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The Cryosphere Discussions

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Interactive Comment

Interactive comment on "Supercooled interfacial water in fine grained soils probed by dielectric spectroscopy" *by* A. Lorek and N. Wagner

Anonymous Referee #1

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This paper focus on measurements of the dielectric properties of supercooled water adsorbed on fine grained soils, to measure the amount of liquid water and ice. The measurement of dielectric properties of earth materials (soils and rocks) is very important for a large variety of applications. Dielectric properties are used as an indirect methods for measuring earth soil moisture, which is an important variable affecting, for instance, the evolution of the earth's boundary layer, therefore affecting weather patterns. Soil moisture is also a key factor for plant growth, microbial activity, earth's energy budget and so forth. For planetary studies, the possibility of detecting the presence of liquid water on other planets (i.e. Mars) is of great interest since water is the primary media for life, and also for future space explorations, where the presence of water would be very advantageous for future missions.

This paper therefore addresses a very relevant topic. The research is well conducted and I recommend publication after revision. There are still some questions that the authors should address before publication. Comments are listed below.

Comments

1. Page 1443. Line 24. It should read 'calorimetry'.

2. Page 1446. Line 3. Include a full stop after ' between. In combinations.....'

3. Page 1446. Lines 12 to 14. I understand the meaning of this statement, but it is not clear as written, ' number of ...in maximum ' ?.

4. Page 1447-1448, lines 13 to line 25. It is always useful for readers who are going to repeat similar experiments to have units included, for each variable. They are standard units, but they would help the reader to check the equations and write computer codes for repeating the calculations.

5. Page 1449, Lines 7 to 15. This dielectric mixing model is usually referred as the Roth's model (Roth et al., 1990). I think the correct citation should be included.

6. Page 1450. Theory. There have been other studies not cited in this paper regarding the evaluation of adsorbed water, where the relaxation frequency of adsorbed water was measured with Nuclear Magnetic Resonance. See Figure 1 of the paper by Boyarskii et al. (2002). I included the citation below. I found several discrepancies in the data between the present paper and previously published data. For instance, Boyarskii et al. (2002) maintained that the water molecule diameter is 2.8 x 10ˆ-10 meters, while the authors use a value of 3.5 x 10ˆ-10 obtained by the work of Mohlmann (2008). Please clarify the origin of the discrepancy.

7. Page 1452. Could the author detail how they removed low frequency electrode polarization effects in their measurement system ? These effects can have serious negative effects on the dielectric measurement.

8. Page 1453, Line 9. Change und with and.

9. Pages 1455 to 1465. Results. Looking at Figure 1 of the paper by Boyarskii et al. (2002), the relaxation times at 27 degrees Celsius, with respect to the data at 20 degrees Celsius presented in this paper, differ of at least two orders of magnitude. I understand that the soils used were different and there is a temperature difference of 7 degrees. However, in the study by Boyarskii et al. (2002), the relaxation frequency of adsorbed water for 2 monomolecular layers of water is 5 x 10ˆ-11 seconds, corresponding to 3.18 x 10ˆ9 Hz (therefore in the GHz range). In the present study for 1.53 mono layers of water and at a temperature of 19.11 Celsius, (Figure 4a, graph on the top left), there seems to be 3 relaxations: (a) a low frequency between 10ˆ2 to 10ˆ3 Hz, probably a Maxwell- Wagner effect, and (b) and (c) two high frequency relaxation occurring above 10ˆ5 Hz therefore in the upper kilohertz to the megahertz range due to absorption and interfacial process.

Indeed at Page 1457, Lines 25-28, The authors distinguish three relaxation processes: two weak "high frequency" processes and a strong low frequency Maxwell-Wagner effects. Clearly, there must be a strong change in relaxation frequencies over a few monolayers, making the analysis difficult, as elucidated by other authors. According to Boyarskii et al. (2002), from 1 to 2 monolayers of water the relaxation time changes of more than one order of magnitude.

However, in this study the two high relaxation frequencies seems to occurs at much smaller values with respect to the study of Boyarskii et al. (2002) even at temperature above zero, and the lack of data of this study at higher frequencies prevent a clear analysis of these effects. I understand that a low temperatures, the effect of ice relaxation may shift the relaxation processes to lower frequencies since the dominant relaxation frequency for ice is in the kilohertz range, but still the difference above zero are striking. The measurement of Boyarskii et al. (2002) are performed on sandy loam and silt, therefore the differences may be due to the very different energy associated with the adsorption process.

10. Another effect that could explain the relaxation peak observed at low frequency (1 KHz) (Figure 4a, left) is the ion-dipole polarization of aqueous solutions. Often Maxwell-Wagner is provided as an explanation for a different physical effect. This effect is described by Buehler et al.(2011) and it is always almost neglected in the studies of dielectric spectroscopy of earth materials, but it can have a significant effect on low frequency measurements. It depends on the ionic-concentration of the aqueous solution and it depends solely on effect due to ions in the liquid solution. However, for frozen soil where ions are excluded from ice and concentrated into the liquid phase, this effect can play an important role, since freezing increases ion concentration in the surrounding supercooled water. Please provide information on electrical conductivity and ion concentrations of the analyzed samples, to asses the effect of ion-dipole effects on the measured relaxation peaks. If the author cannot track the paper since it is published in a conference proceeding, I would be happy to provide a copy.

11. Overall, I suggest to the authors to discuss the results of Boyarskii et al. (2002) and Buehler et al.(2011), with respect to the present study, since the measured and modeled relaxation times are quite different in these studies, and they could shed light on the effect of ion-dipole effects, adsorption energy and specific surface on dielectric properties.

12. In general, for future studies, I suggest to repeat measurements at higher frequencies and also for coarser materials, since these data seem incomplete to obtain a full understanding of the processes involved. Moreover, the ion-dipole polarization should be taken into account if experimental conditions are such to determine significant effects of ion-concentrations.

Bibliography

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Buehler M., D. Cobos and K. Dunne, 2011. Dielectric constant and Osmotic Potential from Ion-Dipole Polarization Measurements of KCl and NaCl-doped Aqueos solutions. ISEMA Proceedings, June 2011. http://www.truebner-instruments.com/isema2013/home

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Please also note the supplement to this comment:
http://www.the-cryosphere-discuss.net/7/C621/2013/tcd-7-C621-2013-supplement.pdf

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Interactive comment on The Cryosphere Discuss., 7, 1441, 2013.

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