

Dielectric spectroscopy of swellable clays at low moisture levels

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Introduction

Clays are widely used in industrial and environmental applications, such as construction of geotechnical barriers of hazardous waste disposal sites. Their importance especially arises from the intrinsic properties of the swellable clay minerals.

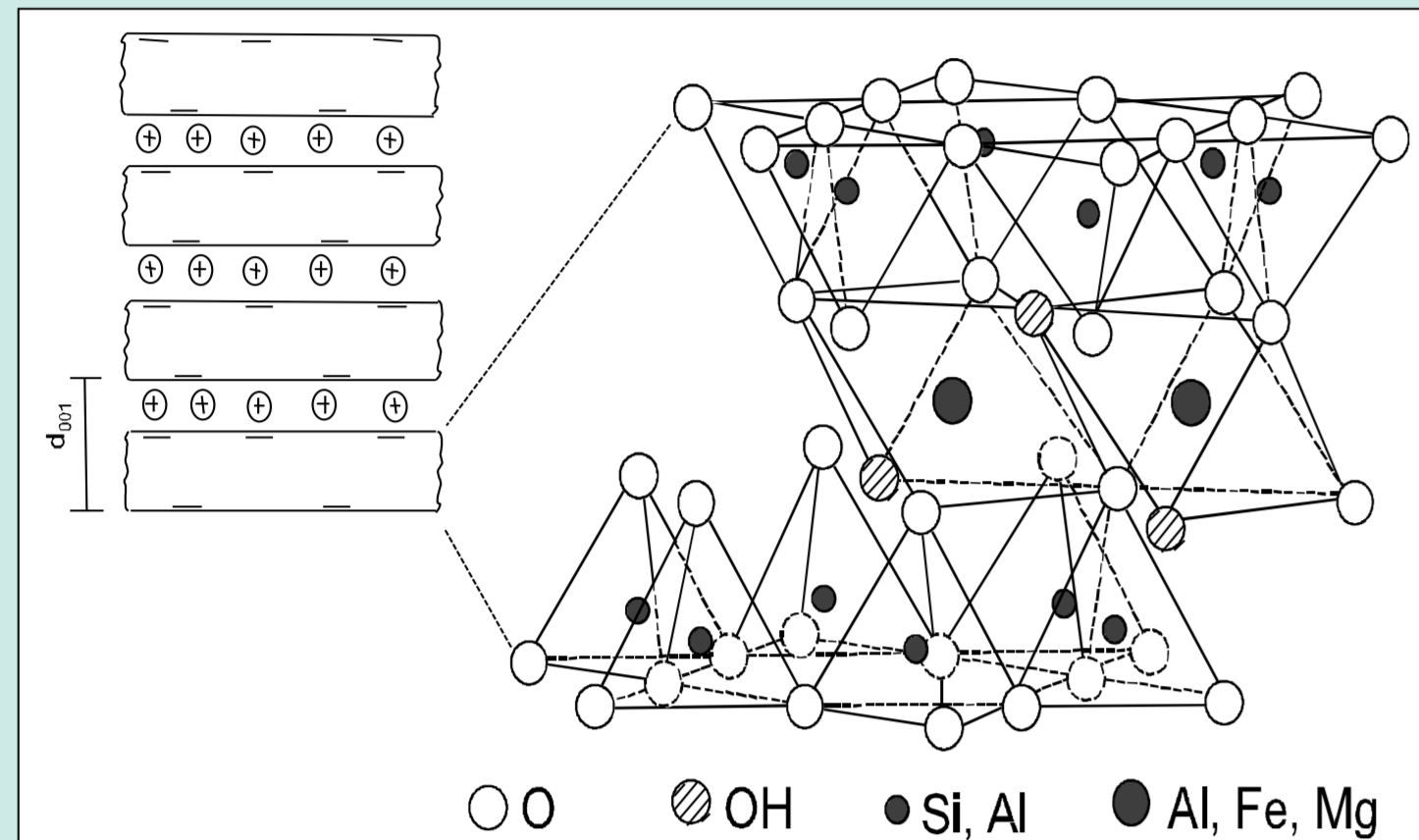


Fig.1: Structure of 2:1 clay mineral, according to Jasmund & Lagaly (1993)

Properties of swellable 2:1 clay minerals

- high specific surface area (A_s), up to 750 m²/g
- high cation exchange capacity (CEC), up to 120 meq/100g
- particles often of colloidal size (< 1 μ m)
- high water uptake capacity, up to 9 g water/g dry clay
- swelling ability connected to variable interlayer spacing that is dependent on relative humidity (r.h.)

