

Review

Dielectric spectroscopy in solution chemistry - advantages and pitfalls

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ABSTRACT

After a brief introduction of background and methods of Dielectric Relaxation Spectroscopy (DRS), an overview of its applications in solution chemistry and soft-matter studies is given. Mainly based on work of the author's laboratory, examples range from pure liquids via solvation/hydration studies to ion-binding and micellar systems.

1. Introduction

With theoretical foundations laid by Peter Debye in his famous book from 1929 [1] Dielectric Relaxations Spectroscopy (DRS) or simply Dielectric Spectroscopy has developed into an important tool for material science [2–8] and biophysics [9]. However, despite early applications in the molecular spectroscopy of solutions, see Ref. [10] and literature cited therein, DRS has remained a niche technique in solution chemistry. Particularly, when the focus is on electrolytes around ambient temperature. Main reasons for that are: (1) technological difficulties to cover the relevant frequency range of ~50 MHz to (ideally) several Tera-Hertz [11,12]; (2) lacking sensitivity (depends on the effective dipole moment but generally concentrations $c \gtrsim 0.05$ mol/L are required to detect ion pairs); and (3) lacking ability to discriminate, as relaxation processes, such as those of contact ion pairs (CIPs) and “slow” water [13], often strongly overlap. Whilst some of these restraints still remain, recent developments in DRS make its application easier now and, in conjunction with information from other methods, allow tackling otherwise inaccessible problems in the physical chemistry of solutions. Based mainly on work done by us in Regensburg over the last decades, these developments should be sketched in this contribution to the EUCMOS2025 Special Issue of the Journal of Molecular Spectroscopy. The reader may excuse the bias of the list of references, which obviously is far from complete.

2. Background

DRS detects the response of a sample to a time-dependent electric field, $\vec{E}(t)$ [4,14]. This polarization, $\vec{P}(t)$, or –scaled by sample volume– the corresponding macroscopic dipole moment, $\vec{M}(t) = \vec{P}(t)/V$, arises from various intra- and intermolecular processes, such as molecular

polarizability, reorientation of permanent molecular dipoles, the formation/decay of dipolar entities, free and/or blocked charge transport etc. Formally, $\vec{M}(t)$ can be written as the product of its time- and space-averaged equilibrium value, $\langle \vec{M}_{\text{eq}} \rangle$, and the associated correlation function $F_p(t) = \langle \vec{M}(t) \cdot \vec{M}(0) \rangle / \langle \vec{M}(0) \cdot \vec{M}(0) \rangle$ describing its time evolution [14]. Since $\vec{M}(t)$ is the vector-sum of the individual moments, $\vec{\mu}_i$, of all dipolar entities, i , present at time t , $F_p(t)$ contains cross-terms, $\vec{\mu}_i(t) \cdot \vec{\mu}_j(0)$. As a consequence, DRS probes the collective dynamics of the sample under study, in contrast to most other spectroscopic techniques, such IR or NMR spectroscopy. Those are generally sensitive to the dynamics of individual molecules. This may pose problems in the interpretation of dielectric spectra but on the other hand also carries additional information [15–18].

Commonly, the response of the sample is not discussed in terms of the above time-domain representation but as a function of the frequency, ν , of an applied harmonic field (of angular frequency $\omega = 2\pi\nu$), as this is the basis of most measurement techniques. Here, the material-specific quantity coupling $\vec{E}(\nu)$ and $\vec{P}(\nu)$ is the frequency-dependent total permittivity, $\hat{\eta}(\nu) = \eta'(\nu) - i\eta''(\nu)$. Frequency-domain and time-domain representation are directly linked via Fourier-Laplace transformation and thus fully equivalent [14].

The total permittivity, $\hat{\eta}(\nu)$, summarizes the contributions of all processes in the sample associated with fluctuations of the macroscopic dipole moment, $\vec{M}(t)$. Most of them, such as the reorientation of molecular dipole moments or blocked charge transport, explicitly depend on time/frequency, whereas free charge transport, characterized by dc-conductivity, κ , does not and thus only contributes to η'' but not η' . In many cases the former contributions are in the focus of DRS, so that it is convenient to split $\hat{\eta}(\nu)$ as

$$\hat{\eta}(\nu) = \epsilon'(\nu) - i[\epsilon''(\nu) + \kappa/(2\pi\nu\epsilon_0)] \quad (1)$$

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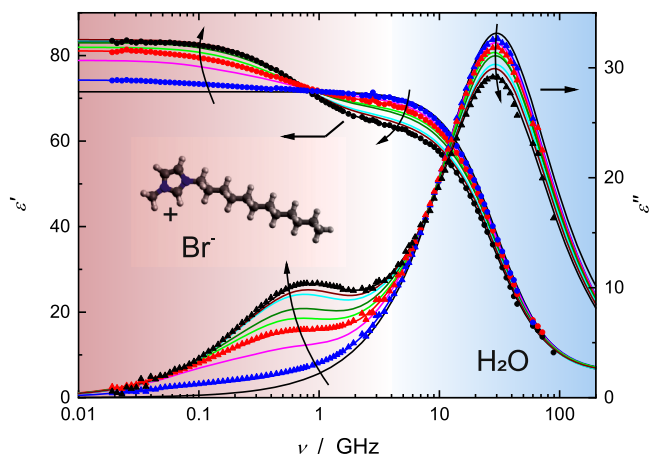


Fig. 1. Spectra of relative permittivity, $\epsilon'(\nu)$, and dielectric loss, $\epsilon''(\nu)$, of aqueous solutions of 1-dodecyl-3-methylimidazolium bromide (coloured symbols) and their fits (lines) as a function of solute concentration, c , at 25°C, with c increasing in arrow direction from 0 to 242.1 mmol/L. Coloured areas indicate solute (purple) and solvent (blue) contributions (see Ref. [19] for details).

where $\epsilon'(\nu)$ and $\epsilon''(\nu)$ are respectively the frequency-dependent relative permittivity and dielectric loss of the sample; $\kappa/(2\pi\nu\epsilon_0)$ is the Ohmic loss due to dc-conductivity and ϵ_0 the permittivity of free space (the electrical field constant). It is $\hat{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$ what we mean with *dielectric spectrum* in the following.

Fig. 1 shows a series of typical $\epsilon'(\nu)$ and $\epsilon''(\nu)$ spectra. In the covered frequency range the relative permittivity, $\epsilon'(\nu)$, drops from the static (relative) permittivity, $\epsilon = \lim_{\nu \rightarrow 0} \epsilon'(\nu)$, to the high-frequency limit, ϵ_∞ , which is nominally only determined by intramolecular polarizability. This dispersion indicates that with increasing ν less and less contributions to $\vec{M}(t)$ are able to follow the external field. Simultaneously, the sample absorbs energy, giving rise to dielectric-loss values $\epsilon''(\nu) > 0$.

