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The microwave absorption of emulsions containing aqueous micro- and nanodroplets: A means to optimize microwave heating

Christian Holtze^a, R. Sivaramakrishnan^b, Markus Antonietti^{a,*}, J. Tsuwi^c, Friedrich Kremer^c, Klaus D. Kramer^d

^a Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, D-14424 Potsdam, Germany
 ^b Physics Department, Humboldt University at Berlin, Newtonstr. 15, D-12489 Berlin, Germany
 ^c Faculty of Physics and Geoscience, University of Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany
 ^d Physics Department, Free University Berlin, Arnimallee 14, D-14195 Berlin, Germany

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Abstract

The microwave absorption at frequencies between 10 MHz and 4 GHz is measured for aqueous brine droplets dispersed in a dielectric medium ($\varepsilon' = 2.0$). By varying the size of the droplets, ion type and ion concentration, it is found that the microwave absorption goes through a maximum which depends on the type of ions and their concentration. The absorption process is attributed to the polarization of the microwave heating in emulsions is discussed.

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1. Introduction

Heating of finely dispersed water droplets in a secondary medium, e.g., oil or air, with adsorbed radiation is of fundamental importance, either for technology, for modern cuisine with the microwave oven, for radar pictures/radar damping or for climate processes. It is however an experimental finding that such systems usually absorb only weakly, i.e., a water in oil emulsion heats up very badly with microwaves, even in spite of the presence of large numbers of water droplets.

The explanation of this observation is to be found in the "effective medium theory" of Maxwell [1] which says that the structure of a multiphasic system is not resolved when the wavelength of radiation is much larger than the characteristic length of the structure. The microwavelength of a typical oven is 10–15 cm (in Germany, 2.45 GHz resp. 12.24 cm, see [2] and therefore 5–9 orders of magnitude larger than the structure of the systems discussed below. Already Garnett [3–5] devel-

Corresponding author. *E-mail address:* markus.antonietti@mpikg.mpg.de (M. Antonietti). oped an equation to calculate the dielectric permittivity of such a system from the bulk properties of single components. If the complex permittivity ε^* of the two components is $\varepsilon_1^* = \varepsilon_1' - i\varepsilon_1''$ and $\varepsilon_2^* = \varepsilon_2' - i\varepsilon_2''$, with 1 indicating the continuous phase, 2 the disperse phase, and *f* the volume fraction of the disperse phase, we can write:

$$\varepsilon_{\text{effective}}^* = \varepsilon_1^* \frac{2\varepsilon_1^* + \varepsilon_2^* + 2f(\varepsilon_2^* - \varepsilon_1^*)}{2\varepsilon_1^* + \varepsilon_2^* - f(\varepsilon_2^* - \varepsilon_1^*)}.$$
(1)

This equation is assumed to be valid for $f \leq 0.2$ and $\varepsilon_1 < \varepsilon_2$. Both conditions are fulfilled in all experiments listed below.

A second, more elaborated equation for two phase systems is the description by Kamiyoshi [5]. It reads:

$$\varepsilon_{\text{effective}}^* = \frac{2\varepsilon_{\text{I}}^* \varepsilon_{\text{II}}^*}{\varepsilon_{\text{I}}^* + \varepsilon_{\text{II}}^*} \tag{2}$$

with

$$\varepsilon_{\rm I}^* = \varepsilon_{\rm I}^* \left[(1+3f) \left/ \left(\frac{2\varepsilon_{\rm I}^* + \varepsilon_{\rm 2}^*}{\varepsilon_{\rm 2}^* - \varepsilon_{\rm I}^*} - f - 0.525 \left(\frac{3\varepsilon_{\rm 2}^* - 3\varepsilon_{\rm I}^*}{4\varepsilon_{\rm I}^* + 3\varepsilon_{\rm 2}^*} \right) f^{10/3} \right) \right]$$
(3)

