Cole type relaxation function is necessary. This means that the relaxation mechanism is characterized by a distribution of relaxation times $H(\tau)$. In this context, the determined relaxation time from the peak frequency is a mean macroscopic relaxation time related to the appropriate microscopic relaxation time due to the assumed relaxation model (Jonscher, 1983). Furthermore, the relaxation time distribution can change with temperature for measurements in a broad temperature range. Therefore the approach in (ii) is applied to the dataset.

**Supercooled
interfacial water in
fine grained soils**

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In case (ii) equation (GDR) is fitted to the dataset based on Eq. (5) at each temperature using a shuffled complex evolution metropolis algorithm (SCEM-UA – Vrugt, 2003). This algorithm is an adaptive evolutionary Monte Carlo Markov chain method and combines the strengths of the Metropolis algorithm, controlled random search, competitive evolution, and complex shuffling to obtain an efficient estimate of the most optimal parameter set, and its underlying posterior distribution, within a single optimization run (Heimovaara et al., 2004).

The algorithm is based on a Bayesian inference scheme. The needed prior information are a lower and upper bound for each of the relaxation parameters ξ . Assuming this non informative prior the posterior density $\rho = (\xi|y, \gamma)$ for ξ conditioned with the measurement y is given by (Vrugt, 2003):

$$\rho = (\xi|y, \gamma) \propto \left[\sum_{k=1}^N \frac{y_k - \hat{y}_k}{\delta} \right]^{-N(1+\gamma)/2} \quad (19)$$

Herein y_k is the k th of m measurements at each frequency for a given temperature and \hat{y}_k is the corresponding model prediction. δ represents the error of the measurements expressed as a standard deviation. The parameter γ specifies the error model of the residuals. The residuals are assumed normally distributed when $\gamma = 0$, double exponential when $\gamma = 1$, and tend to a uniform distribution as $\gamma \rightarrow -1$. In (iii) the approach is extended to frequency and temperature. In Fig. 7 the results of these two approaches are represented. In Table 3 the results of the simultaneous analyses according to method (iii) for both soils is summarized.

For an analysis of the relaxation behavior the measurements of the soils with highest water content (1.53 or 1.96 monolayers) was used (see Table 3). In case of the clay soil the experimental results (Fig. 4a) indicate three relaxation processes in the investigated frequency-temperature-pressure range: two weak high frequency processes α and β (associated with different binding states of water in the porous material) and a strong low frequency process γ associated with counter ion relaxation, Maxwell–Wagner effects and ice. For the analysis of the volcanic ash also these three processes were

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



used to model the relaxation behavior regardless the weak dispersion and no clear indication of a relaxation peak in the investigated frequency-temperature-pressure range. However, the results of the simultaneous analysis suggest a γ process below the measurement window. The strong γ process of the clay soil exhibits an apparent activation energy of 51 kJ mol^{-1} and shows a clear deviation from simple Debye behavior. This is a clear indication of an overlapping of different relaxation mechanisms. Furthermore, the analysis of the relaxation behavior indicates an increase of the relaxation time distribution with decreasing temperature (Fig. 8), which suggests that the relaxation time distribution is a measure of the coexistence of liquid like water and ice.

The β process is visible in the low temperature range below -50°C with apparent activation energy of 41 kJ mol^{-1} . For an analysis of the α process the frequency range has to be extended to higher frequencies. However, based on the inverse modeling technique appropriate apparent activation energy of 32 kJ mol^{-1} was estimated. Furthermore, a narrow relaxation time distribution was observed. In Fig. 9 the results of the relaxation behavior with the different approaches is represented in comparison to results of other studies. It becomes clear that the characterization of the observed relaxation processes is inconsistent. Investigations in the frequency range below 10 MHz were carried out by (Bergman and Swenson, 2000) on a swelling clay (vermiculite) in the frequency range from 10 MHz to 10 MHz, and temperature range from -140°C to -68°C . The study aimed to characterize the relaxation behavior of hydrated interlayer water. Three relaxation processes were observed and associated with a Maxwell-Wagner effect (low frequency range), supercooled interlayer water (intermediate range) and ice (high frequency). In comparison the authors performed measurements on pure ice, which coincide with the high-frequency process.

Auty and Cole (1952), Johari and Jones (1976) and Bittelli et al. (2004) determine an activation energy of 55 kJ mol^{-1} for de-ionized ice, which is distinctly higher than E_a obtained by (Bergman and Swenson, 2000) with 32 kJ mol^{-1} . Hence, the association of the α -process with ice-relaxation seems to be reasonable in comparison to the results of dielectric spectroscopy on swelling clay by Bergman and Swenson (2000).

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



However, the results are inconsistent with the results of de-ionized ice from Auty and Cole (1952), results of different soils by Bittelli et al. (2004) and of contaminated ice from Grimm et al. (2008). Moreover, the transition from free bulk water to supercooled interface water as a function of the distance from particle surface (Speedy and Angell, 1976; Swenson et al., 2002) as well the fast water reorientation (Sciortino et al., 1996; Buchner et al., 1999; Kaatze, 2007a,b) in soils were not sufficiently characterized. In the current development stage the bandwidth of the measurement systems is restricted and therefore the relaxation behavior cannot be fully characterized. This issue needs to be addressed in further broadband studies. However, in this study, a mixture approach based on a power law model (CRIM) according to Eq. (12) is suggested to separate fluid like water and ice at a measurement frequency of 350 kHz. In this frequency range two processes are active (beta, gamma).

Figure 10 illustrates the temperature dependence of $\varepsilon'_{r,eff}$ for 0.7, 1.17 and 1.53 monolayers water at a frequency of 350 kHz. For this frequency the values have shown the lowest dielectric losses (Fig. 4a) and are sufficient to reflect the dielectric properties of the clay soil.

The 0.7 L line shows over the entire temperature range an almost linear decrease for $\varepsilon'_{r,eff}$. Only the lower part is a little bit flattened. Probably, the permittivity of the bound water ε_W approaches to the permittivity of dry soil ε_G and thus, influence on the whole permittivity of the soil $\varepsilon^*_{r,eff}$ decreases. There is no evidence indicating ice formation. The same results for the 1.17 L line, except that the higher water content extends the linear part of the permittivity down to -70°C . Only the stronger falling course of the 1.53 L line below 0°C could be an indication of ice formation.

Figure 11 shows the temperature dependence of $\varepsilon'_{r,eff}$ for 1.37, 1.71 and 1.96 monolayers water on JSC Mars 1 at the same frequency of 350 kHz. The $\varepsilon_{r,eff}$ values showed also the lowest dielectric losses at this frequency.