3. Methods

DRS is arguably the technique offering the largest range of accessible timescales, ranging from tens of femtoseconds to hours or even longer. Obviously, this cannot be spanned by a single instrument [4]. However, often a more limited time window is sufficient to cover the processes of interest. The relevant timescale of the systems in the focus of this contribution, namely low-to-moderate molar-mass solutes dissolved in polar molecular solvents, is in the order of pico- to nanoseconds, so that MHz to GHz, better even THz frequencies should be covered. Since values of $\nu \gtrsim 50$ GHz are still difficult to access, at present only a few specialized laboratories routinely probe the associated short-time dynamics. For technical details regarding instrumentation the reader is referred to the review of Kaatzte [20].

After correcting $\hat{\eta}(\nu)$ for eventual Ohmic loss, $\kappa/(2\pi\nu\epsilon_0)$, the first step in the evaluation $\epsilon'(\nu)$ and $\epsilon''(\nu)$ is their simultaneously fit by relaxation models intended to describe the shape of the spectrum. For solution spectra sums

$$\hat{\epsilon}(\nu) = \sum_{i=1}^n \frac{S_i}{(1 + (i2\pi\nu\tau_i)^{1-\alpha_i})^{\beta_i}} + \epsilon_\infty \quad (2)$$

of n individual relaxation processes, i , generally yield the best fit. Each mode, i , is determined by its amplitude (relaxation strength), S_i , its relaxation time, $\tau_i = 1/(2\pi\nu_i^{\text{pk}})$, defined by the frequency, ν_i^{pk} , of the corresponding loss peak, and by eventual shape parameters, $0 \leq \alpha_i < 1$ and $0 < \beta_i \leq 1$. The simplest (Lorentzian) band shape is given by the Debye (D) equation with $\alpha_i = 0$ and $\beta_i = 1$. Typical fits are shown as solid lines in **Figs. 1, 2 a & b**, and **3**, with the latter two indicating also the individual contributions to $\epsilon''(\nu)$.

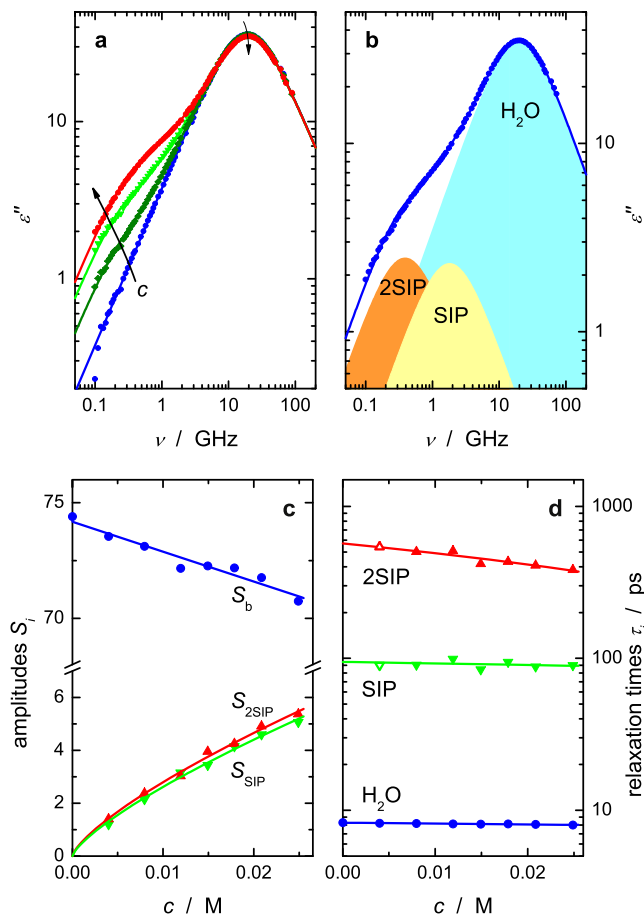


Fig. 2. (a) Dielectric loss spectra, $\epsilon''(\nu)$, of aqueous $\text{Eu}_2(\text{SO}_4)_3$ solutions (symbols) and their fits with the D+D+D model in the concentration range $0 \leq c / \text{mol/L} \leq 0.0249$. (b) Dielectric loss of 0.0209 mol/L $\text{Eu}_2(\text{SO}_4)_3(\text{aq})$ with shaded areas indicating the resolved contributions of solvent-separated ion pairs (2SIPs), solvent-shared ion pairs (SIPs), and bulk-like water. Panel (c) shows the associated relaxation amplitudes, $S_{2\text{SIP}}$, S_{SIP} , S_b ; panel (d) the relaxation times, $\tau_{2\text{SIP}}$, τ_{SIP} , τ_b , as a function of c (see Ref. [21] for details).

At this point a warning is appropriate. By assuming a large enough number, n , of modes and playing with their shape parameters, α_i and β_i , an apparently perfect fit can be achieved for any spectrum. Particularly, when only $\epsilon'(\nu)$ or $\epsilon''(\nu)$ is adjusted. The simultaneous fit of relative permittivity and associated dielectric loss spectrum reduces ambiguity. Nevertheless, so far this is just a formal description of $\hat{\epsilon}(\nu)$ based on numerical criteria, with no guarantee that this “optimum” relaxation model has any physical meaning. Additional arguments, based on information from other techniques, such as scattering experiments, molecular spectroscopy, or thermodynamic measurements, are required for assigning the resolved modes to physical processes [21]. The direct comparison of experimental data with dielectric spectra obtained from molecular-dynamics simulations is gaining increasing importance here [16,22–24].

