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Broadband dielectric response of the ionic liquid *N*-methyl-*N*-ethylpyrrolidinium dicyanamide

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Dielectric relaxation measurements as a function of temperature, and of concentration in a non-coordinating solvent, the first reported for an ionic liquid, indicate a crossover in the relaxation mechanism due to varying levels of ion aggregation and the interplay of formation kinetics and relaxation dynamics of associates.

The significance of ionic liquids (ILs) as exciting new materials with potential applications in chemical synthesis, batteries, separations, and so on, is attested to by the plethora of papers, reviews and monographs that have appeared in recent years.[1–4] Most of the work in this area to date has been understandably in synthesis, reactions and, to a lesser extent, the characterization of the general physical properties of these diverse and fascinating liquids.

One of the most important attributes of any new solvent is its relative permittivity or dielectric constant, ε.[5] This is because ε plays a central role in determining the degree of ionization of dissolved solutes,[6,7] which in turn is critical for many of the solvent's prospective technological applications. Dielectric constants have also been widely used for the correlation and prediction of solvent behaviour.[7–9]

In spite of this importance, with the notable exception of a recent preliminary study by Wakai *et al.*,[10] who reported ε values for five imidazolium-based ILs at 25 °C, no direct measurements of the ε values of ILs have been reported and nothing is known about their temperature dependence. A number of estimates of effective polarity have been made based on solvatochromic probes.[11] However these estimates are only approximate and mostly indicate a higher polarity (similar to acetone to methanol) than the direct measurements,[10] which suggest polarities more akin to tetrahydrofuran and *tert*-butyl alcohol.

As for all highly conducting liquids, ε cannot be measured for ILs using traditional capacitance methods operating in the kHz and MHz range as the cells employed are in essence short-circuited. The only viable method for determining ε for such liquids is dielectric relaxation spectroscopy (DRS) in the microwave (GHz) region.[12,13] The quantity so measured is the complex permittivity $\hat{\varepsilon}(\nu)$, which consists of an in-phase component $\varepsilon'(\nu)$, known as the dielectric dispersion, and an out-of-phase component $\varepsilon''(\nu)$, the dielectric loss, with $\hat{\varepsilon}(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$.[14] The static dielectric constant is obtained as the zero frequency limit of the dispersion curve: $\varepsilon = \lim \varepsilon'(\nu \rightarrow 0)$. For a liquid of conductivity σ, only the total loss $\eta''(\nu) = \varepsilon''(\nu) + \sigma/(2\pi\nu\varepsilon_0)$ can be measured, where ε_0 is the permittivity of free space. The conductivity can be obtained as an adjustable parameter from a fit of the experimental loss curve. The values so calculated are equal (within 1–2%) to those obtained by conventional conductometric measurements.[14]

In addition to providing access to static properties, DRS probes the contributions from any dipolar species present, thus providing insights into solution equilibria, structures and dynamics. Activation energies can be derived from the temperature dependence of the dielectric response, but are lacking for ILs as the specialized equipment and techniques required are outside the capabilities of most laboratories.[12,13]

For this first study into the concentration and temperature dependence of an ionic liquid a coaxial reflection technique was used over a frequency range $\nu_{\min} \leqslant \nu/\mathrm{GHz} \leqslant 20$.† The value of $\nu_{\min}$ was governed by the conductivity of the sample solution (and hence the temperature and concentration) but was in the range $0.3 \leqslant \nu_{\min}/\mathrm{GHz} \leqslant 2$. Nitrogen, a mercury short, and benzonitrile were used as the dielectric standards for the pure IL and its more concentrated mixtures with dichloromethane (DCM). For the more diluted solutions, DCM was used as an additional reference.

The IL chosen for the present study was *N*-methyl-*N*-ethylpyrrolidinium dicyanamide, $\mathrm{p}_{1,2}$dca. This compound is characterized by a low viscosity, which makes it particularly attractive for various applications in synthetic chemistry.[15] Compared to common IL anions such as $\mathrm{BF_4}^-$ or $\mathrm{PF_6}^-$, dicyanamide has a permanent dipole moment and thus facilitates the investigation of liquid dynamics by dielectric spectroscopy.

Quantitative analysis of the DR spectra of neat ILs is not trivial, as noted by Wakai *et al.*[10] In essence, DR spectra reflect the presence and molecular motions of all dipolar species present. In associated liquids, however, such motions are highly correlated and therefore cannot always be assigned to a well-defined dipole but rather reflect the kinetics of network rearrangement. Especially for liquids that have many interaction sites, leading to a variety of possible dipolar aggregates of similar stability, DR is not likely to be governed by reorientation phenomena of discrete, stable species at typical DR time scales. To further investigate possible contributions to the spectrum of the neat IL it is useful to study the effects of temperature and dilution (with a suitable solvent).