The 1.96 L line shows like the 1.71 L line an almost linear decrease of the permittivity over the whole temperature range. In contrast the 1.37 L line decreases linearly up to approximately -20°C , turns into a plateau phase, and continues to decrease

from approximately -50°C . At the plateau, the dielectric behavior of dry soil could already dominate the processes. Evidence for ice formation at the three curves was not detected.

Both soils clay and JSC Mars 1 have not shown indications for freezing except the 1.53 L line of the clay soil in Fig. 10. Either the water remains in a liquid state, or the effect of ice formation is overlaid by other polarization effects. In both soils the permittivity decreases for temperatures greater than 0°C . This "temperature effect" has already been described by Stacheder (1996).

The 1.53 L line of the clay soil was analyzed in Sect. 5.2. Interfacial water content below 0°C could be calculated and ice formation substantiated. All further investigated water contents in this paper remain probably in the liquid like state down to -70°C .

5 Discussion

High frequency electromagnetic measurements techniques for in situ soil moisture estimation such as Time Domain Reflectometry (TDR) are mostly based on an empirical relationship between measured apparent permittivity ϵ_{app} and volumetric water content (e.g. Topp et al., 1980). Under this circumstance, these techniques assume a slight temperature dependence of ϵ_{app} in the temperature range above 0°C , which is a justified assumption for specific soils (e.g. Stacheder, 1996). For this reason, the decrease of ϵ_{app} below 0°C is solely ascribed to the freezing of liquid water. Therefore, measured permittivity is assumed to be a function of the volume fraction of soil and the residual liquid water. This simplified calculation leads to incorrect results (Yoshikawa and Overduin, 2005) also because below 0°C the liquid water content depend on the total water content of the soil sample (Oliphant, 1985). However, Seyfried and Murdock (1996) have investigated the differences between experimental data obtained with empirical equations or theoretical mixing-models such as the CRIM-equation (12) based on TDR-measurements. The results confirm the dependence of the liquid water content below

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



0°C on the total water content. Reliable conclusions for the differences between experimental data and theoretical models were not drawn by Seyfried and Murdock (1996).

On the other hand, theoretical models based on the Claypeyron-equation (cf. Seyfried and Murdock, 1996) or the sandwich-model (Sect. 2.1) provide a physical theory for the calculation of the interfacial water content and show no dependence on the total water content. These findings were further supported by the empirical approach for interfacial water contents below 0°C suggested by Anderson and Tice (1973):

$$\ln(w) = 0.2618 + 0.5519 \cdot \ln(S_{sp}) - 1.449 \cdot S_{sp}^{-0.264} \cdot \ln(T_m - T_s). \quad (20)$$

Hence, for swelling clays, the mentioned calculations by Seyfried and Murdock (1996) consequently have resulted to incorrect results due to neglecting the temperature effect (Sect. 4). This further suggests, to be the reason for the unsatisfying results in the determination of ice contents in clays by Bittelli et al. (2004).

In section 5.2 a new approach for simultaneous ice and liquid water content estimation in soils based on experimental data from the clay soil will introduced (Lorek, 2008). This approach explicitly takes the temperature effect into account. The ice and water content of the clay soil than was estimated with the CRIM or Birchak-equation (12) for the 1.53 L line in Fig. 10. However, appropriate soil parameters in Eq. (13) have to be determined prior to the application of Eq. (9).

5.1 Estimation of the solid phase permittivity ϵ_G

In Table 4 the permittivity of the solid phase of the clay soil and JSC Mars 1 are summarized. The values were either calculated using formulas of Dobson et al. (1985), Olhoeff et al. (1975), Campbell (2002) or taken from literature.

The measured permittivity $\epsilon_{r,eff}$ of the clay soil and JSC Mars 1 at the lowest water contents of 0.179 and 0.314 monolayers are 1.803 and 1.994, respectively (Fig. 12). The appropriate volume fractions were calculated with the equation $\Theta_G = m_G \cdot S_{sp} / \theta_{Soil}$ and $\Theta_W = d_1 / ((4 \cdot S \cdot l \cdot v) / (\pi \cdot d_3^2))$. The resulting volume fractions are for the clay soil

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$\Theta_A = 0.6838 \text{ m}^3/\text{m}^3$, $\Theta_W = 0.0107 \text{ m}^3/\text{m}^3$, $\Theta_G = 0.3055 \text{ m}^3/\text{m}^3$ and for JSC Mars 1 $\Theta_A = 0.7077 \text{ m}^3/\text{m}^3$, $\Theta_W = 0.0139 \text{ m}^3/\text{m}^3$ and $\Theta_G = 0.2784 \text{ m}^3/\text{m}^3$.

For the dry clay soil a ε_G value of 4.33 was calculated with Eq. (13). The calculated ε_G value for dry JSC Mars 1 is 5.87. These values are in reasonable accordance with the data in Table 3 and support the reliability of the approach.

5.2 Estimation of the ice and liquid water content of the clay soil below 0 °C

Figure 13 illustrates the calculated ε'_W curve for 0.7, 1.17 and 1.53 monolayers water based on Eq. (13). For decreasing temperatures above 0 °C the permittivity falls in all three cases nearly linear. This can be explained by the temperature effect mentioned in Sect. 4 through which lower water content leads to a stronger decrease of the permittivity. The 0.7 L curve shows the strongest decrease with a flatter line at lower temperatures. This behavior is supposed to be associated with the reduced influence of the temperature effect with decreasing number of monolayers. The 1.17 L curve has down to -55 °C an almost linear decrease. The 1.53 L curve shows a different behavior with a stronger decrease below 0 °C which suggests a phase transition.

To determine the ice content in the soil based on available data of ε'_W , it is necessary to estimate the permittivity ε'_{IW} of bound water or (without freezing) interfacial water. Assuming supercooling of all available water (without ice formation) below 0 °C the decrease of the ε'_{IW} values for dropping temperature is further linear, the known linear decrease can be used for temperatures below 0 °C. Due to the lack of experimental data of the electromagnetic properties of interfacial water, the ε'_{IW} values between the 0.7, 1.17 and 1.53 L lines have been extrapolated from temperatures above 0 °C. Using the assumption stated before, the determined decreases are extended down to lower temperatures and represent thereby the permittivity of the interfacial water content for different monolayers. Figure 14 shows the calculated curves from Fig. 13 compared to the deduced curves without ice formation.

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



6 Conclusions

A parallel plate capacitor has been developed to obtain isothermal dielectric spectra of fine grained soils in the frequency range from 10 Hz to 1.1 MHz at martian like temperatures down to -70°C (Lorek, 2008). Two martian analogue soils have been investigated: a Ca-Bentonit (specific surface of $237\text{ m}^2\text{ g}^{-1}$, up to 9.4 % w/w gravimetric water content) and JSC Mars 1, a volcanic ash (specific surface of $146\text{ m}^2\text{ g}^{-1}$, up to 7.4 % w/w). The dielectric relaxation behavior was analyzed with three different methods: (i) based on the temperature dependence of characteristic frequencies such as the maximum frequency in the imaginary part of the complex effective permittivity, (ii) based on inverse modeling technique by means of fitting the frequency dependency of the complex permittivity at each measured temperature, and (iii) a simultaneous fit of the frequency and temperature dependence.