For solutions of low- to moderate-molar-mass solutes in polar solvents the detected relaxation processes, i , are generally arising from the reorientation of permanent molecular dipole moments, μ_i . In this case amplitudes, S_i , can often be evaluated with the equation

$$S_i = \frac{\epsilon}{\epsilon + A_i(1 - \epsilon)} \times \frac{N_A}{3k_B T \epsilon_0} \times c_i \times \mu_{\text{eff},i}^2 \quad (3)$$

to obtain the concentration, c_i , or alternatively, the effective dipole moment,

$$\mu_{\text{eff},i} = g_i^{1/2} \times \mu_i / (1 - f_i \alpha_i) \quad (4)$$

of the causing species [25,26]. In Eqs. (3) & (4) A_i is the shape-dependent cavity factor ($A_i = 1/3$ for spheres), f_i the reaction-field factor, and α_i the polarizability of the dipole; N_A , k_B and T have their usual meaning [26]. The empirical factor g_i accounts for possible orientational correlations of the i -dipoles. For low to moderate solute concentrations $g_i \approx 1$ can be reasonably assumed, so that $\mu_{\text{eff},i}$ can be obtained from geometrical models or —preferably— quantum-chemical calculations [27,28]. Eqs. (3) & (4) are not only valid for dipoles reorienting via rotational diffusion (small-angle random jumps of the dipole vector) but also for systems where dynamics is governed by hydrogen-bonding, such as water or alcohols. It also includes short-lived species, such as ion pairs, provided their lifetime is at least comparable to their rotational correlation time [13]. However, note that Eqs. (3) & (4) assume a rigid dipole and neglect specific intra- and intermolecular interactions [29]. Also, for larger aggregates, such as micelles [19,30], different relaxation mechanisms and associated expressions for S_i apply.

4. Applications

As already indicated, DRS yields the cooperative dynamics of the studied system. Thus, in conjunction with other methods, particularly computer simulations and experimental methods determining molecular-level structure (e.g. scattering experiments), and molecular (single-particle) dynamics (e.g. NMR, IR pump-probe anisotropy experiments), deep insights into intermolecular interactions of liquids and solutions can be gained.

4.1. Neat liquids

Regarding intermolecular interactions in pure dipolar liquids, the major focus is on understanding the interplay between molecular-level structure and dynamics and its implications on macroscopic properties. The liquid-state dynamics of rigid molecules interacting only through dipole-dipole and van-der-Waals interactions, such as dichloromethane [31], acetonitrile [32], or nitromethane [33], is governed by rotational diffusion. This can be viewed as small-angle random jumps of the orientation of the molecular dipole vector, exposed to an essentially isotropic frictional force determined by the macroscopic viscosity of the liquid. Note, that cross-correlations become increasingly important on supercooling, complicating the dynamics of such apparently simple liquids [15].

This so-called Stokes-Einstein-Debye (SED) behaviour breaks down when directional forces, such as hydrogen bonds (HBs) become relevant [34]. For instance, the dielectric spectrum of water exhibits at least two [32], possibly three [35] relaxation processes: Weak contributions at ~ 600 GHz (relaxation time ~ 0.3 ps) and ~ 140 GHz (~ 1.1 ps), and the dominant process situated at ~ 18 GHz (~ 8.3 ps) around room temperature. Reason is the fluctuating three-dimensional HB-network formed by this liquid. According to Laage et al. [36], water dynamics is characterized by fast (~ 0.3 ps) $\sim 60^\circ$ -flips of individual H_2O molecules changing H-bond allegations. These jumps generate a cascade of dipole swings in their surroundings leading to the slow (~ 8.3 ps) collective re-settlement of the local H-bond network [37]. The intermediate 1.1 ps mode would represent the full reorientation of individual H_2O molecules [35]. However, note that also alternative models of water relaxation were proposed, such as the coupling model of Ngai [38].

Whilst cooperative dynamics of water is rather fast due to the three-dimensional structure of the H-bond network, liquids forming two- (formamide [39], diols [40]) or one-dimensional aggregates (mono-alcohols [41], secondary amides [39,42]) exhibit considerably longer relaxation times but simultaneously also significantly larger static permittivities than expected from their molecular dipole moments. The latter is a consequence of the preferably parallel dipole alignment, whereas the slow dynamics reflects the reduced probability to find new energetically equivalent (or better) H-bond partners. Discussions on the detailed relaxation mechanism are still vivid [43–45]. Interesting from a chemist's

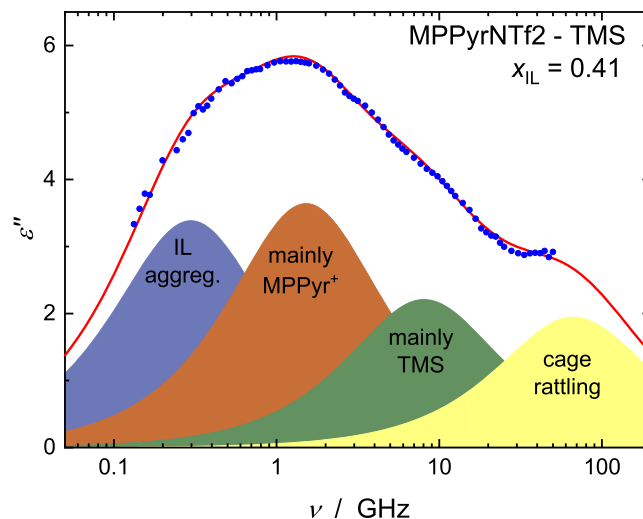


Fig. 3. Dielectric loss spectrum, $\epsilon''(\nu)$ (symbols), of a mixture (mole fraction $x_{\text{IL}} = 0.41$) of the ionic liquid (IL) MPPyrNTf₂ with sulfolane (teramethylsulfone, TMS) at 30 °C and its fit with the D + D + D + D model (line) [83]. Shaded areas indicate the resolved modes, $i = 1 \dots 4$, tentatively assigned to IL aggregates (1), cation reorientation (2), TMS reorientation (3), and cage-rattling (4), based on previous IL + solvent studies.

point of view is the link between H-bond dynamics and catalytic activity of fluorinated mono-alcohols [46].

Because of numerous potential applications ionic liquids (ILs), i.e. room-temperature molten salts, are intensively studied for about two decades now. It may suffice to cite here the review of Wang et al. [47] focusing on their structure and dynamics. In the early years, DRS studies focused on static permittivity, ϵ , as for conducting systems extrapolation of $\epsilon'(\nu)$ to $\nu \rightarrow 0$ is the only way to determine this fundamental quantity [48]. Charge transport is still intensively studied [7,49–51] but also the relaxation mechanisms behind the complex dielectric spectra. For aprotic ILs this may be roughly sketched in the direction of increasing time as cage-rattling, intramolecular flexibility, ion reorientation and cage-escape [11,52]. For protic and pseudo-protic ILs additionally proton transfer comes into play [53]. Deep eutectic solvents (DES), i.e. mixtures of a salt, where one of the ions acts as H-bond donor, with a neutral (solid or liquid) H-bond acceptor, such as ethaline (1:2 molar ratio mixture of choline chloride and urea), exhibit a similar rich and complex behaviour [54–58]

