

DIELECTRIC SPECTRA OF SOME COMMON SOLVENTS IN THE MICROWAVE REGION. WATER AND LOWER ALCOHOLS

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Precise complex permittivity spectra of the hydrogen-bonding liquids water, methanol, ethanol, 1-propanol, and 2-propanol have been determined in the frequency range 0.95–89 GHz. It is shown that the dielectric relaxation behaviour of water is governed by two exponentials, whereas three discrete dispersion steps are found for the alcohols.

1. Introduction

One of the fundamental questions, important to the understanding of liquid state systems is the reorientational dynamics of the solvent which, for polar liquids, can be probed by dielectric relaxation experiments [1]. From the frequency-dependent complex permittivities, $\hat{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$, obtained with this technique, relaxation times τ_j and dispersion amplitudes $\Delta\epsilon_j$ of the underlying relaxation processes can be extracted, which do not only provide a wealth of information on equilibrium systems like pure liquids [2] or electrolyte solutions [3,4], but also have a major influence on the rate of chemical reactions in the liquid phase. The theoretical treatment of electron transfer reactions, a rapidly developing field in recent years [5–9], clearly reveals the influence of solvent dynamics on the frequency factor of the reaction. The contributions of collisional and dielectric friction to this solvent effect seem to be equally important.

The modelling of the dielectric friction term is still a matter of discussion. Experimental evidence from time-resolved solvation studies [10,11] or electrochemical exchange kinetics data [12,13] clearly show the inadequacy of a continuum treatment of the solvent dielectric relaxation by a simple exponential with time constant τ . Especially alcohols suggest an effective relaxation time much smaller than the lon-

gitudinal relaxation time, $\tau_L \approx (\epsilon_\infty/\epsilon)\tau$, extracted from available dielectric data.

It is evident, that precise dielectric relaxation data covering the complete time scale of solvent dynamics are needed for the comparison of the present theories on electron transfer reactions with experimental studies, and for the calculation of reliable orientational correlation functions necessary for testing liquid models. There is an appreciable number of permittivity data in the microwave range up to ≈ 50 GHz and, to a lesser extent and mostly for simple liquids, also in the far infrared. In the intermediate frequency range between 50 and 300 GHz ($1.6\text{--}10\text{ cm}^{-1}$), however, data are scarce. Since the analysis of dielectric data, even in an empirical approach, critically depends on the maximum frequency accessible [14], no reliable information on motions in the 0.5 to 3 ps time scale can be deduced from the existing data.

In the course of our dielectric relaxation experiments on electrolyte solutions, we have shifted the maximum frequency accessible in our laboratory to 89 GHz. A complete survey of the orientational correlation function is now possible for systems, where low frequency dispersive far-infrared spectra are available. For the other systems the dynamics can be probed down to ≈ 1.5 ps with sufficient reliability. Our aim in this and following Letters is to report the dielectric relaxation parameters which yield the best reproduction of the complex permittivity spectra of

pure liquids studied in the context of our investigations on electrolyte solutions, here on water and the short chain alcohols methanol, ethanol, 1-propanol, and 2-propanol.

The arguments which led us to prefer a relaxation model as the best representation of the data are mainly based on the results from systematic studies on electrolyte solutions which will be published separately. We therefore abstain in this communication from a detailed discussion of the possible physical basis of the relaxation processes extracted from the spectra. Nevertheless, we hope that the results will be helpful as reference data for those doing research on reorientational and reaction dynamics in liquid systems.

2. Experimental and data analysis

The dielectric spectra presented were determined at $25.00 \pm 0.01^\circ\text{C}$ in the frequency range $0.95 \leq \nu \leq 89$ GHz using the method of travelling waves, which allows an independent determination of the attenuation coefficient α and the wavelength λ_M in the sample at a given frequency ν . These quantities, which permit a straightforward calculation of the complex permittivity, need only relative measurements of length and signal intensity, so that calibration errors can be minimized. Due to the limited band width of waveguides, unavoidable for signal transmission in the microwave range, six measuring lines are used in our laboratory to cover the above frequency range. A description of the 1–40 GHz equipment, which allows an accuracy better than 1.5% for ϵ' and 2.5% for ϵ'' is given in ref. [14]. The E-band (60–90 GHz) set up is constructed in a similar way, with the mechanical constraints required by the short wavelength (3.3–5 mm in air) taken into account. This allows to determine α and λ_M with a precision better than 1%. Due to lacking standards, the accuracy of ϵ' and ϵ'' can only be estimated from scarce permittivity data of liquids found in the literature for this frequency range and from the internal consistency of our data over the entire frequency range studied. Approximately 3%, depending somewhat on the system studied, are probably realistic for both ϵ' and ϵ'' . A detailed description of the equipment will be given elsewhere [15].