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and

$$\varepsilon_{\mathrm{II}}^{*} = \varepsilon_{2}^{*} \bigg[1 + 3(1 - f) \bigg/ \bigg(\frac{2\varepsilon_{2}^{*} + \varepsilon_{1}^{*}}{\varepsilon_{1}^{*} - \varepsilon_{2}^{*}} - (1 - f) - 0.525 \bigg(\frac{3\varepsilon_{1}^{*} - 3\varepsilon_{2}^{*}}{4\varepsilon_{2}^{*} + 3\varepsilon_{1}^{*}} \bigg) (1 - f)^{10/3} \bigg) \bigg].$$
(4)

Both approaches do hold for spherical droplets. Sillars extended the Maxwell–Wagner theory for non-spherical inclusions ("Maxwell–Wagner–Sillars theory"), taking already the interfacial polarization into account [6]. A comparison and comprehensive summary of different effective media models is found in the review article of Hanai [7]). In the present context, it is important to denote that all these equations are not sensitive to the size of the droplets, at least as long as their size is sufficiently small (and still sufficiently large to have bulk-water properties).

It was Wagner [8] who pointed out that such heterophasic systems should possess an additional dielectric relaxation due to an interface polarization. The Maxwell–Wagner polarization is to be found as an additional relaxation mode: the droplets act as permanent dipoles at low frequencies, whereas at high frequencies, the ions cannot follow the orientation of the outer field, and no contribution to the permittivity in this frequency domain is observed. At intermediary frequencies, a dispersion peak is to be found, with the frequency corresponding to ion mobility, but not to the size of the droplets.

A more complicated relaxation and absorption behavior is to be expected when the electric field drives droplet deformation, droplet–droplet interactions and flocculation [9,10]. As the systems discussed below are stable and do not change their colloidal (and dielectric) characteristics throughout the experiments (employing sufficiently weak fields), discussion of those effects is omitted in the present context.

In real world systems such as low fat margarine [11] or crude oil [12] such relaxations play a major role and contribute to the unexpectedly high energy uptake of such systems. The assignment of the dielectric loss mechanism to the molecular structure in such systems is however at least unclear to us and relies on very distinct assumptions for the flocculation process. To support these more practical examinations, it is the purpose of the present contribution to employ recent progress in the synthesis of stable, narrowly distributed water-in-oil emulsions for the generation of model dispersion droplets with controlled size and compositions. Specifically, we want to use the complementary techniques of high shear generated inverse miniemulsions [13,14] and membrane emulsification to cover the relevant size range from 100 nm to 10 µm droplet diameter for a number of salts and salt concentrations. The frequency-dependent permittivity of these nano- and microdroplets is then determined to shed light on the effects underlying the anomalous high uptake of radiowave and microwave radiation in compartmentalized systems.

2. Experimental

2.1. Preparation of emulsions

For the precise characterization of the size dependence, emulsions with well defined diameter and dispersity which do not undergo Ostwald ripening or coalescence are mandatory. For the smaller droplets in the range of 100-1000 nm, the technique of miniemulsification, as described in [13,14], was employed. It is stressed that the added salts, needed to amplify the surface polarization effects, also act as osmotic droplet stabilization agent. The pure salt solutions could be dispersed by ultrasound saturation as described in Ref. [13], and the miniemulsions turned out to be stable over the timescale of months, as checked by dynamic light scattering. As effective inverse surfactants, both KLE 3736 [15] as well as Lubrizol U (from Lubrizol Co.) were selected. KLE 3736 is a non-ionic surfactant based on hydrogenated isoprene as the hydrophobic part and polyethylene oxide as the hydrophilic part. Lubrizol U is made of end-functionalized polyisobutylene and a polyamidoamine moiety. Both surfactants are oil-soluble and show, as oil solutions, only a weak dissipative dielectric behavior by themselves. KLE 3736 was applied for all miniemulsion experiments, whereas Lubrizol U (available on larger scales) was used for membrane emulsification. From reference experiments we however know that the efficiency of both surfactants with respect to emulsion stability and droplet sizes is about the same.