4.2. Solutions — solvent relaxation and solvation numbers

For solutions of electrolytes or non-electrolytes in a polar solvent, the relaxation behaviour of the latter is affected by the balance of solvent-solvent and solute-solvent interactions. With increasing solute concentration the process(es) assigned to the —more-or-less unperturbed— bulk solvent usually exhibit a decrease in amplitude, $S_b(c)$ (Fig. 2c), and possibly a relaxation-time shift. Using the value for the pure solvent, $S_b(0)$, to determine its effective dipole moment, the DRS-detected bulk-solvent concentration, $c_b(c)$, at solute concentration, c , can be calculated from $S_b(c)$ with Eq. (3). Comparison with the analytical solvation concentration, $c_s(c)$, then yields the effective total solvation (hydration for solvent water) number, $Z_i = (c_s - c_b)/c$, as the total number of dynamically affected solvent molecules per equivalent of solute. Note, that for electrolytes $S_b(c)$ first needs to be corrected for kinetic depolarization [59]. Such numbers have been determined in our laboratory for aqueous [13,21,60] and non-aqueous electrolytes [33], as well as other solutes ranging from sugar-alcohols [61] and neurotransmitters [62] to supra-molecular hosts [63] and hydrophilic polymers [64] to mono-clonal antibodies [65]. Hydration/de-hydration effects are also important to understand surfactant systems [66,67]. For instance, the

4.4. Micelles, confinement, ...

Confinement in general and in particular the nano- to mesoscopic structures arising from surfactant aggregation often lead to characteristic changes in dynamics [91]. This is especially the case when ions are involved, either directly for ionic surfactants, or indirectly when small amounts of salt are added to monitor structure changes.

Aqueous solutions of ionic micelles, such as those formed by 1-dodecyl-3-methylimidazolium bromide ($[C_{12}MIM]Br$), exhibit a pronounced contribution in the ~ 0.1 -3 GHz region of their dielectric spectra (Fig. 1). This can be resolved into two Debye modes, with the lower-frequency mode assigned to fluctuations of the diffuse counterion cloud surrounding the charged micelles and the higher-frequency relaxation arising from the surface-hopping of condensed counterions [92]. The surface-diffusion coefficient of the counterions deduced from the latter suggests that at least for dodecyltrimethylammonium [92] and $[C_{12}MIM]$ surfactants [19] triflate (trifluoromethanesulfonate, TfO^-) counterions partly insert into the micellar core, whereas halide ions stay in the interfacial layer. Almost certainly, this is the major reason for the low efficiency of $[C_{12}MIM]TfO$ in micellar catalysis [19,93].

For aggregates of non-ionic surfactants generally only contributions arising from the dynamics of the polar headgroup can be detected but no aggregate-specific relaxation processes [95]. However, small amounts of added "monitor ions" give rise to Maxwell-Wagner-type modes when charge transport is blocked by confinement [96]. This was for instance used to study the percolation transition of water-in-oil microemulsions formed by (oligo)ethylene glycol surfactants [97]. Dielectric spectra of reverse micelles with ionic surfactants are generally rather complicated (Fig. 4) [94,98]. One may argue whether mode 4 (tentatively assigned to the reorientation of headgroup-counterion pairs) is really required to describe this particular sample. However, relaxations 1, 2, 3, 5 & 6 definitely are. Modes 5 and 6 are assigned to water residing inside the pool and to H_2O molecules interacting with the interface. Relaxation 1 is due to the exchange of ions between colliding reverse micelles, similar to the situation in Ref. [97]. According to our interpretation, modes 2 and 3 are comparable to the micelle-specific modes of normal micelles, however with flipped dynamics. Because of the small pool size, ion-cloud fluctuations (3) are now faster than surface hopping (4). However, this interpretation needs a crosscheck by other methods, preferably computer simulations.

5. Concluding remarks

In the frequency range relevant to solution chemistry, DRS will almost certainly remain a niche technique. However, with the availability of broad-band vector network analyzers (VNAs) now more potential users are expected. Here, the first pitfall for newcomers opens: VNAs require calibration with (at least) three standards. Open- and short-circuit calibration pose no major problem, as long as experiments can be performed under open atmosphere. However, the third standard should be preferably a liquid with dielectric properties similar to the sample. Unfortunately, the selection of standard liquids that are accurately characterized by absolute measurements of $\hat{\epsilon}(\nu)$ is limited. Particularly, when temperatures away from room temperature should be investigated.

The second pitfall was already mentioned: This is the choice of the relaxation model, Eq. (2), used to fit $\hat{\epsilon}(\nu)$. Goodness of the fit is a necessary but not a sufficient criterion to decide whether the chosen model is meaningful or not. Particularly, when the covered frequency is limited, which is more than often the case in solution studies. The spectra of Figs. 3 and 4 are examples for that. To check whether the chosen model is self-consistent, a series of measurements, varying temperature or, in solution studies preferred, sample composition, is necessary. Obviously, also the inference from the obtained amplitudes and relaxation times should fit into existing knowledge or be backed by information gained with other methods. This is of particular importance, as the assignment of resolved modes to physical processes is often prob-

lematic. Here, molecular-dynamics simulations are becoming more and more important as they allow disentangling self- and cross-correlations [16,18,51]. However, note that for (reasonable) quantitative agreement polarizability has to be properly taken into account [16,24].

The author hopes that, despite the just sketched pitfalls for active and prospective DRS users, he was able to convince readers with this personally biased review, that DRS can provide otherwise inaccessible information relevant in solution chemistry and for soft-matter studies in general. This is especially true, when DRS results are carefully combined with inference from other methods, may these be thermodynamic or transport measurements, scattering experiments or computer simulation. Although not always explicitly stated, this was the strategy followed in many of the cited papers.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