All liquids presented in this communication were used as solvents for studies on electrolyte solutions. An essential requirement in these studies is the high purity of the solvent; especially the water content has to be kept to a minimum [16]. Therefore all our samples were thoroughly purified with recommended procedures and handled under nitrogen, leaving impurity contents, including water traces, less than 50 ppm for the alcohols. The water sample was purified with a Millipore line. Its conductance after removal from the dielectric cells was $< 10^{-6} \Omega^{-1} \text{cm}^{-1}$.

In addition to the results from our measurements in the microwave range up to 89 GHz we have included into the discussion of the dielectric properties the far-infrared spectra up to about 300–500 GHz ($10\text{--}16 \text{ cm}^{-1}$) of those liquids where data are available. In this region, where librational motions and inertial effects do not contribute appreciably to liquid dynamics, the best fit of the data is always achieved by an appropriate (though not necessarily physically reasonable) empirical relaxation model. We used the Debye equation ($\alpha_j=0$; $\beta_j=1$), the Cole–Cole equation ($0 \leq \alpha_j < 1$; $\beta_j=1$), the Cole–Davidson equation ($\alpha_j=0$; $0 < \beta_j \leq 1$), as well as some appropriate sums of these equations [1]

$$\hat{\epsilon}(\omega) = \epsilon_\infty + (\epsilon - \epsilon_\infty) \sum_{j=1}^n \frac{g_j}{[1 + (i\omega\tau_j)^{1-\alpha_j}]^{\beta_j}} \quad (1)$$

Here n is the number of separable dispersion steps j of weight

$$g_j = \frac{\epsilon_j - \epsilon_{\infty j}}{\epsilon - \epsilon_\infty}, \quad \epsilon_{\infty j} = \epsilon_{j+1},$$

and relaxation time τ_j contributing to the total dispersion from the static value $\epsilon = \epsilon_1$ to $\epsilon_\infty = \lim_{\omega \rightarrow \infty} \epsilon'$. The parameters $\alpha_j > 0$ and $\beta_j < 1$ describe either a symmetric or asymmetric distribution of relaxation times for process j .

For data fitting a non-linear least squares routine [17] is applied, which minimises the error function

$$\chi^2 = \frac{1}{2m-l} \sum_{i=1}^m \left[\left(\frac{\delta\epsilon'_i}{\sigma(\epsilon'_i)} \right)^2 + \left(\frac{\delta\epsilon''_i}{\sigma(\epsilon''_i)} \right)^2 \right], \quad (2)$$

where m is the number of data triples (ν , ϵ' , ϵ''), l is the number of adjustable parameters, $\delta\epsilon_i$ and $\sigma(\epsilon_i)$

are the residuals and the standard deviations of the individual data points, respectively.

For all liquids presented in figs. 1 and 2 the best relaxation model is a sum of Debye equations ($n=2$ (water) or 3 (alcohols)). In neither case superior results could be achieved by an increase of the number of dispersion steps, n , or by the use of the Cole-Cole or Cole-Davidson equation or other empirical equations such as the Fröhlich or Havriliak-Negami equation (cf. ref. [1]).

3. Results and discussion

Table 1 shows the best fit parameters, the maximum frequency, ν_{\max} , used in the data analysis, and the quantity χ^2 for water, methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), and 2-propanol (2-PrOH). Also listed is the static permittivity of the liquids, ϵ_s , determined by conventional low frequency measurements. The comparison with the permittivities extrapolated to zero frequency from the dielectric spectra, ϵ , shows excellent agreement with deviations less than 0.5% even for the propanols, where the critical frequency, $\nu_c = 1/2\pi\tau_1$, is distinctly below the minimum frequency (0.95 GHz) of our experiments. This may be taken as an indication of the quality of our $\hat{\epsilon}(\nu)$ data and lends credit to the other parameters extracted from the fit.