For continuous membrane emulsification, a home-made setup based on a commercial ultrafiltration cell was used.

To obtain droplets with a narrow size distribution, the volume streams through and along the membrane and the corresponding shear forces must be similar in each element of the cell. This was realized by a spiral channel design (Fig. 1), which also gives sufficient mechanical support to the commercial sintered glass or ceramic separation membrane. We operate this cell under controlled flow and cross-flow rates, where the flow is controlled by a volume-controlled, low-pulsation peristaltic pump, while the cross-flow is controlled by the pressure of nitrogen onto the fluid sitting on the membrane. This crossmembrane flow has to be determined in an independent experiment for each applied membrane, where the security specifications of the used ultrafiltration cell restrict the cross-pressure to 10 bar. Usually, a relative flow rate of 0.1 is applied, thus resulting in 9.1 vol% dispersion where droplet-droplet interactions are only weak.

As membranes, we used hydrophobized HITK ceramic membranes (Hermsdorfer Institut für Technische Keramik e.V.) with formal pore diameters of 200, 600, and 1000 nm, and a membrane diameter of 76 mm, but a variety of other membranes can be taken, too. For some asymmetric membranes with very fine top-layer pores, a leak volume loss along the membrane (and out of the sealed volume) is observed, the consideration of which would require an improved construction of the seal-rings. As this was only salt–water, we refrained from those changes, but had to consider the loss for calculating the relative phase volumes.



Fig. 1. (Left side) Photograph of the spiral channel shape for guiding the continuous phase below the emulsification membrane. The continuous phase containing the surfactant is added in the center with a controlled flow speed and is loaded with the droplets on its way out of the cell. The relative volume fraction of disperse phase is controlled by the relative volume flow of the two phases. (Right side) Explosion chart of the whole pressurized cell. The cross-membrane flow is adjusted by the gas pressure on the cell which can be up to 10 bar.

Droplet sizes of three miniemulsions,	produced with different amounts of	f surfactants, as determined by	dynamic light-scattering (DLS)

Name	Surfactant (mg)	Intensity mean (nm)	Volume mean (nm)	Number mean (nm)	Gaussian width (%)
KLE 100	100	256	257	251	8
KLE 200	200	125	93	64	34
KLE 1000	1000	148.5	112.5	72	34.3

Note. The intensity-, volume-, and number-mean of the droplet diameters and the Gaussian width expressed as a standard deviation are given. The amounts of surfactant refer to the mass of KLE 3736 that was used to disperse 2 g of aqueous 1 M NaCl-solution in 20 g of paraffinic Isopar M.

2.2. Dielectric experiments

Table 1

Dielectric measurements were performed at 25 °C using a combination of two measuring systems: an HP Impedance Analyzer HP4291B covering the frequency range 1 MHz to 1.8 GHz and a Rhode & Schwarz network analyzer for the frequency up to 4 GHz. For measurements above 40 MHz the sample capacity was determined at the end of a high precision coaxial cable (3.25-mm-diameter solid rigid probe), while for frequencies down to 1 MHz the sample was placed in a carefully designed sample cell composed of two capacitor plates. The sample thickness was determined by 50-µm glass fibers placed between the plates. For each sample measured, the permittivity and dielectric absorption were taken at each frequency at a constant temperature. To diminish noise and fluctuation, each data set represents sampling over 100 measurements. The bandwidth was 1 kHz. The accuracy in measuring ε'' was better than 10^{-4} . As stirring throughout the measurements was not possible, due to the sensitive probe, certain variations in the volume fraction of the disperse phase due to sedimentation have to be considered. Height-dependent measurements throughout sedimentation of the droplets when measuring directly after stirring partly allow excluding highly biased measurements.