Generative AI and AI-assisted technologies were not used.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] P.J.W. Debye, *Polar Molecules*, Chemical Catalogue, reprinted by Dover Publications, New York, 1929.
- [2] D. Craig, *Dielectric Analysis of Pharmaceutical Systems*, Taylor & Francis, London, 1995.
- [3] Y. Feldman, T. Skodvin, J. Sjöblom, *Dielectric spectroscopy on colloidal systems — a review*, in: P. Becher (Ed.), *Encyclopedia Handbook of Emulsion Technology*, 5, Marcel Dekker, New York, 2001.
- [4] F. Kremer, A. Schönhalz (Eds.), *Broadband Dielectric Spectroscopy*, Springer, Berlin, Germany, 2003.
- [5] K.L. Ngai, *Relaxation and Diffusion in Complex Systems*, Springer, New York, 2011.
- [6] F. Kremer (Ed.), *Dynamics in Geometrical Confinement*, Springer, Berlin, Germany, 2014.
- [7] M. Paluch (Ed.), *Dielectric Properties of Ionic Liquids*, Springer, Berlin, Germany, 2016.
- [8] F. Kremer, M. Tress, *Dielectric spectroscopy: yesterday, today and tomorrow*, *Appl. Sci.* 15 (2025) 6954. <https://doi.org/10.3390/app15136954>
- [9] V. Raicu, Y. Feldman (Eds.), *Dielectric Relaxation in Biological Systems: Physical Principles, Methods, and Applications*, Oxford University Press, Oxford, U.K., 2015.
- [10] N.E. Hill, W.E. Vaughan, A.H. Price, M. Davies, *Dielectric Properties and Molecular Behaviour*, Van Nostrand Reinhold Co., London, 1969.
- [11] T. Sonnleitner, D.A. Turton, S. Waselikowski, J. Hunger, A. Stoppa, M. Walthert, K. Wynne, R. Buchner, *Dynamics of RTILs: a comparative dielectric and OKE study*, *J. Mol. Liq.* 192 (2014) 19–25. <https://doi.org/10.1016/j.molliq.2013.09.019>
- [12] A.K. Singh, L.C. Doan, D. Lou, C. Wen, N.Q. Vinh, *Interfacial layers between ion and water detected by terahertz spectroscopy*, *J. Chem. Phys.* 157 (2022) 054501. <https://doi.org/10.1063/5.0095932>
- [13] R. Buchner, G. Hefter, *Interactions and dynamics in electrolyte solutions by dielectric spectroscopy*, *Phys. Chem. Chem. Phys.* 11 (2009) 8984–8999. <https://doi.org/10.1039/b906555p>
- [14] C.F.J. Böttcher, P. Bordewijk, *Theory of Electric Polarization*, Vol. 2, Elsevier, Amsterdam, 1978.
- [15] K. Moch, P. Münzner, R. Böhmer, C. Gainaru, *Molecular cross-correlations govern structural rearrangements in a nonassociating polar glass former*, *Phys. Rev. Lett.* 128 (2022) 228001. <https://doi.org/10.1103/PhysRevLett.128.228001>
- [16] P. Honegger, O. Steinhauser, C. Schröder, *Collective spectroscopy of solvation phenomena: conflicts, challenges, and opportunities*, *J. Phys. Chem. Lett.* 14 (2023) 609–618. <https://doi.org/10.1021/acs.jpcllett.2c03574>
- [17] D.V. Matyushov, R. Richert, *From single-particle to collective dynamics in supercooled liquids*, *J. Phys. Chem. Lett.* 14 (2023) 4886–4891. <https://doi.org/10.1021/acs.jpcllett.3c00959>