The experimental results indicate three active relaxation processes in the investigated frequency-temperature-pressure range: two weak high frequency processes α and β (associated with different binding states of water in the porous material) and a strong low frequency process γ associated with counter ion relaxation, Maxwell-Wagner effects and ice. To characterise the dielectric relaxation behaviour, a generalized fractional dielectric relaxation model (Wagner et al., 2007, 2011) was applied assuming three active relaxation processes with relaxation time of the i th process according to an Eyring's equation (Wagner and Scheuermann, 2009). The strong γ process exhibits an apparent activation energy of 51 kJ mol^{-1} and shows a clear deviation from simple Debye behavior. This is a clear indication of an overlapping of different relaxation mechanisms. Furthermore, the analysis of the relaxation behavior indicates an increase of the relaxation time distribution with decreasing temperature, which suggests that the relaxation time distribution is a measure of the coexistence of liquid like water and ice. The β process is visible in the low temperature range below -50°C with apparent activation energy of 41 kJ mol^{-1} . For an analysis of the α process, the frequency range has to be extended to higher frequencies. However, based on the

TCD

7, 1441–1493, 2013

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



inverse modeling technique, appropriate apparent activation energy of 32 kJ mol^{-1} was estimated. Furthermore, a narrow relaxation time distribution was observed.

The real part of effective complex soil permittivity at 350 kHz was used to determine ice and liquid-like water content by means of the CRIM or Birchak equation (Lorek, 2008). There is evidence that swelling clay soil (Ca-Bentonite) down to -70°C has a interfacial water content of 1.17 monolayers and JSC Mars 1 an interfacial water content of 1.96 monolayers. The results of the experimental investigations as well as the analysis show that the technique is suitable to estimate fluid like water content in soils below 0°C . However, the developed analysis strategy is the first step to a rigorous physical approach for estimation of fluid like water and ice simultaneously. (i) the frequency range has to be broaden to higher (up to 10 GHz) and lower frequencies (down to the mHz range) and (ii) the spectrum of soils has to be broaden (mixtures of silt and clay with variation in clay mineralogy) and (iii) the effect of water content and pore water chemistry has to be systematically evaluated.

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TCD

7, 1441–1493, 2013

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Jänchen, J., Morris, R. V., Bish, D. L., Janssen, M., and Hellwig, U.: The H₂O and CO₂ adsorption properties of phyllosilicate-poor palagonitic dust and smectites under martian environmental conditions, *Icarus*, 200, 463–467, 2009b.

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Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Merriam, J. B.: Induced polarization and surface electrochemistry, *Geophysics*, 72, 157–166, 2007.
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- 30

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Supercooled
interfacial water in
fine grained soils**

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Table 1. (1) Excerpt from Edasil data sheet (Agrimont GmbH); (2) Soil parameters for Bentonite (BET method with N_2 and H_2O measurement performed at the Federal Institute for Materials Research and Testing (BAM)).

		Chemical composition		Mass %
Montmorillonite ¹	65–70 %			
Cation exchange capacity Na ¹	0.65 mmolL ⁻¹	SiO ₂		56
Cl ¹	1.09 mmolL ⁻¹	Al ₂ O ₃		16
Grain size < 63 μm ¹	90–93 %	Fe ₂ O ₃ , CaO, MgO		every 4
Grain size > 63 μm ¹	7–10 %	K ₂ O		2
Spec. surface (N ₂ ²)	50.3 m ² g ⁻¹	Na ₂ O		0.4
Spec. surface (H ₂ O ²)	237 m ² g ⁻¹			
Pore size ²	5.641 nm			
Absolute desity ²	2.38 gcm ⁻³			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Table 3. Summary of the determined relaxation parameters of the two soils at the highest water content based on the simultaneous analyses according to method (iii).

	Clay soil	JSC-Mars I		
RMSE [-]	0.26		0.28	
monolayers	1.53		1.96	
ε_U [-]	1.90	(± 0.015)	1.7	(± 0.05)
$\Delta\varepsilon_\alpha$ [-]	0.005	(± 0.0002)	0.003	(± 0.0001)
$E_{a,\alpha}$ [kJ mol ⁻¹]	32.00	(± 0.01)	22.3	(± 2.1)
$1-a_\alpha$ [-]	0	–	0	–
$\Delta\varepsilon_\beta$ [-]	5.21	(± 0.12)	1.43	(± 0.07)
$E_{a,\beta}$ [kJ mol ⁻¹]	36.7	(± 0.4)	39.8	(± 0.2)
$1-a_\beta$ [-]	0.793	(± 0.005)	0.875	(± 0.009)
$\Delta\varepsilon_\gamma$ [-]	24.90	(± 0.38)	10.8	(± 1.1)
$E_{a,\gamma}$ [kJ mol ⁻¹]	51.98	(± 0.06)	67.7	(± 1.3)
$1-a_\gamma$ [-]	0.153	(± 0.005)	0.703	(± 0.007)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 4. Summary of the solid phase permittivity ϵ_G (cf. Lorek, 2008).

Literature	Material	Spec. density	Frequency	ϵ_G
Dobson-formula	clay/JSC Mars 1	2.38 gcm ⁻³ / 2.64 gcm ⁻³	1.4–18 GHz	4.18/ 4.65
Olhoeft-formula	clay/JSC Mars 1	2.38 gcm ⁻³ / 2.64 gcm ⁻³	> 100 kHz	4.78/ 5.67
Campbell-formula	clay/JSC Mars 1	2.38 gcm ⁻³ / 2.64 gcm ⁻³	–	4.96/ 5.91
Robinson (2004a)	Montmorillonite	2.67 gcm ⁻³	0.001–1.75 GHz	5.5

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

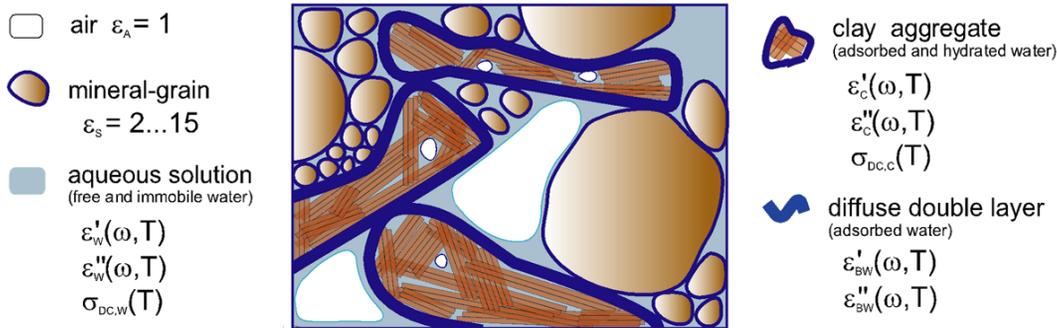


Fig. 1. Simplified schematic illustration of the structure of an unsaturated soil sample indicated are the contributions of the single components to the dielectric material properties in terms of a complex effective relative permittivity $\epsilon_{r,eff}^* = \epsilon'_{r,eff} - j \cdot \epsilon''_{r,eff}$ with real $\epsilon'_{r,eff}$ and imaginary part $\epsilon''_{r,eff}$ (cf. Wagner and Scheuermann, 2009).