It was possible in all cases to describe the relaxation curves with a slightly broadened Debye relaxation, i.e., the processes can be described by a single relaxation time. A stretching exponent of 0.95 (instead of 1 for a single mode process) was sufficient to catch the experimental broadening. Therefore, only the relaxation times, but not the exact shape of the relaxation curves are discussed below.

3. Results

The properties of the different miniemulsions analyzed in this work as well as their characteristics, as determined by DLS, are summarized in Table 1.

To extend the accessible size range, we also applied membrane emulsification through the 200-, 600-, and 1000-nm membranes. The corresponding flow parameters are summarized in Table 2.

Optical microscopy of the dispersions resulting from the two larger membranes is depicted in Fig. 2.

It is seen that the droplets are well dispersed, stable, and sufficiently homogeneous (note that the smallest droplet size cannot be depicted with light microscopy). The remaining polydispersity is assumed to be coupled to the polydispersity of the membrane pores. The droplet size is about three times the size of the pores and does under our applied condition practically not depend on the flow rates. The factor 3.5 confirms similar observations described in the literature [16]. According to expectations, also the salt concentration does not influence the droplet size. That way, stable emulsions with microdroplets composed of 0.1, 0.25, 1, and 4 M NaCl solutions as well as 0.25 M MgSO₄ and 0.25 M HCl solutions were made.

In simple heating experiments within a microwave oven for prescreening, both the smallest miniemulsions as well as the weakly controlled, crude preemulsions show practically no absorption and heating, whereas for all other systems, the heating rate increases with the droplet size. This is already a very quick indication for the size dependence of the microwave absorption in inverse aqueous emulsions.

 Table 2

 Applied parameter sets for the membrane emulsification

Pore size (nm)	Transmembrane pressure (bar)	Volume stream of the continuous phase (ml/min)	Diameter of droplets (µm) (light microscopy)
200	2.5	3.125	<1
600	2	1.875	2.0
1000	0.9	1.875	3.5



Fig. 2. Light microscopy characterizing the droplet sizes and size distributions of two of the emulsions made by membrane emulsification: (left) 600-nm membrane; (right) 1000-nm membrane. Disperse phase is 1 M NaCl in H_2O in Isopar M (continuous phase), stabilized by Lubrizol U. Scale bars represent 200 μ m, each. The overall volume fraction of water droplets is 9.1 wt%. The non-statistical distribution on the right picture is due to sedimentation and weak interaction, the droplets could be easily redispersed.



Fig. 3. Frequency-dependent complex permittivity of a miniemulsion of 1 M NaCl solution with d = 125 nm droplet size in Isopar at 25 °C.

Determination of the frequency-dependent permittivity of the smallest 125 nm miniemulsion in capacitor geometry resulted in the data shown in Fig. 3.

Indeed, both the real and loss part of the permittivity throughout the spectrum are very low. At the lower frequency side, there are weak indications for the onset of a conductivity contribution, but the spectrum as a whole is still very close to a dielectrically inert medium. This is why nanoscopic water droplets in inverse emulsions cannot be heated by microwaves, although they easily contain 10% of water as a potential absorber: the effective absorption cross-section is too low. This reference experiment also indicates that the effects described below are not due to the employed surfactants. As seen in Table 1, the smallest miniemulsions also contain the largest amounts of surfactant, but show the weakest dielectric absorption. This is why we can strictly exclude surfactant specific dissipation mechanism.