- [18] M. Paluch, K. Koperwas, Z. Wojnarowska, Determination of self and cross contributions to the dipole-dipole correlations function from analysis of dielectric measurements, *J. Mol. Liq.* 382 (2023) 121907. <https://doi.org/10.1016/j.molliq.2023.121907>
- [19] S. Friesen, T. Buchecker, A. Cognigni, K. Bica, R. Buchner, Hydration and counterion binding of [C₁₂MIM] micelles, *Langmuir* 33 (2017) 9844–9856. <https://doi.org/10.1021/acs.langmuir.7b02201>
- [20] U. Kaatz, Measuring the dielectric properties of materials. Ninety-year development from low-frequency techniques to broadband spectroscopy and high-frequency imaging, *Meas. Sci. Technol.* 24 (2013) 012005. <https://doi.org/10.1088/0957-0233/24/1/012005>
- [21] S. Friesen, S. Krickl, M. Luger, A. Nazet, G. Hefter, R. Buchner, Hydration and ion association of La³⁺ and Eu³⁺ in aqueous solution, *Phys. Chem. Chem. Phys.* 20 (2018) 8812–8821. <https://doi.org/10.1039/C8CP00248G>
- [22] J.H. Ryu, J.W. Yu, T.J. Yoon, W.B. Lee, Understanding the dielectric relaxation of liquid water using neural network potential and classical pairwise potential, *J. Mol. Liq.* 397 (2024) 124054. <https://doi.org/10.1016/j.molliq.2024.124054>
- [23] F. Papst, S. Baroni, How salt solvation slows water dynamics while blue-shifting its dielectric spectrum, *J. Phys. Chem. Lett.* 16 (2025) 7915–7920. <https://doi.org/10.1021/acs.jpclett.5c01401>
- [24] R.A. Bone, K. Schwarz, Computational dielectric spectroscopy shows that water/methanol mixtures form hybrid hydrogen bonding networks, *J. Chem. Phys.* 164 (2026) 094502. <https://doi.org/10.1063/5.0320783>
- [25] A. Eiberweiser, A. Nazet, G. Hefter, R. Buchner, Ion hydration and association in aqueous potassium phosphate solutions, *J. Phys. Chem. B* 119 (2015) 5270–5281. <https://doi.org/10.1021/acs.jpcc.5b01417>
- [26] C. Akilan, N. Rohman, G.T. Hefter, R. Buchner, Temperature effects on ion association and hydration in MgSO₄(aq) by dielectric spectroscopy, *ChemPhysChem* 7 (2006) 2319–2330. <https://doi.org/10.1002/cphc.200600342>
- [27] A. Eiberweiser, A. Nazet, S. Kruchinin, M. Fedotova, R. Buchner, Hydration and ion binding of the osmolyte ectoine, *J. Phys. Chem. B* 119 (2015) 15203–15211. <https://doi.org/10.1021/acs.jpcc.5b09276>
- [28] V. Agieienko, R. Buchner, Urea hydration from dielectric spectroscopy: old findings confirmed, new insights gained, *Phys. Chem. Chem. Phys.* 18 (2016) 2597–2607. <https://doi.org/10.1039/c5cp07604h>
- [29] J.P. Gabriel, M. Tress, W. Kossack, L. Popp, F. Kremer, Molecular heterogeneities in the thermal expansivity of polyalcohols, *J. Chem. Phys.* 154 (2021) 024503. <https://doi.org/10.1063/5.0036067>
- [30] C. Baar, R. Buchner, W. Kunz, Dielectric relaxation of cationic surfactants in aqueous solution. 2. solute relaxation, *J. Phys. Chem. B* 105 (2001) 2914–2922. <https://doi.org/10.1021/jp004450p>
- [31] J. Hunger, A. Stoppa, A. Thoman, M. Walther, R. Buchner, Broadband dielectric response of dichloromethane, *Chem. Phys. Lett.* 471 (2009) 85–91. <https://doi.org/10.1016/j.cplett.2009.02.024>
- [32] T. Fukasawa, T. Sato, J. Watanabe, Y. Hama, W. Kunz, R. Buchner, The relation between dielectric and low-frequency raman spectra of hydrogen-bond liquids, *Phys. Rev. Lett.* 95 (2005) 197802. <https://doi.org/10.1103/PhysRevLett.95.197802>
- [33] A. Nazet, L. Weiß, R. Buchner, Dielectric relaxation of nitromethane and its mixtures with ethylammonium nitrate: evidence for strong ion association induced by hydrogen bonding, *J. Mol. Liq.* 228 (2017) 81–90. <https://doi.org/10.1016/j.molliq.2016.09.008>
- [34] M. Becher, R. Horstmann, S. Kloth, E.A. Rössler, M. Vogel, A relation between the formation of a hydrogen-bond network and a time-scale separation of translation and rotation in molecular liquids, *J. Phys. Chem. Lett.* 13 (2022) 4556–4562. <https://doi.org/10.1021/acs.jpclett.2c00821>
- [35] N.Q. Vinh, L.C. Doan, N.L.H. Hoang, J.R. Cui, B. Sindle, Correlation between macroscopic and microscopic relaxation dynamics of water: evidence for two liquid forms, *J. Chem. Phys.* 158 (2023) 204507. <https://doi.org/10.1063/5.0142818>
- [36] D. Laage, G. Stirnemann, F. Sterpone, R. Rey, J.T. Hynes, Reorientation and allied dynamics in water and aqueous solutions, *Annu. Rev. Phys. Chem.* 62 (2011) 395–416. <https://doi.org/10.1146/annurev.physchem.012809.103503>
- [37] A. Offei-Danso, U.N. Morzan, A. Rodriguez, A. Hassanali, A. Jelic, The collective burst mechanism of angular jumps in liquid water, *Nat. Commun.* 14 (2023) 1345. <https://doi.org/10.1038/s41467-023-37069-9>
- [38] K.L. Ngai, Interpretation of the GHz to THz dielectric relaxation dynamics of water in the framework of the coupling model, *J. Mol. Liq.* 253 (2018) 113–118. <https://doi.org/10.1016/j.molliq.2018.01.039>
- [39] J. Barthel, K. Bachhuber, R. Buchner, J.B. Gill, M. Kleebauer, Dielectric spectra of some common solvents in the microwave region. Dipolar aprotic solvents and amides, *Chem. Phys. Lett.* 167 (1990) 62–66. [https://doi.org/10.1016/0009-2614\(90\)85071-J](https://doi.org/10.1016/0009-2614(90)85071-J)
- [40] S. Schrödle, R. Buchner, W. Kunz, Effect of the chain length on the inter- and intramolecular dynamics of liquid oligo(ethylene glycol)s, *J. Phys. Chem. B* 108 (2004) 6281–6287. <https://doi.org/10.1021/jp037937h>
- [41] T. Böhmer, C. Gainaru, R. Richert, Structure and dynamics of monohydroxy alcohols — milestones towards their microscopic understanding, 100 years after Debye, *Phys. Rep.* 545 (2014) 125–195. <https://doi.org/10.1016/j.physrep.2014.07.005>
- [42] C. Gainaru, S. Bauer, E. Vynokur, H. Wittkamp, W. Hiller, R. Richert, R. Böhmer, Dynamics in Supercooled Secondary Amide Mixtures: dielectric and hydrogen bond specific spectroscopies, *J. Phys. Chem. B* 119 (2015) 15769–15779. <https://doi.org/10.1021/acs.jpcc.5b10034>
- [43] T. Böhmer, F. Papst, J.P. Gabriel, R. Zeißler, T. Blochowicz, On the spectral shape of the structural relaxation in supercooled liquids, *J. Chem. Phys.* 162 (2025) 120902. <https://doi.org/10.1063/5.0254534>
- [44] S. Cheng, S. Patil, S. Cheng, Hydrogen bonding exchange and supramolecular dynamics of monohydroxy alcohols, *Phys. Rev. Lett.* 132 (2024) 058201. <https://doi.org/10.1103/PhysRevLett.132.058201>