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



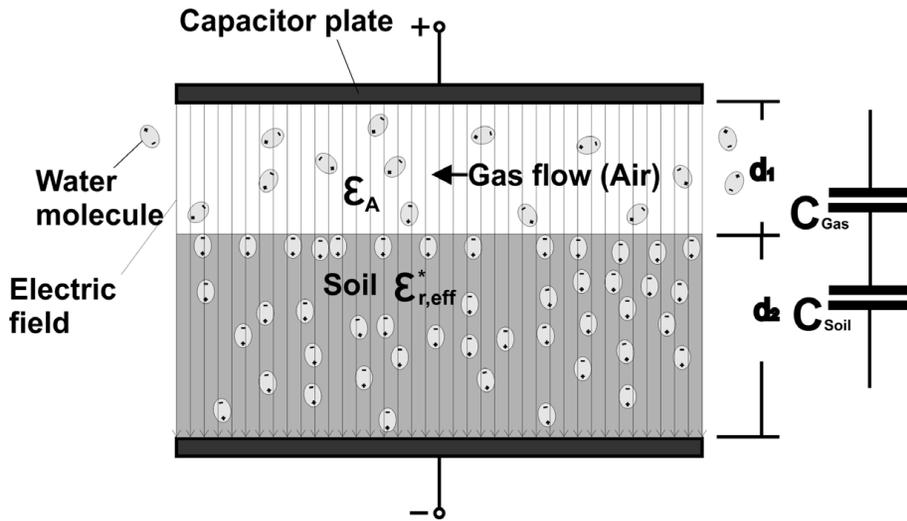


Fig. 2. Schematic diagram of the capacitor with defined air gap over investigated material.

Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

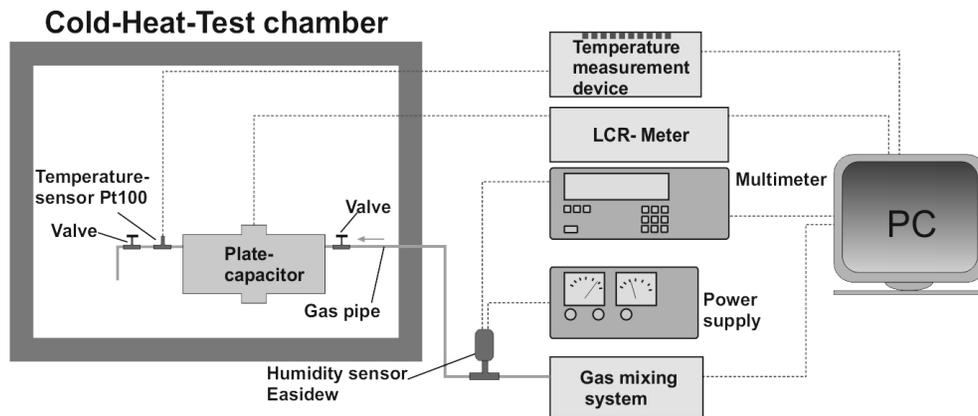


Fig. 3. Measurement system.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

⏪ ⏩
⏴ ⏵
Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

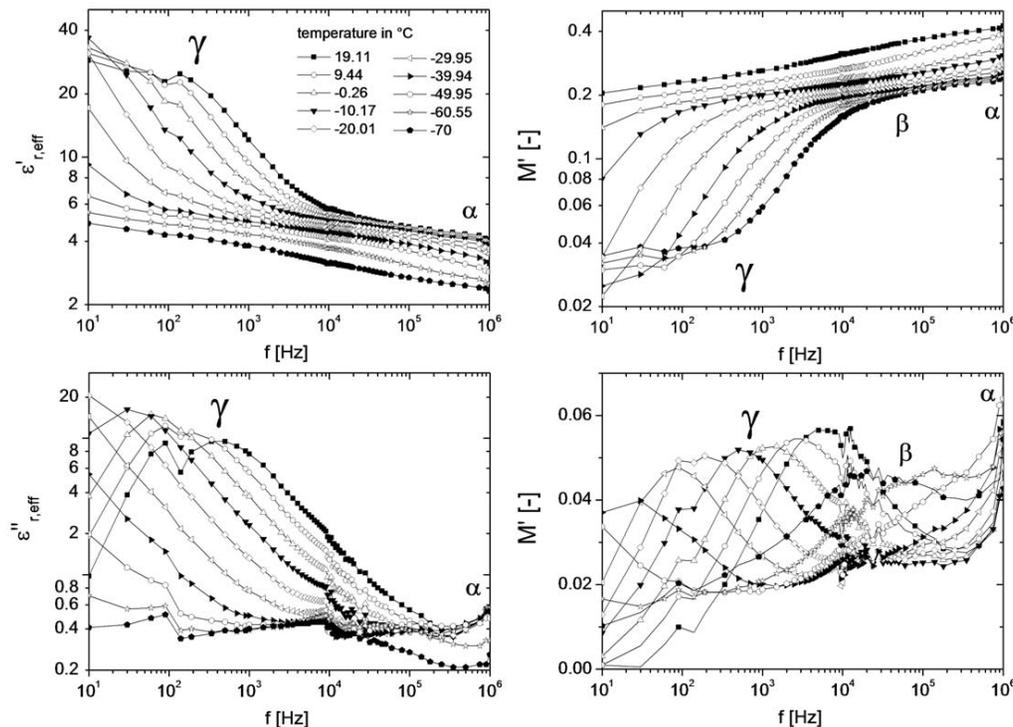


Fig. 4a. (Top) real part and (bottom) imaginary part of the complex effective permittivity $\epsilon_{r,eff}^*$ or complex modulus $M^* = 1/\epsilon_{r,eff}^*$ of the clay sample in case of a constant water content of 1.53 monolayers water measured in the temperature range from -70 to 20°C .