We calculated with the above given equations the effective complex permittivity for such an emulsion system at 1 GHz, where the effects of conductivity and ion polarization are lowest, to compare these data with the effective medium theory. Using independently measured values for Isopar/surfactant solutions (the surfactant does not significantly contribute to the dielectric loss behavior) of $\varepsilon_1^* = 1.96 - 0.0004i$ and for pure 1 M NaCl of $\varepsilon_2^* = 56 - 168i$ (100 MHz), we obtain with Maxwell– Garnett $\varepsilon_{\text{effective}}^* = 2.37 - 0.0048i$ while the Kamiyoshi equation gives $\varepsilon_{\text{effective}}^* = 4.7 - 0.01i$. The measured value for the 125-nm miniemulsion (see Fig. 3) is $\varepsilon_{\text{measured}}^* = 2.51 - 0.0045i$. It is mentioned here that the Kaymoshi formula was derived to take care of higher concentrations of up to f = 0.5: it is apparent from our results that this formula does not fit well with our real system, including impurities and interfaces. Nonetheless, the measured values are sufficiently close to the calculated values to state that surface polarization plays no important role in such systems. Although the interface area of such systems is the highest in the whole series, the droplets are obviously too small to be significantly polarized, and Maxwell-Wagner effects simply do not exist for such small aqueous nanodroplets.

Whereas the miniemulsion with d = 150 nm diameter only showed a weak relaxation peak, it is fully expressed in the system with d = 256 nm, see Fig. 4.

Here, a pronounced relaxation process with a strong loss peak centered at about 200 MHz is found. Note that due to this process, the dielectric loss increases to about 14 which is by a factor 300 higher than the smaller miniemulsions compared at 200 MHz with an otherwise unaltered chemical composition. As such relaxations in previous work were often attributed to droplet flocculation or destabilization of the emulsion by



Fig. 4. Frequency dependence of the complex permittivity of a miniemulsion of 1 M NaCl solution with d = 256 nm in Isopar. A pronounced surface polarization is found which does not depend on time and field treatments and is therefore a property of the spherical droplets themselves.

the electric field, we repeated the measurements after different waiting time and electric loading of the sample. Essentially, all four measurements can be superimposed (with small, unsystematic frequency shifts of the peak position). This proves that this effect is not related to flocculation, and that we indeed characterize the properties of the single, spherical droplets. In addition, we can exclude effects of sedimentation and aggregation for those small particle sizes. Characterization of the miniemulsions with dynamic light scattering after the dielectric treatment also gave no indications for structural alterations throughout the process (data not shown).

We also varied the surfactant in such inverse emulsions to exclude effects of the stabilizer. The surfactant usually taken for stabilization of miniemulsions is a block copolymer made of hydrogenated polybutadiene and polyethyleneglycole, whereas the surfactant more favorable for membrane emulsification is a smaller block structure between polyisobutylene and a hydrophilic amine copolymer [17]. In principle, one might expect an influence of the chemical structure of the hydrophilic block on the surface polarization, as the interaction and immobilization of ions can depend on the specific chemical structure of the surface. The experiments in the overlap region of size however reveal that inverse emulsions stabilized with these two polymers behave rather similar (data not shown, as practical identical to Fig. 4). In case of the applied very high salt concentrations, it is therefore the influence of the free ions which drives the surface polarization.

Further variation of the size towards larger droplets was performed on the base of the membrane emulsified systems. Fig. 5 shows the relaxation behavior of the systems with 2.1 and 3.6 μ m diameter. Essentially, the relaxation behavior is monomodal and is similar to the one of the 0.25 μ m dispersions, except that the amplitude of the Maxwell–Wagner surface polarization is increasing with increasing size, and that the peak shifts from about 200 MHz (0.25 μ m) to 1.7 GHz (2.1 μ m) and 0.9 GHz (3.6 μ m). The position of the peak however de-



Fig. 5. Frequency dependence of the dielectric permittivity of two emulsions with different droplet sizes but the same type and molar concentration of electrolyte (1 M NaCl). The low frequency permittivity increases with increasing droplet diameter, and the position of the maximum of ε'' shifts to lower frequencies.

pends strongly and in a complicated fashion on salt type and concentration, as it will be shown later, and can therefore not straightforwardly to be discussed.