Accordingly, measurements were performed over a range of temperatures from 15 to 55 °C. The spectrum of pure $\mathrm{p}_{1,2}$dca

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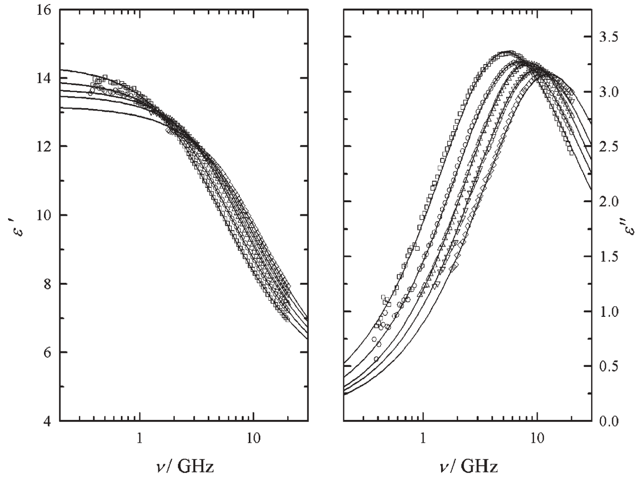

Fig. 1 Complex dielectric spectra (left: ε′; right: ε″) of $p_{1,2}$dca at temperatures from 15 (□) to 55 °C (◇). Solid lines represent HNE fits.

obtained as function of temperature (Fig. 1) could, after subtraction of the conductivity contribution be fitted using the Havriliak–Negami equation (HNE, eqn (1)),[14]

$$\hat{\varepsilon}(\nu) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{[1 + (\mathrm{i}\ 2\pi\nu\ \tau_0)^\alpha]^\beta} \qquad (1)$$

where ε_∞ is the infinite frequency permittivity, τ_0 is the average relaxation time, and α and β are empirical relaxation-time distribution (shape) parameters.

The static dielectric constant for $p_{1,2}$dca so obtained follows an exponential relationship: $\ln\varepsilon = a - b \cdot T$ (a = 3.254, b = 0.00205 K^{-1}; R^2 = 0.982; Fig. 2a) over this temperature range. The value at 25 °C, ε = 13.96 ± 0.28, was within the range of 9 to 15 reported by Wakai *et al.* for their imidazolium-based salts and clearly indicates that neat ILs are in general solvents of modest polarity, with dielectric constants corresponding roughly to those of medium chain-length ketones or alcohols.[5]

The effect of temperature on the average relaxation time (Fig. 2b), reflected in the frequency shift of the maximum in the loss spectra (Fig. 1), can be described by an Arrhenius equation (eqn (2)),

$$\ln(\tau_0/s) = \ln(\tau^*/s) + \frac{E_\mathrm{a}}{RT} \qquad (2)$$

where E_a is the average activation energy of the relaxation process. The plot of $\ln(\tau)$ *vs* T^{-1} (Fig. 2b) is closely linear (R^2 = 0.9997) and gives E_a = 18.6 kJ mol^{-1}. This value is typical for cooperative dipole rearrangements in hydrogen bonded liquids (H_2O: 15.9 kJ mol^{-1},[16] MeOH: 13.0 kJ mol^{-1},[17] EtOH 19.9 kJ mol^{-1}[17]).

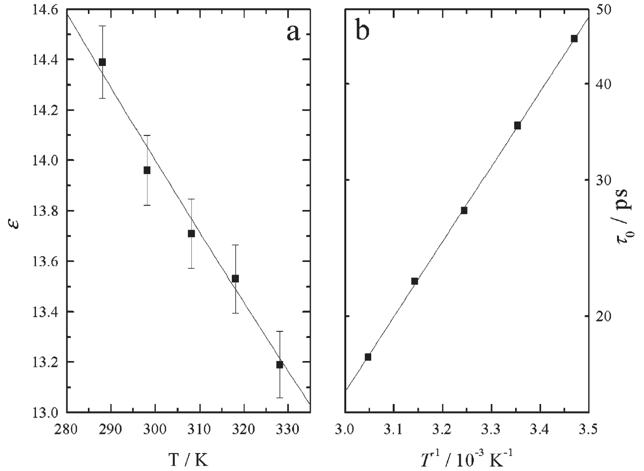

Fig. 2 Temperature dependence of (a) the dielectric constant (error bars: ±1%) and (b) the relaxation time (note the logarithmic scale) derived from fits to the HNE.

Analysis of the HNE shape parameters α (the symmetric broadening) and β (the asymmetric broadening) reveals that α (0.13 ± 0.01) was unaffected by temperature whereas β increased slightly from 0.64 at 15 °C to 0.71 at 55 °C. This indicates a redistribution of the total dielectric response towards shorter relaxation times with temperature, maybe arising from a higher population of high frequency modes, possibly analogous to the ~2.6 and ~0.24 ps processes described[18] for a related IL. With increasing temperature the dispersion curve moves towards higher frequencies. However, the band shape of the present dielectric spectra is not fully revealed by the current experiments, which are limited to 20 GHz. Further measurements at higher frequencies, which require different apparatus, will ultimately be needed.