Dielectric spectroscopy can be used as a non-destructive and fast approach to evaluate clay-water interactions.

Complex permittivity and conductivity are connected to water content and charge carrier mobility, which allows to evaluate clays in different applications.

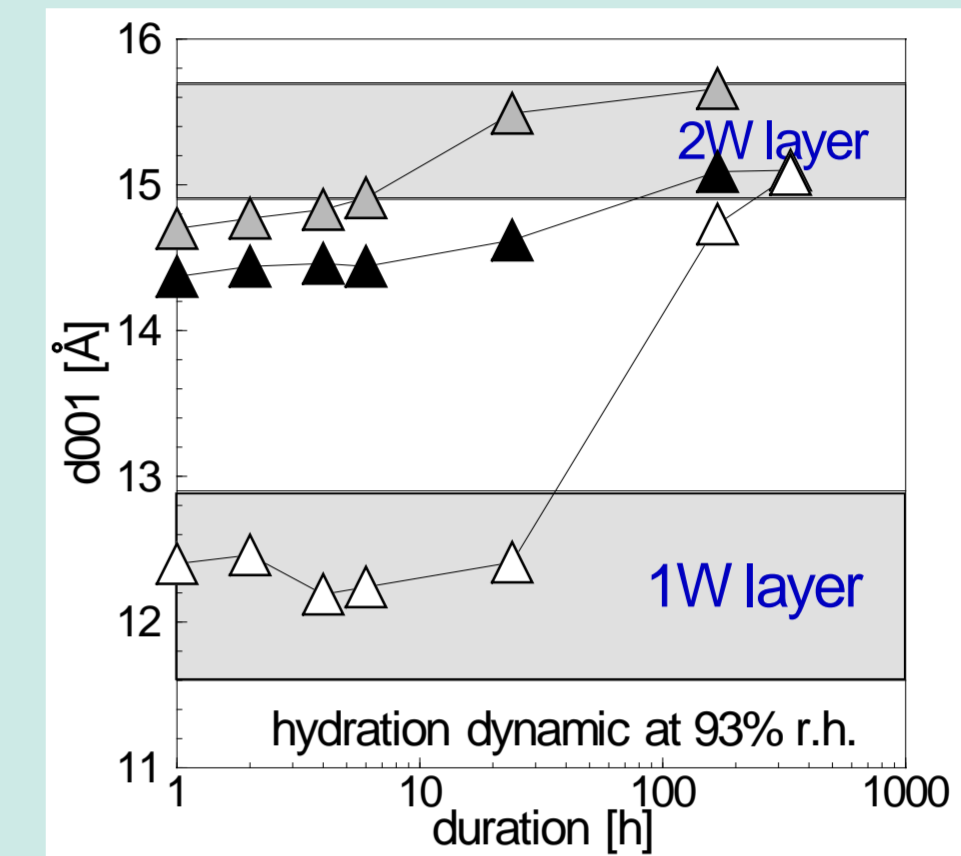


Fig.2: Varying interlayer spacing due to stepwise hydration of interlayer cations of benP (▲), Na-rich benP (△) and Ca-rich benP (▲).

Material & methods

Two bentonites (benCal, benP) provided by Süd-Chemie AG, Germany and containing different amounts of swellable clay minerals of the smectite group, were studied at different low moisture level states by equilibrating them above saturated salt solutions to 11% (LiCl), 43% (K₂CO₃) and 93% r.h. (KNO₃). Gravimetric water contents (W_{gt}), i.e. the weight of the water divided by the dry weight, were determined by dynamic heating with Simultaneous Thermal Analysis (STA 449C Aeolos, Netzsch, Germany) and a heating rate of 10K/min.