At the same time, the low frequency permittivity increases from 18 over 24 to 28. Although both the interface area and the number of droplet number is getting smaller with increasing size, the surface polarization still increases. All the loss peaks are comparably narrow: as compared to the ideal Debye shape, the extra peak broadening is only 5%, which can already be attributed to the small, but finite droplet size distribution.

Controlled droplets larger than 3.6 μ m were not accessible to us within the described techniques, but dielectric measurements were also performed on crude preemulsions prepared with a high energy stirrer, which leads to polydisperse emulsions with droplets larger than 10 μ m. In this case, the low frequency permittivity is lowered ($\varepsilon \approx 8$, data not shown). Macroscopic emulsions therefore show the classical behavior of an effectively averaged system, again, i.e., the anomalous heating and surface relaxations vanish with decreasing surface area.

For the largest controlled droplets in our series of $3.6 \,\mu m$ size, we also varied the sodium chloride concentration. The resulting data are shown in Fig. 6.

The dielectric loss is strongest and the low frequency permittivity is highest for the lowest salt concentration. This might be expected for a long range fluctuation driven mechanism, where lowest osmolarity allows the highest fluctuations of the salt concentration, due to the lower osmotic compressibility. The position of the dielectric loss peak however shifts in an systematic fashion: it moves from 2.2 GHz at lowest concentration to 800 MHz at 1 M NaCl back to 2 GHz at highest salt concentration. Further experiments are certainly needed to reveal the origin of these reproducible peak shifts.

Another relevant experiment is the variation of the chemical nature of the electrolyte. It is classically expected that the frequency of the loss peak depends on ion mobility, whereas the strength of the Maxwell–Wagner polarization will depend on the polarizability of the ionic fluid.



Fig. 6. Frequency dependence of the dielectric permittivity of emulsions with the same droplet size and electrolyte (NaCl) but different molar concentrations. The low frequency permittivity decreases with increasing ion concentration, and the position of the maximum of ε'' depends on the ion concentration.



Fig. 7. Frequency dependence of the dielectric permittivity of emulsions with the same droplet size but different salts with equal molar concentrations. The position of the maximum of ε'' as well as the low frequency permittivity depends on the type of ion. The measurements were performed with the coaxial probe.

As electrolytes, NaCl, MgSO₄, and HCl were employed. It is repeated that the equivalent conductivity of H⁺ is at least by a factor of 7 higher as the one of all other cations $(\lambda_0^+(H^+) =$ $349.8 \text{ S cm}^2/(\text{mol} \times z)$, as compared to $(\lambda_0^+(\text{Na}^+) = 50.1 \text{ S cm}^2/(\text{mol} \times z)$, see Ref. [18]. It is also important to state that in membrane emulsification, the droplet size does not depend on the added amount and type of salt, at least within the precision of our measurements. This goes well with the observation of an about constant ratio of droplet diameter to pore diameter, i.e., a pure hydrodynamic control of the geometry.

The resulting data are shown in Fig. 7. For the H^+ -system, indeed the dielectric mode due to surface polarization is strongest, but appears at about 0.7 GHz and therefore at the lowest frequency of all species. This observation clearly hints to a coupled behavior of the ion fluctuations, i.e., it is not the mobility of the single proton which counts but the behavior of a strongly coupled, local "ionic plasmon," which indeed can be



Fig. 8. Frequency dependence of the dielectric permittivity of emulsions with the same droplet size to elaborate the possibility of having surface polarization relaxation in pure water emulsions. The relaxation strength is small but measurable.

much stronger in case of the proton, due to its interactions with the water structure. This observation hints to the fact that the position of such loss peaks will turn out difficult, as only little is known about local ion fluctuations at interfaces.

The maximum of the loss peak for $MgSO_4$ is located at 1.6 GHz, while the corresponding one of NaCl solution is at 2.2 GHz. It is also interesting to note that the surface polarizability of the double divalent salt is by an order of magnitude lower, as it can be expected on the base of its strongest ionic interactions.