The accuracy of the other parameters can only be estimated. For the liquids where no far-infrared data are available they are still hampered by the incomplete frequency coverage. The relaxation time of the main dispersion step, τ_1 , can be given within 1–2%. For the alcohols the parameters ϵ and τ_1 of this step show almost no change when compared to results from applying a two Debye model to a frequency

range restricted to 18 GHz ([14], [3] and literature quoted therein). In contrast, the high frequency parameters are critically affected by the frequency range. The uncertainty of ϵ_∞ is less than 5%, whereas that of the other parameters is probably in the of range 5% to 10% or even worse, depending on the relative magnitude of the corresponding dispersion amplitude.

Water. The dielectric properties of water were studied extensively in the past [20]. It was found, that the relaxation behaviour up to at least 60 GHz is governed by a single exponential ($\epsilon=78.36$, $\tau=8.27$ ps, $\epsilon_\infty=5.16$). On the high frequency side a second process is discussed controversially, and in a recent paper [21] it was suggested, that one Debye process suffices to fit the data up to 500 GHz.

Below 40 GHz our data also follow a single exponential. However, when analyzing the complete $\hat{\epsilon}(\nu)$ data set together with the far-infrared results of Hasted et al. [22], interpolated to 25°C, systematic deviations are found for a Debye or Cole-Cole fit. Only the assumption of an additional exponential ($\tau_2=1.02$ ps) yields a satisfactory result (cf. fig. 1). This is corroborated by our electrolyte studies which reveal a concentration dependence of τ_2 and $\Delta\epsilon_2$ corresponding to a distinct high frequency process.

Alcohols. Since the pioneering work of Garg and Smyth [23] the existence of three distinct dispersion processes, although based on a limited number of high frequency data, is well established for 1-propanol and its higher homologues. A similar behaviour must also be expected for methanol and ethanol, and indeed, there was early evidence for fast relaxation modes [24]. Data, however, were too scarce for an unambiguous separation of the relaxation steps.

With the information available now, including far-infrared data in the case of methanol [25], it turns

Table 1
Dielectric relaxation parameters of water and lower alcohols at 25°C

	ϵ_s	ϵ	τ_1 (ps)	ϵ_2	τ_2 (ps)	ϵ_3	τ_3 (ps)	ϵ_∞	ν_{\max} (GHz)	χ^2
H ₂ O	78.36 ^{a)}	77.97	8.32	6.18	1.02			4.49	409	0.10
MeOH	32.63 ^{b)}	32.50	51.5	5.91	7.09	4.90	1.12	2.79	293	0.0030
EtOH	24.35 ^{b)}	24.32	163	4.49	8.97	3.82	1.81	2.69	89	0.0056
1-PrOH	20.439 ^{c)}	20.43	329	3.74	15.1	3.20	2.40	2.44	89	0.0006
2-PrOH	19.385 ^{a)}	19.40	359	3.47	14.5	3.04	1.96	2.42	89	0.0005

^{a)} Ref. [18], ^{b)} Ref. [16], ^{c)} Ref. [19].

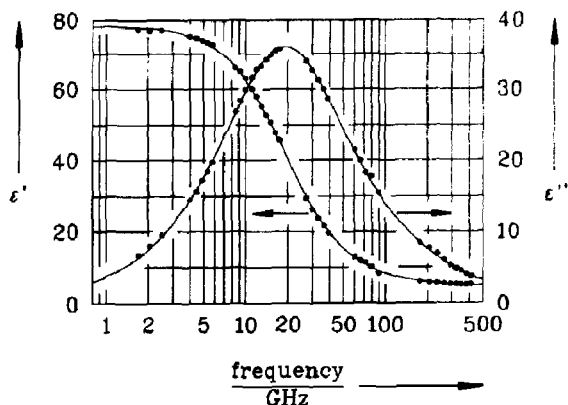


Fig. 1. Dielectric dispersion ($\epsilon'(\nu)$) and loss ($\epsilon''(\nu)$) spectrum of water at 25°C. Far-infrared data ($\nu > 150$ GHz) are obtained by interpolation from the data in ref. [22]. The solid lines are calculated with a two Debye relaxation model using the parameters of table 1.

out, that the assumption of three superimposed Debye processes gives the best description of the dielectric behaviour of all the alcohols studied here (cf. fig. 2). Taking a Cole-Cole distribution for the main dispersion step plus a high frequency exponential increases χ^2 by approximately a factor of two, and other models give an even worse fit, all of them showing systematic deviations from the data points.

The reasonable trend of ϵ_∞ when going from methanol to the other alcohols suggests that the lack of far-infrared data is not critical in the parameter estimation for ethanol and the propanols. This is corroborated by our relaxation times of 1-propanol, which agree very well with the results of Dutuit et al. [26] ($\tau_1 = 340$ ps; $\tau_2 = 15.3$ ps; $\tau_3 = 2.5$ ps), obtained by an elaborate analysis of time domain data below 12 GHz. The discrepancy to our ϵ_j parameters is due to their limited frequency coverage.