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

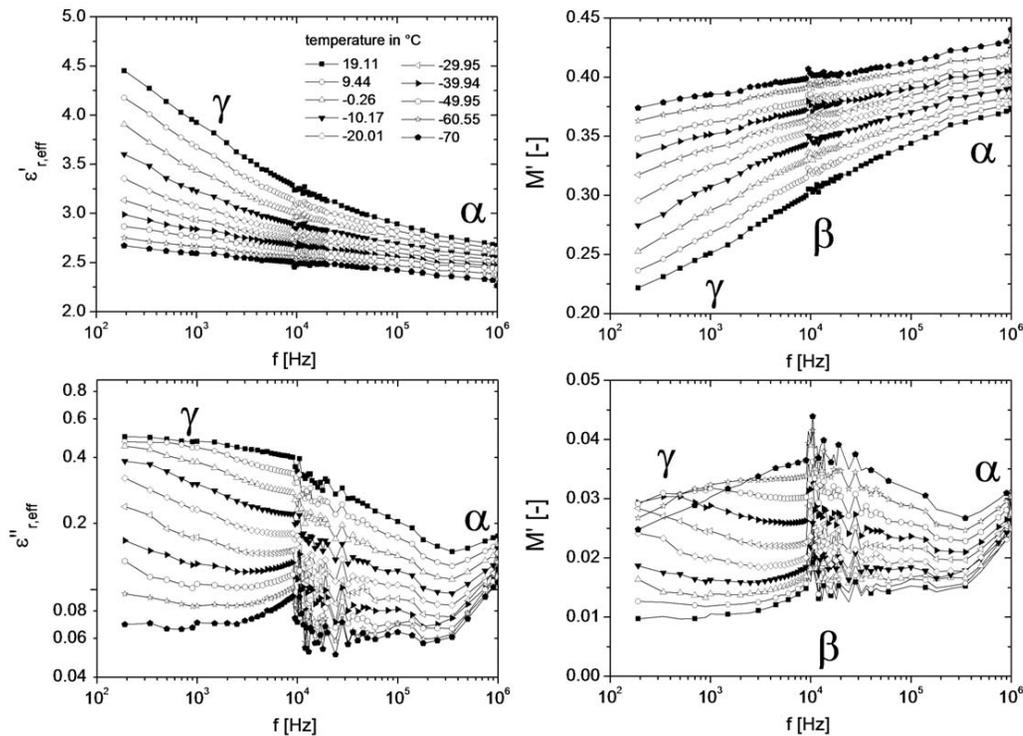


Fig. 4b. Complex effective permittivity $\varepsilon_{r,\text{eff}}^*$ or complex modulus $M^* = 1/\varepsilon_{r,\text{eff}}^*$ of the volcanic ash at a constant water content of 1.96 monolayers.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

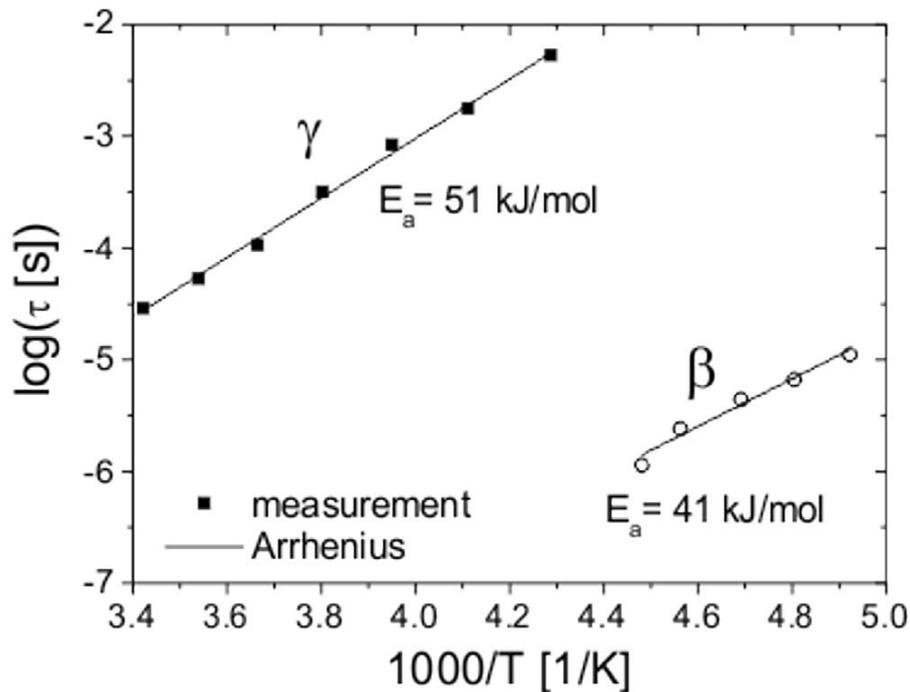


Fig. 5. Arrhenius representation of the relaxation time $\tau = f_{\max}^{-1}$ for the two processes β, γ obtained from the appropriate maximum frequency f_{\max} .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

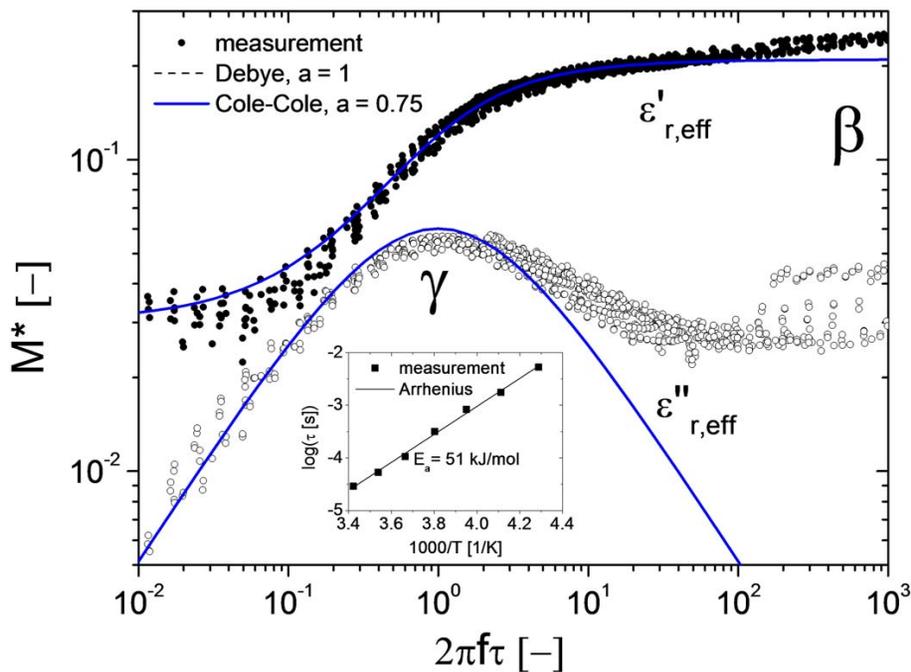


Fig. 6. Master curve of the complex modulus M^* for the γ -process.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