It is interesting to compare those loss peaks with the ones of pure polar organic solvents and their mixtures [19]. Pure formamide exhibits its molecular relaxation at about 4.5 GHz, whereas butanol as a locally coupled system shows at peak at 250 MHz. The butanol relaxation is in the same frequency range, underlining that all the described relaxation effects are presumably very local and on the size scale of a few dielectrically coupled molecules, e.g., single ions and their coupled hydration shells. Water droplets of a certain size apparently contain permanently oriented salt dipoles which however relax locally.

For practical reasons (e.g., to estimate the dielectric properties of fog and clouds), also the case of ion-poor water is of interest. As polarization was strongest for the lowest examined ion concentrations as well as for the H⁺ ions, it is allowed to expect a surface polarization already for the natural ion concentrations of 2×10^{-7} (pure water) to $10^{-5.5}$ (water in contact with air).

These experiments are not simple within the present experimental design, as such droplets in the absence of an osmotic agent (the added ions) undergo quite rapidly Ostwald ripening. Nevertheless, the data of a set of experiments with 2.1-µm-sized droplets are presented where it was tried to characterize the emulsions directly after the preparation. The resulting data are shown in Fig. 8, but their reproducibility has to be seen in the light of the co-occurring Ostwald-ripening of droplets.

A weak, but observable Maxwell–Wagner relaxation even in these droplets was found, well above the calculated value for ε^*

from the effective medium theory. This is relevant for damping radar and microwave radiation, but however not sufficient to drive microwave heating of reactions. On the other hand, it must be underlined that the salt miniemulsion with 120 nm droplets had still a lower absorption of radiation. The best way to make an emulsion dielectrically inactive is therefore the presence as a sufficiently small nanostructure.

4. Discussion and conclusion

By using the miniemulsion approach for making nanosized droplets and membrane emulsification for manufacturing micrometer droplets, applying block copolymer stabilizers, it was possible to generate a whole set of model water-in-oil emulsions which were used to characterize the Maxwell–Wagner surface polarization at liquid/liquid interfaces in dependence of droplet size, salt type and concentration.

Only for the droplets with 120 nm droplet diameter, we observed a dielectric behavior close $\varepsilon_{\text{effective}}^* = 2.37 - 0.0048i$ to the effective medium theory. Although the surface area is biggest in this case, the droplet size is too small to allow effective charge separation and surface polarization. This observation is important, as it means that 100-nm-sized water droplets cannot contain effectively oriented salt dipoles. Therefore, the best way to construct a dielectrically inert liquid multiphase system is to adopt a structural size of 100 nm and below.

At larger droplet sizes, the strength of the Maxwell–Wagner polarization increases with increasing droplet diameter in the range accessible with the present applied membranes (up to 3.6 μ m). Obviously, the extent of salt dipole orientation in the droplets more than counterbalances the decreasing surface area, at least within the composition range examined here. As the specific surface area of an emulsion increases with D^{-1} , this is somewhat unexpected, but unequivocally proven by the experiments.

The fact that dielectric absorption decreases again when the droplet size is further increased was tested with crude emulsions made by stirring. These emulsions are ill-defined with respect to dispersion state, but constituted from droplets certainly larger than 10 μ m. Here, only weak microwave absorption was found. Future experiments using for instance microfluidic devices for controlled generation of larger droplets [20,21] will have to be performed to clarify the precise maximum of microwave absorption in dependence of composition and type of ion.

It was already mentioned that Skodvin et al. made similar observations with crude oil and model alphaltene emulsions using 3–5 wt%. NaCl in water (0.7 M) as a disperse phase [22–24]. The dielectric absorption was on a similar level, however at much higher contents of water droplets. In these publications, the data were explained on the base of droplet flocculation models. As our emulsions turned out to be stable throughout our (low energy) measurements, we conclude that such intermolecular effects are not needed to explain the anomalous high microwave absorption rates: simple Maxwell–Wagner polarization in each droplet is sufficient to explain the observed energy

dissipation, while interdroplet effects can of course not be excluded.

