Dielectric relaxation spectroscopy of ion–solvent interactions in formamide and N-methylformamide

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Abstract

In this contribution, which complements a previous publication on the dielectric relaxation of electrolytes in N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) [Wurm B., Münsterer M., Richardi J., Buchner R., Barthel J., J. Mol. Liq. 119 (2005) 97], we explore the effect of the electrolytes Bu_4NClO_4, $LiClO_4$, $NaClO_4$, and $NaCl$ on structure and dynamics of formamide (FA) and N-methylformamide (NMF) at 25 °C.
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1. Introduction

Dielectric relaxation spectroscopy (DRS) which involves the measurement of the complex dielectric permittivity

$$\hat{\varepsilon}(v) = \varepsilon'(v) - i\varepsilon''(v) \tag{1}$$

with ε' as relative permittivity and ε'' as loss of the sample as a function of the frequency v of an applied electromagnetic wave, is especially suited for investigating the cooperative dynamics of H-bonding systems [2–4]. Additionally, the technique allows the determination of solvation numbers and is a powerful method to detect possible ion–ion interactions [3,5–7]. Note, that for an electrolyte solution only the total loss

$$\eta''(v) = \varepsilon''(v) + \kappa/(2\pi v \varepsilon_o) \tag{2}$$

is measurable, where $\kappa/(2\pi v \varepsilon_o)$ represents the conductivity contribution from the electrolyte; κ is the specific conductivity of the sample and ε_o is the permittivity of free space [8].

2. Experimental and data analysis

The dielectric permittivity, $\varepsilon'(v)$, and total loss, $\eta''(v)$, spectra were recorded at 25.00 °C in the frequency range $0.2 \leq v/GHz \leq 89$

with a set of four waveguide interferometers (≥ 8.5 GHz) [5,9] and a time-domain reflectometer (TDR, ≤ 6 GHz) [10]. An accuracy of 2% in ε' and ε'', relative to the static permittivity of the sample, ε, was achieved. A typical set of spectra is shown in Fig. 1. The conductivity, κ, of the samples was determined with capillary cells according to Ref. [11]. The densities, ρ, were determined with a vibrating-tube densimeter (Paar DMA). Viscosities, η, were measured with an Ubbelohde viscometer (Schott). The data for ρ, κ, and η are summarized in Table 1.

All conceivable relaxation models based on $1 \leq N \leq 4$ relaxation processes were fitted to the experimental $\hat{\varepsilon}(v)$ by a procedure described in Ref. [12]. For all solutions in FA and NMF, except NaCl in FA, it was found that $\hat{\varepsilon}(v)$ is best fitted by the superposition of a dominating Cole–Cole (CC) equation (amplitude $S_{s1} = \varepsilon_s - \varepsilon_{s1}$ relaxation time τ_{s1}, width parameter α_{s1}) with a small high-frequency contribution that can be formally described with a Debye (D) equation ($S_{s2} = \varepsilon_{s1} - \varepsilon_{\infty}$, τ_{s2}) so that

$$\hat{\varepsilon}(v) = \frac{\varepsilon_s - \varepsilon_{s1}}{1 + (i2\pi v \tau_{s1})^{1-\alpha_{s1}}} + \frac{\varepsilon_{s1} - \varepsilon_{\infty}}{1 + i2\pi v \tau_{s2}} + \varepsilon_{\infty} \tag{3}$$

For consistency all $\hat{\varepsilon}(v)$ data of the pure solvents accumulated in our laboratory were pooled and also fitted with Eq. (3). The spectra of the investigated electrolytes in NMF did not allow us a self-consistent separation of the intermediate solvent mode at ~ 20 GHz ($\tau \approx 8$ ps) detected in Refs. [13,14] and associated with

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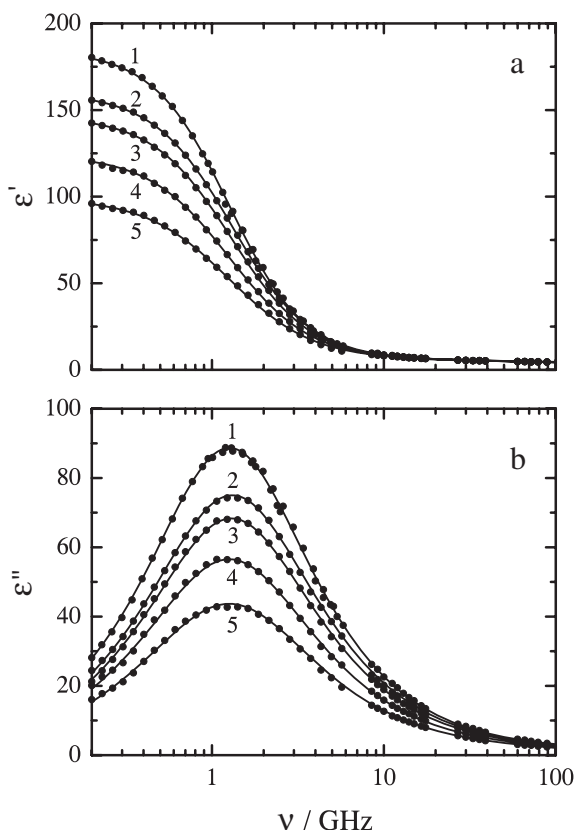 *E-mail address:* Josef.Barthel@chemie.uni-regensburg.de (J. Barthel).

Fig. 1. Permittivity, $\varepsilon'(\nu)$ (a), and loss spectra, $\varepsilon''(\nu)$ (b), of Bu$_4$NClO$_4$ solutions in N-methylformamide at 25 °C and concentrations $c=0.0$ mol L^{-1} (1); 0.15 mol L^{-1} (2); 0.24 mol L^{-1} (3); 0.46 mol L^{-1} (4); 0.76 mol L^{-1} (5).

the reorientation of individual NMF molecules. The relaxation time distribution parameter α_{s1}, which accounts for deviations from Debye relaxation on the low-frequency side of the experimental spectra masks this intermediate NMF relaxation.