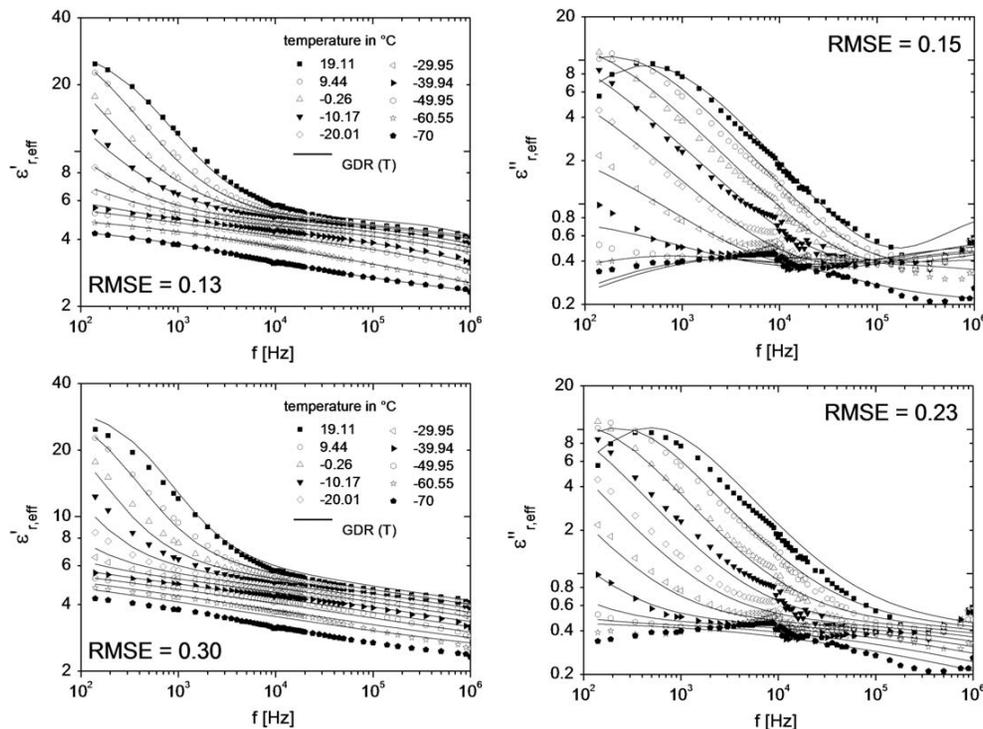


Fig. 7. Complex effective permittivity of the clay sample in case of a constant water content of 1.53 monolayers water measured in the temperature range from -70 °C to 20 °C parameterized with the GDR (top) at each temperature and (bottom) in combination with Eqs. (6) or (12) simultaneously.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

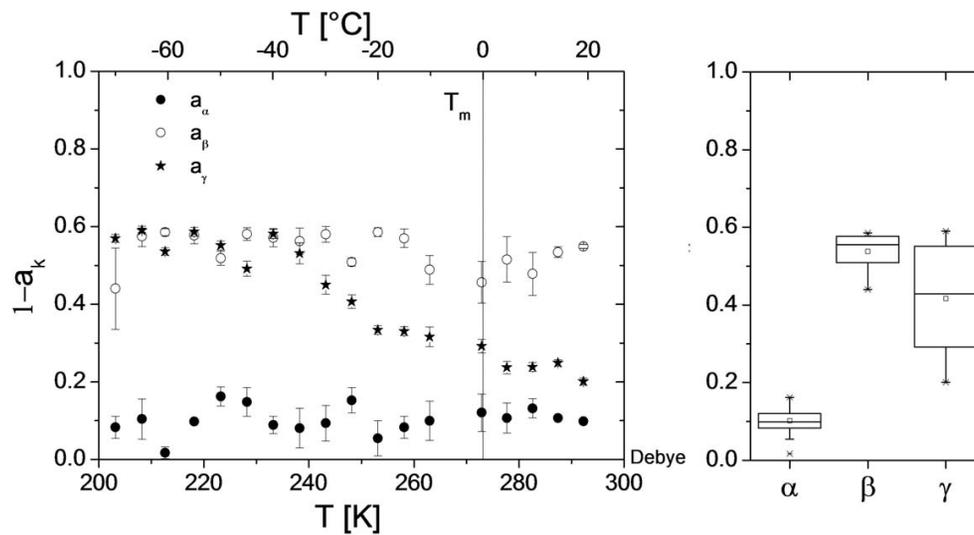


Fig. 8. Dependence of the distribution parameter α_k of the k th process on temperature.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

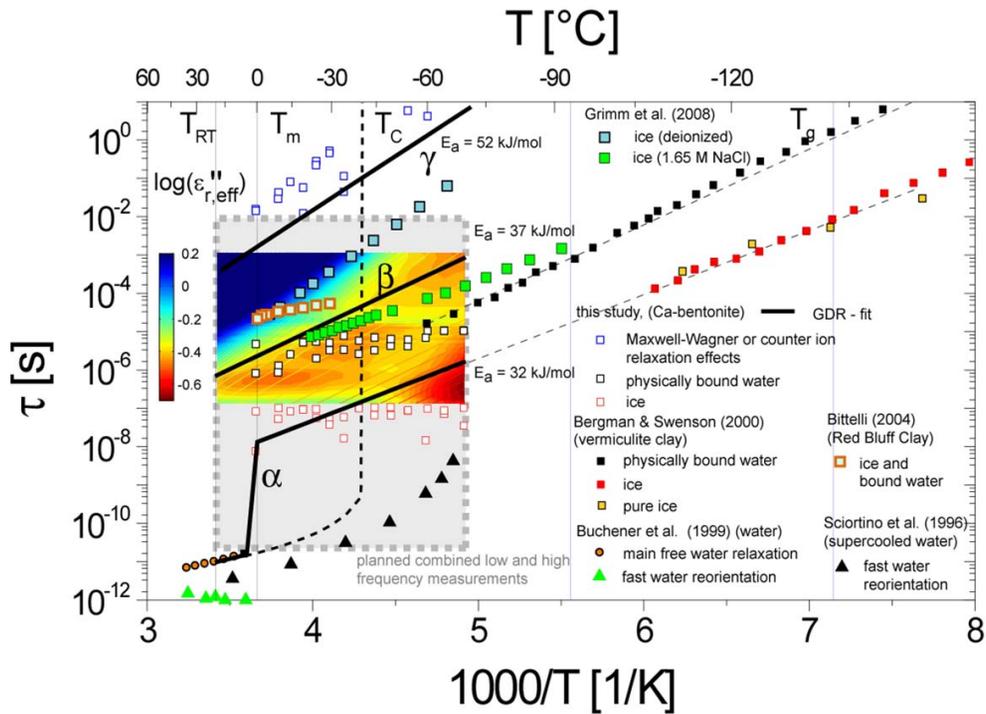


Fig. 9. Relaxation map of the Ca-Bentonite (1.53 water monolayers) in comparison to results from aqueous solution with different electrolyte concentrations, ice, as well as clay soils. The contour-plot represents the measured imaginary part of the relative complex effective permittivity.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