- [45] V.G. Artemov, A. Ryzhov, E. Carlsen, P.O. Kapralov, H. Ouerdane, Nonrotational mechanism of polarization in alcohols, *J. Phys. Chem. B* 124 (2020) 11022–11029. <https://doi.org/10.1021/acs.jpcc.0c09380>
- [46] F. Caporaletti, L. Gunkel, M.A. Fernández-Ibáñez, J. Hunger, S. Woutersen, Fast collective hydrogen-bond dynamics in hexafluoroisopropanol related to its chemical activity, *Angew. Chem. Int. Ed.* 63 (2024) e20241609. <https://doi.org/10.1002/anie.202416091>
- [47] Y.-L. Wang, B. Li, S. Sarman, F. Mocci, Z.-Y. Lu, J. Yuan, A. Laaksonen, M.D. Fayer, Microstructural and dynamical heterogeneities in ionic liquids, *Chem. Rev.* 120 (2020) 5798–5877. <https://doi.org/10.1021/acs.chemrev.9b00693>
- [48] H. Weingärtner, The static dielectric permittivity of ionic liquids, *J. Mol. Liq.* 192 (2014) 185–190. <https://doi.org/10.1016/j.molliq.2013.07.020>
- [49] F. Papst, Z. Wojnarowska, M. Paluch, T. Blochowicz, On the temperature and pressure dependence of dielectric relaxation processes in ionic liquids, *Phys. Chem. Chem. Phys.* 23 (2021) 14260–14275. <https://doi.org/10.1039/d1cp01636a>
- [50] T. Cosby, C.D. Stachurski, R.A. Mantz, P.C. Trulove, D.P. Durkin, Elucidating the interplay of local and mesoscale ion dynamics and transport properties in aprotic ionic liquids, *Phys. Chem. Chem. Phys.* 25 (2023) 6351–6362. <https://doi.org/10.1039/d2cp05863d>
- [51] F. Joerg, J. Sutter, L. van Damm, K. Kanellopoulos, J. Hunger, C. Schröder, Comparative analysis of dielectric spectra in protic ionic liquids: experimental findings and computational molecular decomposition, *J. Mol. Liq.* 396 (2024) 123834. <https://doi.org/10.1016/j.molliq.2023.123834>
- [52] D.A. Turton, J. Hunger, A. Stoppa, G. Hefter, A. Thoman, M. Walther, R. Buchner, K. Wynne, Dynamics of Imidazolium Ionic Liquids from a Combined Dielectric Relaxation and Optical Kerr Effect Study: evidence for mesoscale aggregation, *J. Am. Chem. Soc.* 131 (2009) 11140–11146. <https://doi.org/10.1021/ja903315v>
- [53] H. Watanabe, T. Umecky, N. Arai, A. Nazet, T. Takamuku, K.A. Harris, Y. Kameda, R. Buchner, Y. Umebayashi, Possible proton conduction mechanism in pseudo-protic ionic liquids: the concept of specific proton conduction, *J. Phys. Chem. B* 123 (2019) 6244–6252. <https://doi.org/10.1021/acs.jpcc.9b03185>
- [54] V. Agieienko, R. Buchner, Is Ethaline a deep eutectic solvent?, *Phys. Chem. Chem. Phys.* 24 (2022) 5265–5268. <https://doi.org/10.1039/d2cp00104g>
- [55] V. Agieienko, V. Neklyudov, R. Buchner, Why does ethaline apparently behave as an ideal binary mixture?, *J. Phys. Chem. Lett.* 13 (2022) 10805–10809. <https://doi.org/10.1021/acs.jpclett.2c02901>
- [56] S. Spittle, I. Alfaray, B.B. Hansen, K. Glynn, W. Brackett, R. Pandian, C. Burda, J. Sangoro, Enhanced dynamics and charge transport at the eutectic point: a new paradigm for the use of deep eutectic solvent systems, *JACS Au* 3 (2023) 3024–3030. <https://doi.org/10.1021/jacsau.3c00420>
- [57] J. Mondal, D. Maji, S. Mitra, R. Biswas, Temperature-dependent dielectric relaxation measurements of (Betaine + Urea + Water) deep eutectic solvent in Hz-GHz frequency window: microscopic insights into constituent contributions and relaxation mechanisms, *J. Phys. Chem. B* 128 (2024) 6567–6580. <https://doi.org/10.1021/acs.jpcc.4c02784>
- [58] A. Schulz, P. Lunkenheimer, A. Loidl, Ionic conductivity of a lithium-doped deep eutectic solvent: glass formation and rotation-translation coupling, *J. Phys. Chem. B* 128 (2024) 3454–3462. <https://doi.org/10.1021/acs.jpcc.4c00412>
- [59] M. Segal, S. Kantorovich, A. Arnold, Kinetic Dielectric Decrement Revisited: phenomenology of finite ion concentrations, *Phys. Chem. Chem. Phys.* 17 (2015) 130–133. <https://doi.org/10.1039/c4cp04182h>
- [60] R. Buchner, W. Wachter, G. Hefter, Systematic variations of ion hydration in aqueous alkali metal fluoride solutions, *J. Phys. Chem. B* 123 (2019) 10868–10876. <https://doi.org/10.1021/acs.jpcc.9b09694>
- [61] I. Płowaś-Korus, R. Buchner, Structure, molecular dynamics and interactions in aqueous xylitol solutions, *Phys. Chem. Chem. Phys.* 21 (2019) 24061–24069. <https://doi.org/10.1039/c9cp04547c>
- [62] S. Friesen, M.V. Fedotova, S.E. Kruchinin, R. Buchner, Hydration of the neurotransmitter γ -Aminobutyric Acid and its isomer α -Aminobutyric Acid, *J. Mol. Liq.* 375 (2023) 121363. <https://doi.org/10.1016/j.molliq.2023.121363>
- [63] N. Moreno, E.F. Vargas, R. Buchner, Ionic effects on supramolecular hosts: solvation and counter-ion binding in polar media, *Phys. Chem. Chem. Phys.* 24 (2022) 2040–2050. <https://doi.org/10.1039/d1cp05444a>
- [64] K. Yanase, R. Buchner, T. Sato, Microscopic insights into the phase transition of Poly(N-isopropylacrylamide) in aqueous media: effects of molecular weight and polymer concentration, *J. Mol. Liq.* 302 (2020) 112025. <https://doi.org/10.1016/j.molliq.2019.11.2025>
- [65] J. Hartl, S. Friesen, D. Johannsmann, R. Buchner, D. Hinderberger, M. Blech, P. Garidel, Dipolar interactions and protein hydration in highly concentrated antibody formulations, *Mol. Pharmaceutics* 19 (2022) 494–507. <https://doi.org/10.1021/acs.molpharmaceut.1c00587>
- [66] Ž. Medoš, N.V. Plechkova, S. Friesen, R. Buchner, M. Bešter-Rogač, Insight into the Hydration of Cationic Surfactants: a thermodynamic and dielectric study of functionalized quaternary ammonium chlorides, *Langmuir* 35 (2019) 3759–3772. <https://doi.org/10.1021/acs.langmuir.8b03993>
- [67] Ž. Medoš, S. Friesen, R. Buchner, M. Bešter-Rogač, Interplay between aggregation number, micelle charge and hydration of catanionic surfactants, *Phys. Chem. Chem. Phys.* 22 (2020) 9998–10009. <https://doi.org/10.1039/d0cp00877j>
- [68] K. Yanase, M. Obikane, T. Ogura, R. Buchner, A. Igarashi, T. Sato, Ion fluctuations and intermembrane interactions in the aqueous dispersions of a dialkylchain cationic surfactant studied using dielectric relaxation spectroscopy and small- and wide-angle X-Ray scattering, *Phys. Chem. Chem. Phys.* 20 (2018) 26621–26633. <https://doi.org/10.1039/c8cp05575k>