As discussed in detail in Refs. [1,15,16], the observed excess absorption at $\nu>50$ GHz is essentially due to inertial effects and cannot be interpreted as a proper relaxation process of distinct physical origin. Also, due to the limited frequency coverage of our experiments, the 'infinite-frequency' limit of the dispersion region, ε_∞, can only be treated as an adjustable parameter. ε_∞ not only contains intramolecular polarizability but partly also inertial effects, librational modes and contributions from the hydrogen-bond dynamics [17,18]. As a consequence, from the parameters of the CC+D model, Eq. (3), we will only discuss the cooperative relaxation time, τ_{s1}, and the total solvent amplitude, $S_s=\varepsilon_s-\varepsilon_\infty$.

Surprisingly, the CC+D model is not appropriate for NaCl solutions in FA, see Fig. 2. The best formal description of the experimental data is achieved with a superposition of three Debye (3D) equations

$$\hat{\varepsilon}(\nu) = \frac{\varepsilon-\varepsilon_s}{1+i2\pi\nu\tau_{IP}} + \frac{\varepsilon_s-\varepsilon_{s1}}{1+i2\pi\nu\tau_{s1}} + \frac{\varepsilon_{s1}-\varepsilon_\infty}{1+i2\pi\nu\tau_{s2}} + \varepsilon_\infty \qquad (4)$$

As will be seen below, the additional low-frequency process of amplitude $S_{IP}=\varepsilon-\varepsilon_s$ and relaxation time τ_{IP} can be reasonably attributed to solute ion pairs (IP).

The parameters of Eqs. (3) and (4) and the corresponding reduced error function, χ_r^2, are summarized in Table 2 for FA solutions and in Table 3 for NMF solutions. Note that with the exception of NaCl/FA the values of the static permittivity of the solution, ε, and of the solvent in the solution, ε_s, are identical.

3. Results and discussion

3.1. Cooperative solvent dynamics

Electrolytes in DMF and DMA induce a rise of the rotational correlation time, $\tau'_{s1}\approx2\tau_{s1}/3$, proportional to the change of solution viscosity. This behaviour is described by the Stokes–Einstein–Debye equation [1] and typical for rotational diffusion of individual solvent molecules in a viscous bath. As can be seen from Figs. 3 and 4 the cooperative solvent relaxation times τ_{s1} of FA and NMF behave differently.

According to Table 1 the viscosity of FA solutions rises significantly with electrolyte concentration in a smooth but salt-specific way (at $c=0.7$ mol L^{-1} $\eta(c)/\eta(0)=1.64$ for Bu$_4$NClO$_4$, 1.29 for LiClO$_4$, 1.45 for NaCl). τ_{s1} also rises for all investigated electrolytes, see Fig. 3. However, for the investigated inorganic salts, including NaClO$_4$ [13], the increase of the solvent relaxation time is only weak ($\tau_{s1}(c)/\tau_{s1}(0)=1.03$ at 0.7 mol L^{-1}) and independent of the cation. On the other hand, Bu$_4$NClO$_4$ induces a major increase, $\tau_{s1}(0.7$ M$)/\tau_{s1}(0)=1.44$, but is still below $\eta(c)/\eta(0)$.

NMF solutions also exhibit an electrolyte-specific rise of solution viscosity with c, see Table 1. However, $\tau_{s1}(c)$ drops significantly when inorganic salts are dissolved. According to Fig. 4, the effect is electrolyte specific, with a significant difference between NaCl and NaClO$_4$, whereas LiClO$_4$ is intermediate. On the other hand, after an apparent minimum of τ_{s1} at low c the solvent relaxation time of Bu$_4$NClO$_4$ solutions resumes the value observed for the pure solvent. In line with the

Table 1
Densities, ρ, conductivities, κ, and viscosities, η, of Bu$_4$NClO$_4$, LiClO$_4$ and NaCl of the solutions at 25°

Solvent: formamide				Solvent: N-methylformamide			
c	ρ	κ	η	c	ρ	κ	η
0	1.12913	0	3.29	0	0.99841	0	1.73
Bu$_4$NClO$_4$				*Bu$_4$NClO$_4$*			
0.14394	1.12388	0.235	3.57	0.15091	1.00124	0.450	1.86
0.27945	1.11979	0.374	3.89	0.24157	1.00241	0.627	1.96
0.49709	1.11269	0.510	4.53	0.45586	1.00522	0.892	2.25
0.79219	1.11034	0.580	5.95	0.75847	1.00925	1.022	2.88
LiClO$_4$				*LiClO$_4$*			
0.13353	1.13592	0.281	3.45	0.11902	1.00702	0.414	1.84
0.30067	1.14683	0.610	3.76	0.31363	1.01955	0.916	2.05
0.65708	1.16274	1.039	4.16	0.56209	1.03544	1.368	2.36
1.04954	1.18549	1.381	4.95	0.9342	1.05909	1.755	2.93
NaCl				*NaCl*			
0.1904	1.1355	0.399	3.62	0.1203	1.0030	0.394	1.84
0.3648	1.1413	0.669	3.97	0.2432	1.0074	0.688	1.99
0.6228	1.1498	0.964	4.59	0.3461	1.0111	0.881	2.12
0.7346	1.1534	1.062	4.89	0.4927	1.0164	1.091	2.33

Units: c in mol L^{-1}; κ in Ω^{-1} m^{-1}; η in 10^{-3} Pa s.