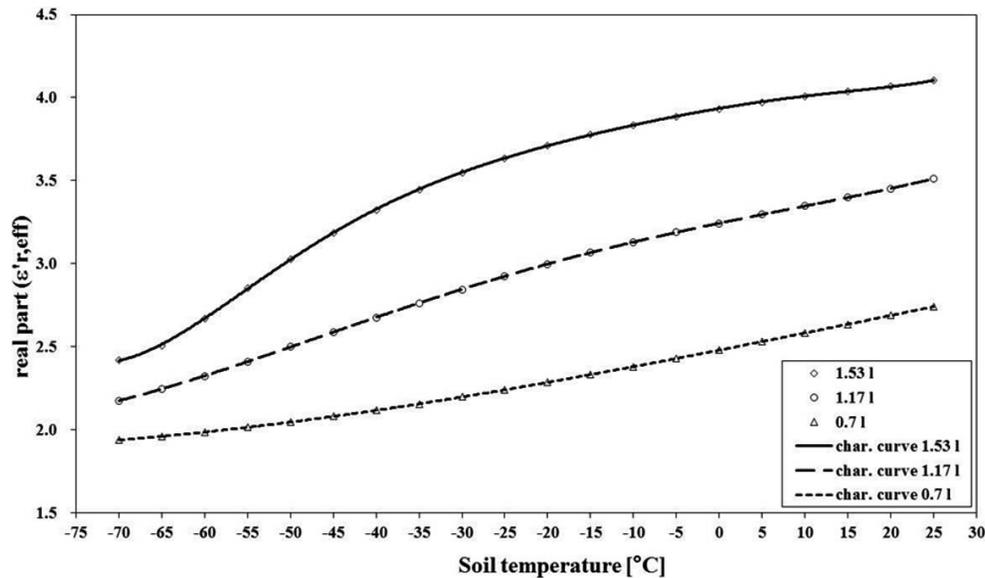


Fig. 10. Dependence of $\epsilon'_{r,\text{eff}}$ for the clay soil at 350 kHz for 0.7, 1.17 and 1.53 monolayers water (l) in a temperature range from -70 to 25°C .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

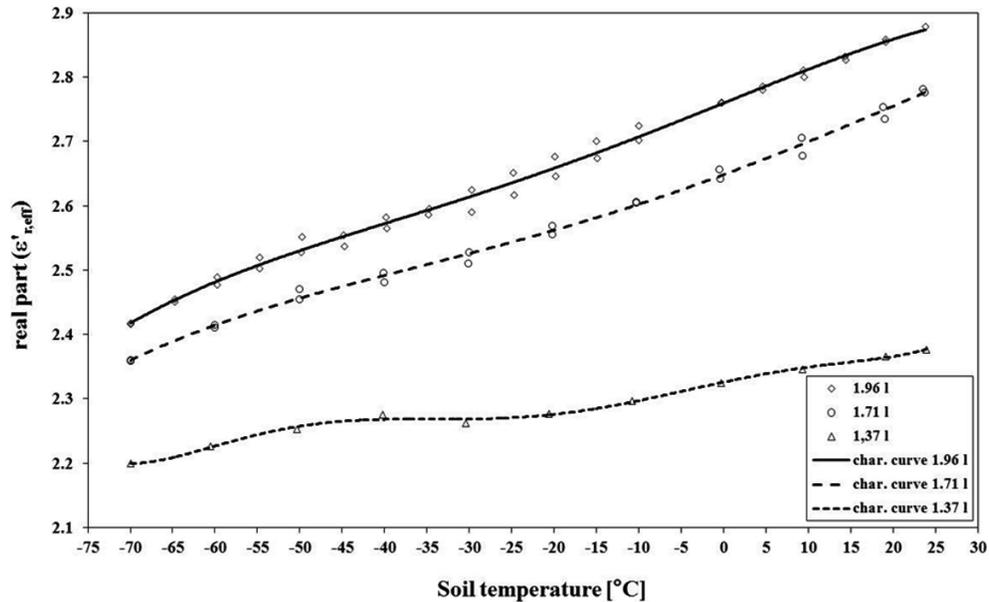


Fig. 11. Temperature dependence of $\epsilon'_{r,\text{eff}}$ for JSC Mars 1 at 350 kHz for 1.37, 1.71, and 1.96 monolayers of water (l) in the range from -70 to 25 °C.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

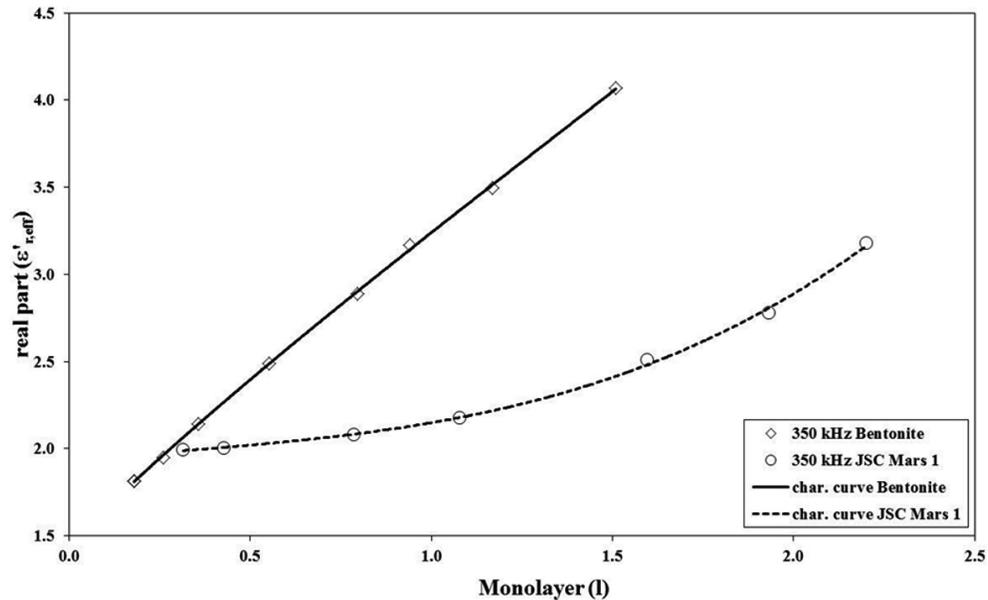


Fig. 12. Characteristic curve of $\epsilon'_{r,\text{eff}}$ in respect to the moisture of the clay soil and JSC Mars 1 at a frequency of 350 kHz and 25 °C.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