All liquids in table 1 show a dielectric behaviour characterized by a sum of exponentials. Due to the huge amplitude of the low frequency process, $\Delta\epsilon_1$, and because of the insufficient frequency range and precision of the existing data, the contribution of the fast processes was not detected in earlier papers. From the evidence of a synopsis of our work, we think that in all cases presented here, the fastest relaxation rate is connected to the dynamics of hydrogen bonding. Indeed, the short relaxation time of water,

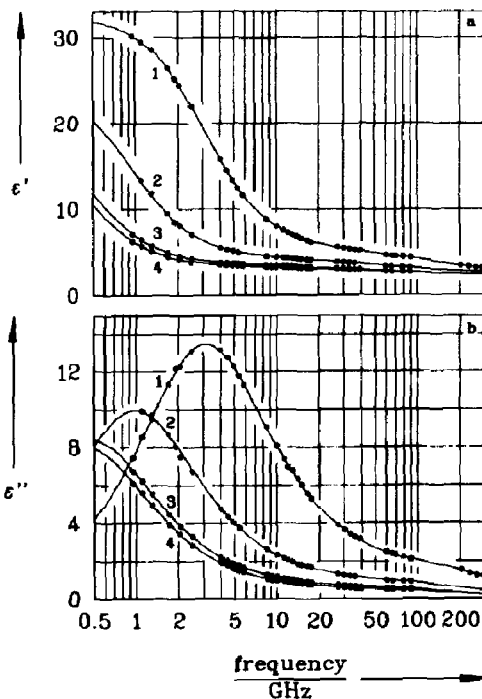


Fig. 2. Dielectric dispersion ($\epsilon'(\nu)$) (a) and loss ($\epsilon''(\nu)$) spectra (b) of methanol (1), ethanol (2), 1-propanol (3), and 2-propanol (4) at 25°C. Far-infrared data for methanol ($\nu > 150$ GHz) are taken from ref. [25]. The solid lines are calculated with a three Debye relaxation model using the parameters of table 1.

$\tau_2 = 1.02$ ps, and the alcohols, $1.1 \leq \tau_3 \leq 2.4$ ps, is close to the life time of a hydrogen bond in water, $\tau_{\text{HB}} = 0.54$ ps, deduced by Conde and Teixeira [27] from Rayleigh scattering experiments. The origin may be a flipping motion of "free" OH groups between two acceptor sites and/or the breaking and reforming of a given hydrogen bond in a translational motion. The dependence of τ_3 on the molecular structure of the alcohols and the fact, that its amplitude, $\Delta\epsilon_3$ markedly exceeds $\Delta\epsilon_2$ do not support the relaxation mechanism suggested by Garg and Smyth [23], who assume only OH-group rotation in alcohol monomers to contribute to $\Delta\epsilon_3$.

The intermediate dispersion step found for the alcohols, $\Delta\epsilon_2$ and τ_2 , is compatible with single molecule reorientation. Evidence from vibrational spectroscopy [28] suggests that the concentration of monomers in short chain alcohols is very low. Therefore mostly molecules on the ends of hydrogen-

bonded chains should contribute to this relaxation mode. Also the ratio of single particles correlation time over viscosity, τ_2^{SP}/η , is not proportional to molecular size. This excludes simple rotational diffusion, which would be expected for the motion of a free molecule.

It is well known [1] that the mechanism responsible for the main dispersion step of the alcohols and also of water involves cooperative motions. It is the low probability for an end-standing molecule of the polymeric alcohol chain to find an appropriate donor/acceptor site on an adjacent chain, which is the rate determining step of this relaxation process. This applies also for water. However, the possibility to form four hydrogen bonds greatly enhances the reorientational motion, yielding a time constant of the cooperative process which is undiscernible from the reorientational time of a water molecule (approximated $3\tau_{\text{NMR}} = 7.5$ ps [29]).

It is evident that even in the framework of empirical relaxation models, the inclusion of far-infrared data is desirable for a precise description of the permittivity spectra, although an upper frequency limit of ≈ 100 GHz gives satisfactory results in most cases. The dispersion amplitude of the high frequency processes both in water and the alcohols are small, nevertheless they might be one reason for the fast electron transfer rates found in these solvents [12].

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