Table 1: Material properties; CEC = cation exchange capacity, $A_{s, out}$ = outer specific surface area; $A_{s, total}$ = total specific surface area.

		benCal	benP
smectite content	%	62	98
CEC	meq/100g	63	119
exchangeable cations	Na	9	50
	K	2	1
	Ca	62	40
	Mg	27	9
clay content (fraction <2 μ m)	wt%	47	79
$A_{s, out}$	m ² /g	72	105
$A_{s, total}$	m ² /g	289	417

Table 2: Gravimetric water contents.

	r.h. [%]		
W_{gt} [%]	11	43	93
benCal	10.3	12.7	18.9
benP	15.6	17.0	30.4

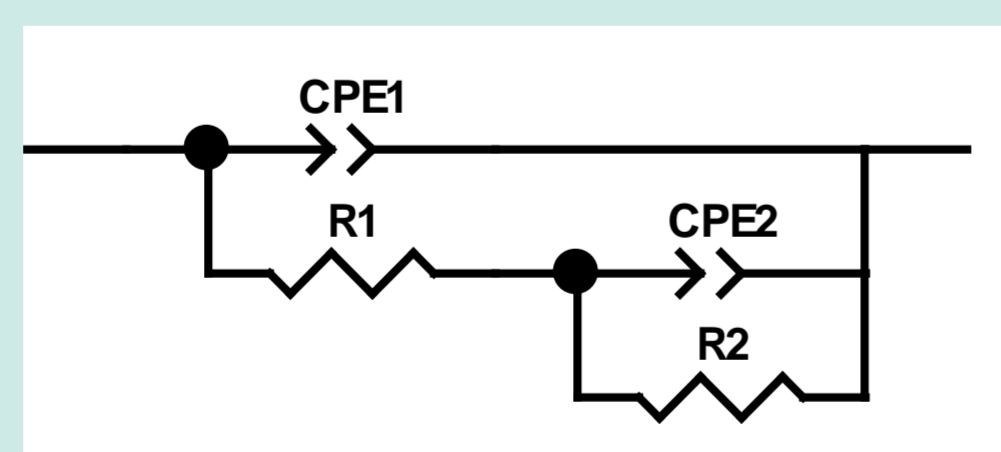


Fig. 3: Equivalent circuit for bentonites at low moisture levels.

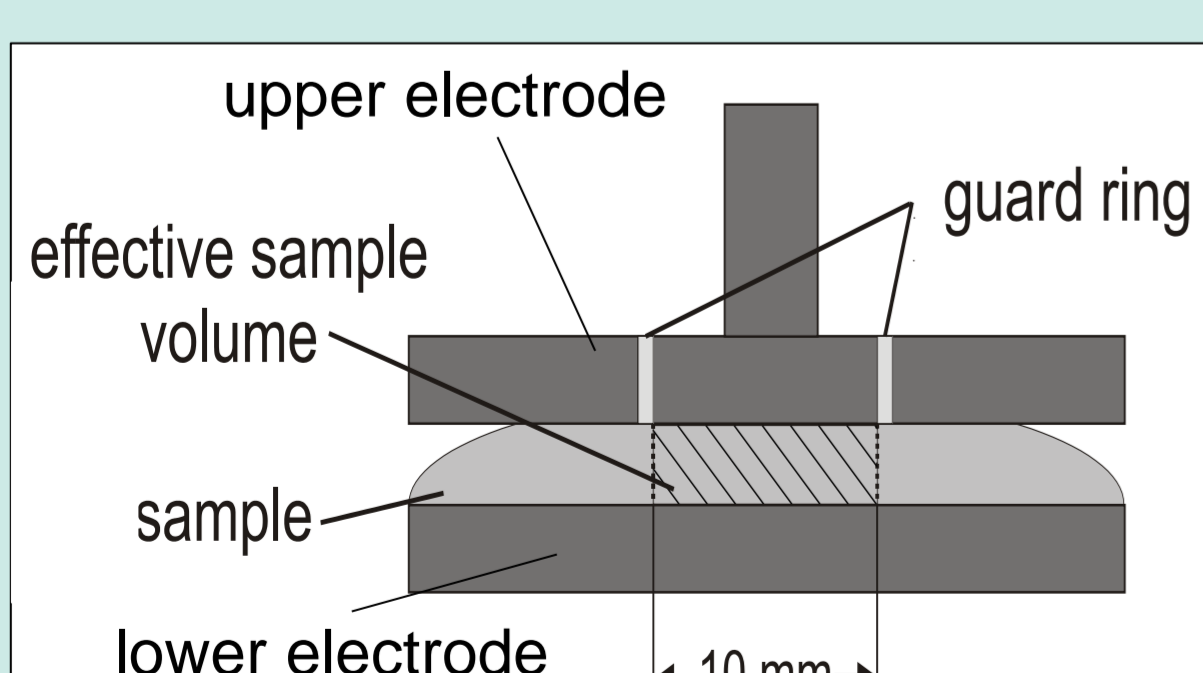


Fig.4: Sample holder and effective sample volume for complex impedance measurement.