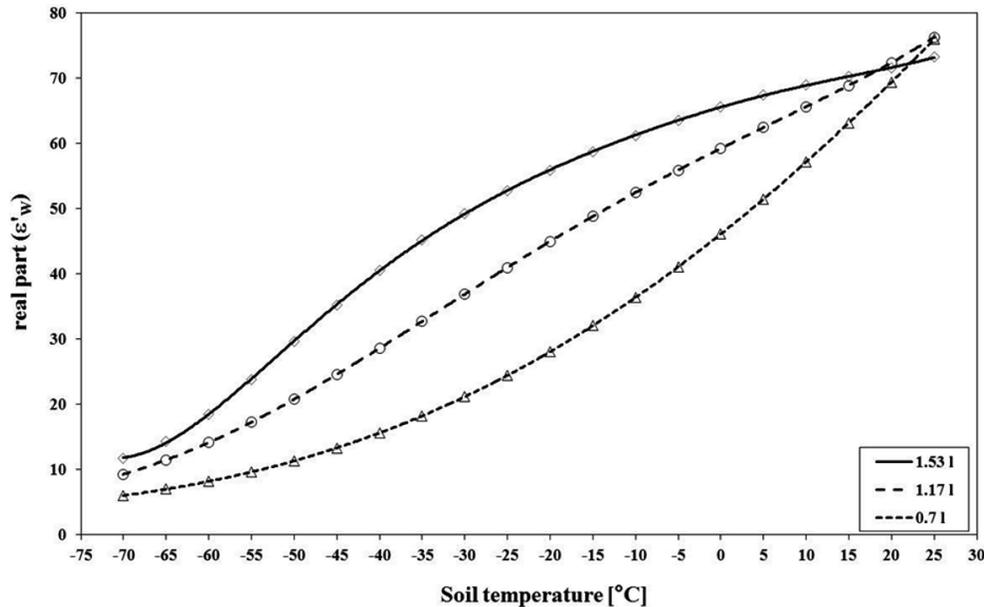


Fig. 13. Calculated real part ϵ'_W of the bound water ϵ_W for 0.7, 1.17 and 1.53 water monolayers for the clay soil in a temperature range from -70 to 25 °C.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

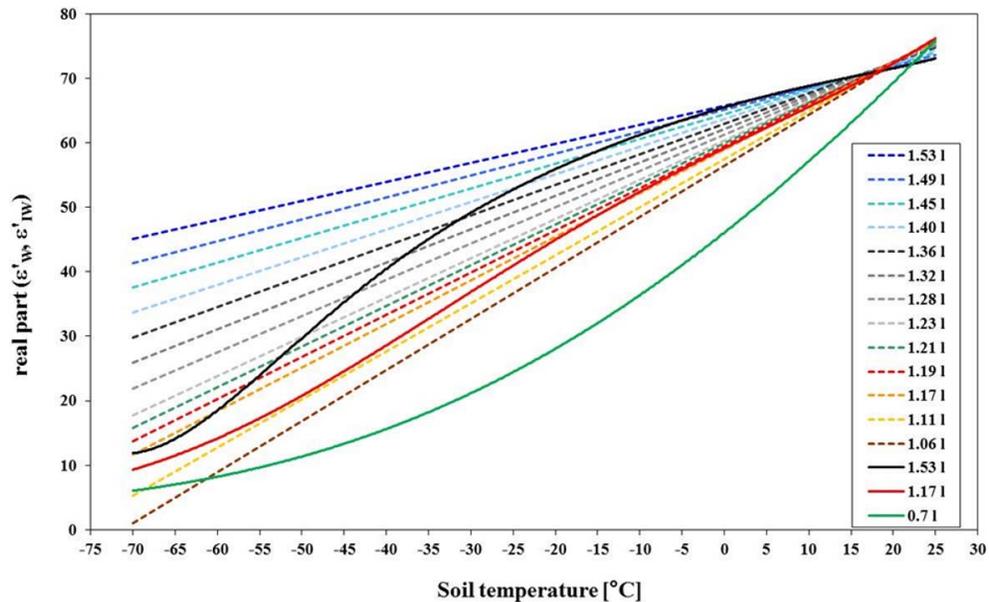


Fig. 14. Figure 13 with deduced linear ε'_{IW} curves representing the permittivity of interfacial water (linear dotted lines).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Supercooled interfacial water in fine grained soils

A. Lorek and N. Wagner

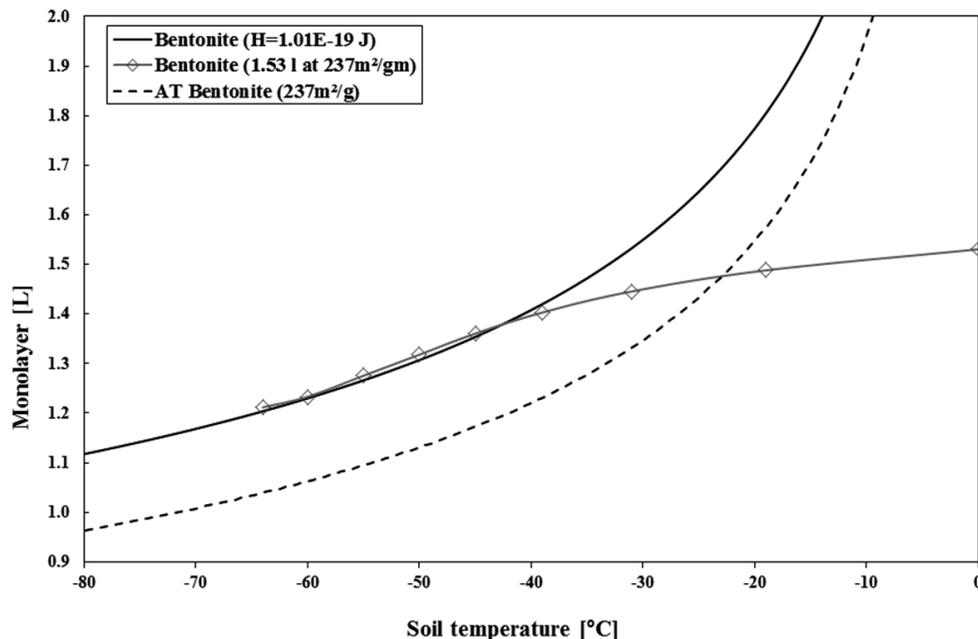


Fig. 15. Interfacial water content of the clay soil based on the sandwich-model (black solid line), the deduced values of the 1.53 L line from Table 5 (gray line) and the Anderson–Tice equation (20) (dotted line).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