An optimization of a potential heating behavior with respect to droplet size, salt and salt concentration revealed that lower concentration of monovalent salts, preferentially H^+ , in ca. 4-µm-sized droplets are ideal to boost surface polarization. From a practical point of view, the addition of such droplets in otherwise unpolarizable media enables the control of microwave and radar absorption rates, e.g., to allow homogeneous heating of industrial food by microwaves or to block radar waves in military operations.

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References

- J.C. Maxwell, Electricity and Magnetics, vol. 1, Clarendon, Oxford, 1892, p. 452.
- [2] M. Nüchter, B. Ondruschka, W. Bonrath, A. Gum, Green Chem. 6 (2004) 128.
- [3] J.C. Garnett, Philos. Trans. R. Soc. London 203 (1904) 385.
- [4] J.L. Greffe, C. Grosse, in: A. Priou (Ed.), Dielectric Properties of Heterogeneous Materials, in: PIER Series, vol. 6, Elsevier, New York, 1992, Chapter 2.
- [5] F. Kremer, A. Schönhals (Eds.), Broadband Dielectic Spectroscopy, Springer-Verlag, Berlin/Heidelberg, 2003.
- [6] R.W. Sillars, J. Inst. Elect. Engrs. 80 (1937) 378.
- [7] T. Hanai, in: P. Sherman (Ed.), Emulsion Science, Academic Press, London, 1968, Chapter 5.
- [8] K.W. Wagner, Arch. Elektrotech. 2 (1914) 371.
- [9] J. Sjöblom, H. Fordedal, T.J. Skodvin, Dispers. Sci. Technol. 20 (1999) 921.
- [10] S.S. Dukhin, V.N. Shilov, Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes, Wiley, New York, 1974.
- [11] T. Skodvin, J. Sjöblom, J.O. Saeten, T. Wärnheim, B. Gestblom, Colloids Surf. A 83 (1994) 75.
- [12] T. Skodvin, J. Sjöblom, J.O. Saeten, O. Urdal, B. Gestblom, J. Colloid Interface Sci. 166 (1994) 43.
- [13] K. Landfester, M. Willert, M. Antonietti, Macromolecules 33 (2000) 2370.
- [14] M. Antonietti, K. Landfester, Prog. Polym. Sci. 27 (2002) 689.
- [15] A. Thomas, H. Schlaad, B. Smarsly, M. Antonietti, Langmuir 19 (2003) 4455.
- [16] U. Lambrich, G. Vladisavljevic, Chem. Ing. Tech. 76 (2004) 376.
- [17] A. Tomlinson, T.N. Danks, D.M. Heyes, S.E. Taylor, D.J. Moreton, Langmuir 13 (1997) 5881.
- [18] Manual of Electrochemical Analysis. Part 3. Electric Conductivity, Sartorius AG, Göttingen, 2004.
- [19] J. Lou, T.A. Hatton, P.E. Laibinis, J. Phys. Chem. A 101 (1997) 5262.
- [20] S.Q. Xu, Z.H. Nie, M. Seo, P. Lewis, E. Kumacheva, H.A. Stone, P. Garstecki, D.B. Weibel, I. Gitlin, G.M. Whitesides, Angew. Chem. Int. Ed. 44 (2005) 724.
- [21] Z.H. Nie, S.Q. Xu, M. Seo, P.C. Lewis, E. Kumacheva, J. Am. Chem. Soc. 127 (2005) 8058.
- [22] T. Skodvin, J. Sjöblom, J. Colloid Polym. Sci. 274 (1996) 754.
- [23] H. Fordedal, J. Sjöblom, J. Colloid Interface Sci. 181 (1996) 589.
- [24] T. Skodvin, J. Sjoblom, J. Colloid Interface Sci. 182 (1996) 190.