Dielectric spectroscopy was performed in a frequency range of 10⁻⁴ to 10⁶ Hz with an Alpha AN Analyzer (Novocontrol) and software WinDETA 5.0. Equivalent circuit modeling was done with ZView (version 3.2c).

Acknowledgements

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Results and discussion

Although the bentonites differ in their mineralogical composition and their material intrinsic properties (Table 1) their dielectric behavior at different adsorbed water states (Table 2) was very similar.

Real permittivity and real conductivity increased with increasing water content. With increasing W_{gt} we observed a significant shift in drop frequency (f_{drop}). A significant dependency from the materials ability to reversibly exchange cations (CEC) could not be distinguished.

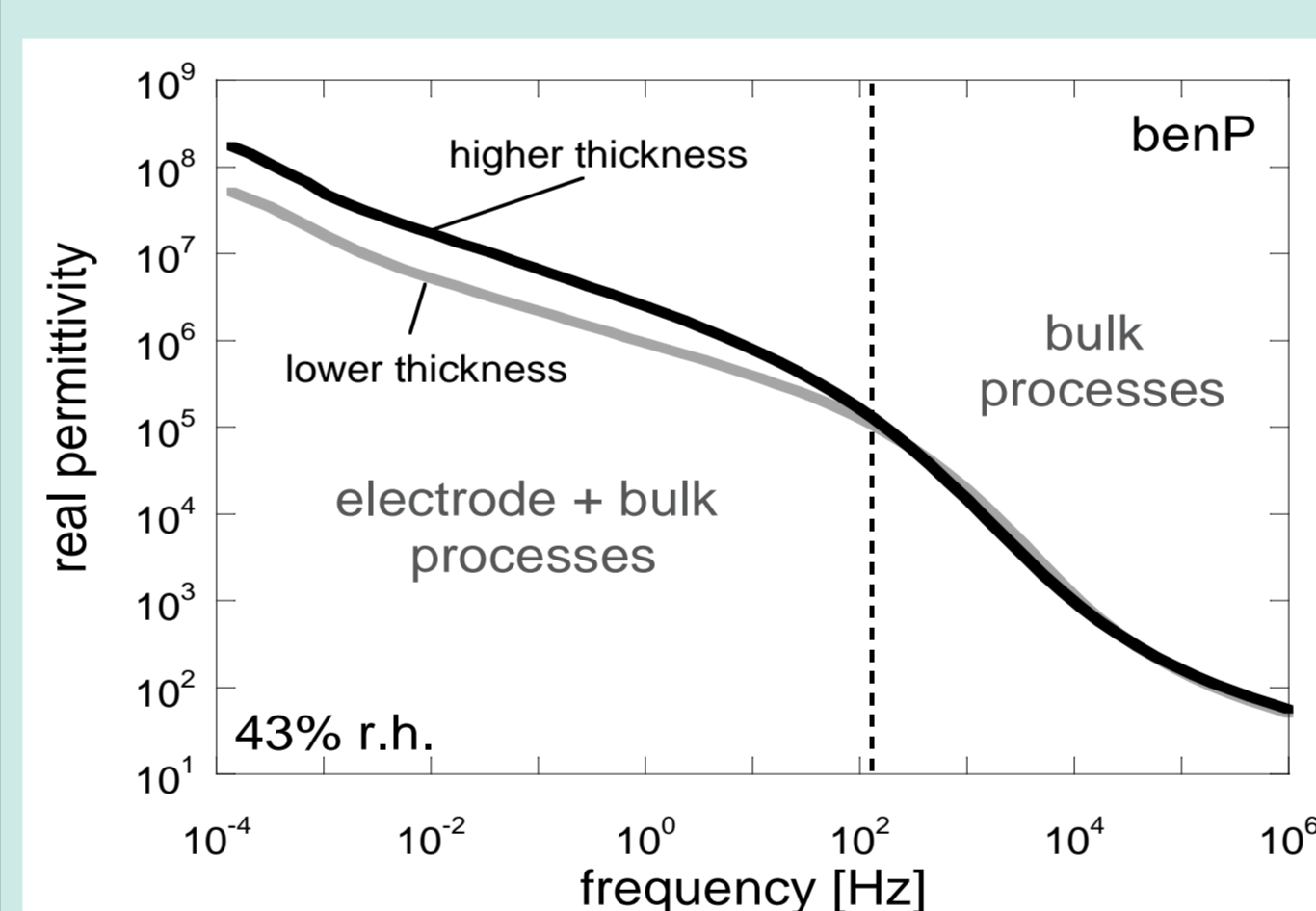


Fig. 7: Real permittivity of benP at 43% r.h. measured at different sample thicknesses (1:1.5) to estimate the limit of bulk and electrode processes.