- [69] C. Baar, R. Buchner, W. Kunz, Dielectric relaxation of cationic surfactants in aqueous solution. 1. solvent relaxation, *J. Phys. Chem. B* 105 (2001) 2906–2913. <https://doi.org/10.1021/jp002884e>
- [70] K. Mazur, R. Buchner, M. Bonn, J. Hunger, Hydration of sodium alginate in aqueous solution, *Macromolecules* 47 (2014) 771–776. <https://doi.org/10.1021/ma4023873>
- [71] I. Persson, Structure and size of complete hydration shells of metal ions and inorganic anions in aqueous solution, *Dalton Trans.* 53 (2024) 15517–15538. <https://doi.org/10.1039/d4dt01449a>
- [72] T. Yamaguchi, Historical development of a study of the structure and dynamics of liquids and solutions, *J. Mol. Liq.* 395 (2024) 123919. <https://doi.org/10.1016/j.molliq.2023.123919>
- [73] R.A. Wheeler, E.E. Dalbey, Structure factor line shape model gives approximate nanoscale size of polar aggregates in pyrrolidinium-based ionic liquids, *Phys. Chem. Chem. Phys.* 27 (2025) 4593–4602. <https://doi.org/10.1039/d4cp04488f>
- [74] S.E. Weitzner, T.A. Pham, C.A. Orme, S.R. Qiu, B.C. Wood, Beyond thermodynamics: assessing the dynamical softness of hydrated ions from first principles, *J. Phys. Chem. Lett.* 12 (2021) 11980–11986. <https://doi.org/10.1021/acs.jpcclett.1c03314>
- [75] Y. Zeng, Y. Jia, T. Yan, W. Zhuang, Binary structure and dynamics of the hydrogen bonds in the hydration shells of ions, *Phys. Chem. Chem. Phys.* 23 (2021) 11400–11410. <https://doi.org/10.1039/d0cp06397e>
- [76] M. Flór, V. Vorobev, V. Mandalaparthi, N.F.A. van der Vegt, P.S. Cremer, S. Roke, Unraveling the molecular pathways for structure “Making” and “Breaking” by ions in water, *J. A. Chem. Soc.* 147 (2025) 37328–37336. <https://doi.org/10.1021/jacs.5c10984>
- [77] D. Laage, T. Elsaesser, J.T. Hynes, Water dynamics in the hydration shells of biomolecules, *Chem. Rev.* 117 (2017) 10694–10725. <https://doi.org/10.1021/acs.chemrev.6b00765>
- [78] W.H. Boeijs, H.J. Bakker, Dynamics of solvating water as a probe of polymers and supramolecular structures, *Chem. Rev.* 126 (2026) 2197–2217. <https://doi.org/10.1021/acs.chemrev.5c00735>
- [79] J. Barthel, R. Buchner, Dielectric permittivity and relaxation of electrolyte solutions and their solvents, *Chem. Soc. Rev.* 21 (1992) 263–270. <https://doi.org/10.1039/CS9922100263>
- [80] M. Eigen, K. Tamm, Schallabsorption in Elektrolytlösungen als Folge chemischer Relaxation II. Meßergebnisse und Relaxationsmechanismen für 2-2-wertige Elektrolyte, *Z. Elektrochem.* 66 (1962) 107–121. <https://doi.org/10.1002/bbpc.19620660206>
- [81] G. Hefter, When spectroscopy fails: the measurement of ion pairing, *Pure Appl. Chem.* 78 (2006) 1571–1586. <https://doi.org/10.1351/pac200678081571>
- [82] J.M.G. Barthel, H. Krienke, W. Kunz, *Physical Chemistry of Electrolyte Solutions-Modern Aspects*, Steinkopff, Springer, Darmstadt, New York, 1998.
- [83] I. Płowaś-Korus, A. Gabryelczyk, A. Świdarska-Mocek, R. Buchner, 2026. In preparation.
- [84] R. Buchner, G. Hefter, Ion hydration and association in aqueous solutions of zinc sulfate by dielectric spectroscopy, *J. Mol. Liq.* 383 (2023) 122146. <https://doi.org/10.1016/j.molliq.2023.122146>
- [85] J. Hunger, R. Buchner, G. Hefter, Ion association and hydration of some heavy-metal nitrate salts in aqueous solution, *J. Phys. Chem. B* 128 (2024) 10238–10246. <https://doi.org/10.1021/acs.jpcc.4c05441>
- [86] O.A. Dmitrieva, M.V. Fedotova, R. Buchner, Evidence for Cooperative Na⁺ and Cl⁻ binding by strongly hydrated proline, *Phys. Chem. Chem. Phys.* 19 (2017) 20474–20483. <https://doi.org/10.1039/C7CP04335J>
- [87] S. Friesen, S.E. Kruchinin, M.V. Fedotova, R. Buchner, Cation-binding of glutamate in aqueous solution, *J. Phys. Chem. B* 128 (2024) 5746–5755. <https://doi.org/10.1021/acs.jpcc.4c02373>
- [88] A. Stoppa, J. Hunger, G. Hefter, R. Buchner, Structure and dynamics of 1-*N*-Alkyl-3-*N*-methylimidazolium tetrafluoroborate + acetonitrile mixtures, *J. Phys. Chem. B* 116 (2012) 7509–7521. <https://doi.org/10.1021/jp302067>
- [89] T. Sonnleitner, V. Nikitina, A. Nazet, R. Buchner, Do H-Bonds explain strong ion aggregation in ethylammonium nitrate + acetonitrile mixtures?, *Phys. Chem. Chem. Phys.* 15 (2013) 18445–18452. <https://doi.org/10.1039/C3CP51773J>
- [90] V. Agieienko, A.R. Harifi-Mood, R. Buchner, Cooperative dynamics and speciation in deep eutectic solvent + DMSO mixtures, *J. Mol. Liq.* 331 (2021) 115790. <https://doi.org/10.1016/j.molliq.2021.115790>
- [91] W.H. Thomson, Perspective: dynamics of confined liquids, *J. Chem. Phys.* 149 (2018) 170901. <https://doi.org/10.1063/1.5057759>
- [92] P.S. Lima, H. Chaimovich, I.M. Cuccovia, R. Buchner, Dielectric Relaxation Spectroscopy shows a sparingly hydrated interface and low counterion mobility in triflate micelles, *Langmuir* 29 (2013) 10037–10046. <https://doi.org/10.1021/la401728g>
- [93] A. Cognigni, P. Gärtner, R. Zirbs, H. Peterlik, K. Prochazka, C. Schröder, K. Bica, Surface-active ionic liquids in micellar catalysis: impact of anion selection on reaction rates in nucleophilic substitutions, *Phys. Chem. Chem. Phys.* 18 (2016) 13375–13384. <https://doi.org/10.1039/C6CP00493H>
- [94] W. Wachter, Cooperative dynamics of didodecyldimethylammonium bromide/water/*n*-dodecane microemulsions: a dielectric relaxation study, Ph.D. thesis, Universität Regensburg, 2007.
- [95] L. Montara, F.S. Lima, I.M. Cuccovia, A. Nazet, D. Horinek, R. Buchner, H. Chaimovich, Specific ion effects on zwitterionic micelles are independent of interfacial hydration changes, *Langmuir* 34 (2018) 11049–11057. <https://doi.org/10.1021/acs.langmuir.8b02115>
- [96] K. Asami, Characterization of heterogeneous systems by dielectric spectroscopy, *Prog. Polym. Sci.* 27 (2002) 1617–1659. [https://doi.org/10.1016/S0079-6700\(02\)00015-1](https://doi.org/10.1016/S0079-6700(02)00015-1)
- [97] S. Schrödle, R. Buchner, W. Kunz, Percolating microemulsions of nonionic surfactants probed by dielectric spectroscopy, *ChemPhysChem* 6 (2005) 1051–1055. <https://doi.org/10.1002/cphc.200400605>
- [98] W. Wachter, R. Buchner, Dielectric spectroscopy into co-ion effects on microemulsion dynamics and phase behavior, *Acta Chim. Slov.* 56 (2009) 53–57.