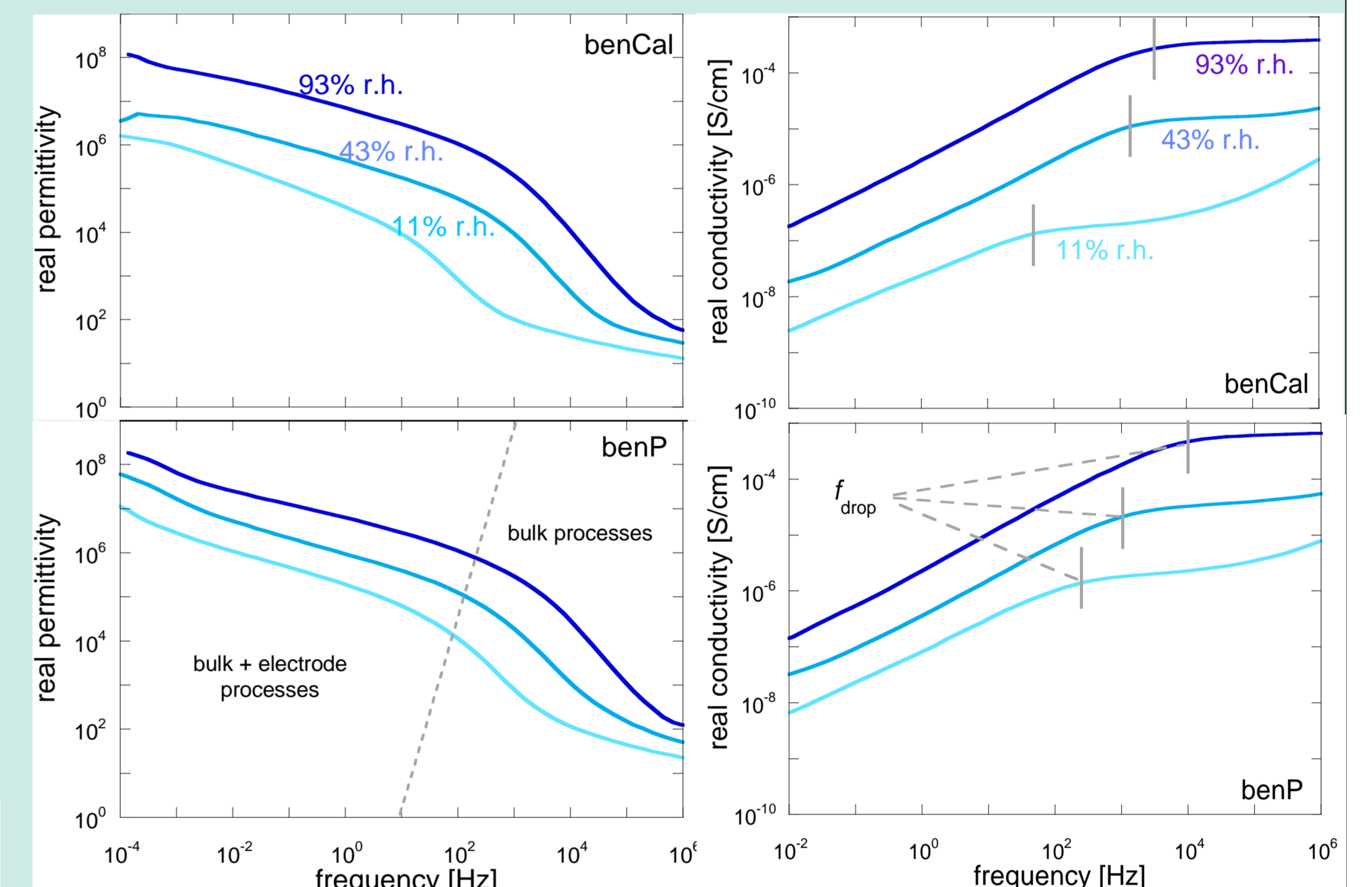


Fig. 5: Real permittivity of bentonites at different r.h..

Fig. 6: Real conductivity of bentonites at different r.h..

Electrode polarization was experimentally proven to occur (Fig. 7). Therefore, the dielectric spectra are dominated by bulk processes at higher frequencies and a mixture of electrode and bulk processes at lower frequencies (Fig. 5 and 6).

Table 3: Equivalent circuit parameters of benP; X² = error estimate.

r.h. [%]	X ²	CPE1-T	CPE1-P	R1	CPE2-T	CPE2-P	R2
11	0.24	8.30E-09	0.64	34678	5.93E-07	0.61	3.27E+07
43	0.23	1.12E-08	0.66	2941	1.93E-06	0.61	1.72E+07
93	0.33	1.66E-10	1.00	176	9.99E-06	0.65	2.80E+06

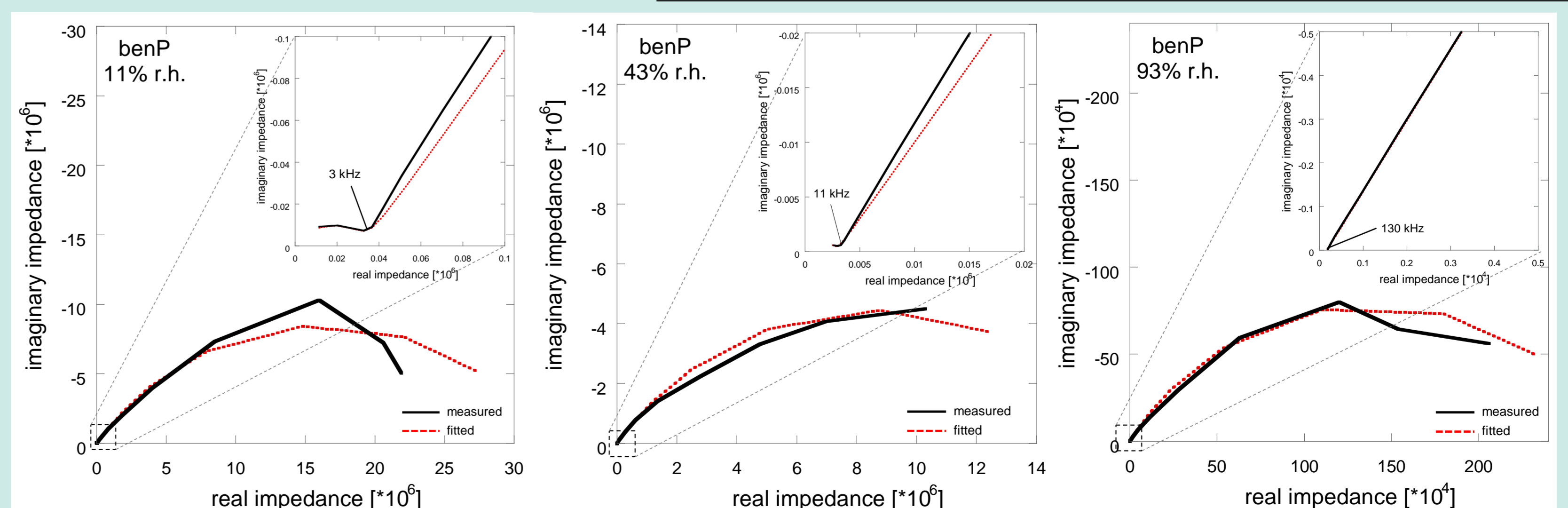


Fig.8: Measured impedance and fitted impedance according to the circuit of Fig. 3 for benP.

The equivalent circuit (Fig.3) gives a preliminary description of the dielectric properties of bentonites (Tab. 3, Fig. 8). The element R1 showed a strong W_{gt} dependency and is together with CPE1 attributed to bulk processes. Regarding CPE2 and R2 we were not able to clearly separate bulk and electrode processes. The bulk relaxation around 10²-10⁴ Hz (Fig. 7), might be due to double layer polarization at the clay-water interfaces. Thus, further modeling is necessary to fully describe the dielectric effects in clays at adsorbed water states.