The spectra of neat $p_{1,2}$dca (Fig. 1) suggest that the mechanism of dielectric relaxation in the IL does not change significantly over the temperature range studied. As noted above, E_a is not temperature dependent and is close to those observed for cooperative network rearrangement processes in other associated dipolar liquids. If a similar mechanism governs the dielectric relaxation of $p_{1,2}$dca, dramatic changes should occur upon dilution with an inert, weakly coordinating solvent.

Dichloromethane (DCM) has been used as a diluent to investigate dielectric relaxation in liquids of medium polarity[19] and $p_{1,2}$dca is fully miscible with DCM. Accordingly, the dielectric spectra of four solutions at concentrations ranging from 0.08 to 1.78 mol L^{-1} were recorded at 25 °C. Pure DCM shows only one significant relaxation mode, at ~2 ps,[19] which is well outside the present region of interest, so the spectra of the $p_{1,2}$dca/DCM mixtures could be easily corrected for the (rather small) contribution from DCM (Fig. 3).

While postponing a detailed analysis of the spectra until high frequency data are known, the general trends observed here still provide insights into the role of ionic aggregates in ILs. The relaxation characteristic of the neat IL, centred at ~7 GHz, is maintained even at significant dilutions (*i.e.* at 1.78 mol L^{-1}, corresponding to an ideal volume fraction of the IL ~0.31; Fig. 3b, curve 2). On further dilution, significant broadening occurs, caused by a new dispersion step at ~1.2 GHz (Fig. 3b, curves 3–5). This process dominates the dielectric spectrum at the two lowest concentrations studied (Fig. 3b, curves 4 and 5). Its frequency maximum is typical for ion pairs or similar aggregates. Note that the noise in these spectra is largely due to the limited signal/noise ratio of the experimental setup for highly conducting samples of low permittivity and is within the limits of error currently achievable by DRS. Futher information, including equilibrium constants between the dipolar species present in the mixtures could be obtained from a detailed analysis of the amplitudes of the individual modes. However, this requires data at higher frequencies not accessible by coaxial reflection techniques to accurately

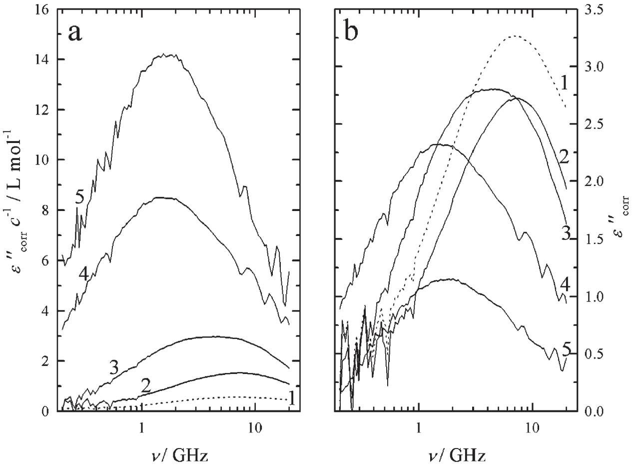

Fig. 3 Dielectric loss spectra of $p_{1,2}$dca–DCM mixtures corrected for the bulk solvent contribution, normalized to $p_{1,2}$dca concentration (3a); unnormalized (3b); 1: neat $p_{1,2}$dca, 2: 1.78 M, 3: 0.94 M, 4: 0.27 M, 5: 0.08 M.

account for the solvent (DCM) contributions. For now, we can give only loss spectra normalized with respect to the IL concentration (Fig. 3a). These spectra show that a higher proportion of IL molecular ions is present as individually contributing dipoles at low concentrations in DCM, assuming relaxation in a constant dielectric medium. The dielectric constant of pure DCM ($\varepsilon = 9.2$) is similar to that of the IL. Those of the mixtures are much higher than expected from simple mixing rules, reflecting changes in the loss curve *via* the Kramers–Kronig relation.[12]

Further evidence for the formation of aggregates can be obtained from the molar conductivities of the mixtures. Whereas neat $p_{1,2}$dca, like many ILs,[20,21] shows a simple exponential dependence ($R^2 = 0.9993$) of the conductivity as a function of temperature far above the glass transition point, a distinct maximum in conductivity for the mixtures was observed at ~1.7 M. Viscosities of $p_{1,2}$dca–DCM mixtures, which will affect the conductivity, have not been measured, but would not be expected to show major departures from simple mixing rules with composition. Therefore the observed maximum in the molar conductivity suggests that the number of charge carriers relative to the total amount of IL in the mixtures peaks at ~1.7 M. At lower concentrations, neutral associates, which were also postulated from the investigation of transport properties,[21] might dominate the solutions in DCM. Such associates still have a net dipole moment, but cannot contribute to charge transport in the mixtures. Similar behaviour has been observed in the molar conductivity trends in polymer electrolyte systems which are notoriously prone to ion-association.[22]

In summary, the main dielectric response of the neat IL appears to reflect the correlated rearrangement of a molecular network, similar to that of non-ionic hydrogen-bonded liquids. There is no evidence of relaxation processes of individual, stable aggregates in the neat IL. Upon dilution with DCM this continues to be the main relaxation process. Aggregates are only formed in much more diluted solutions giving rise to a dielectric dispersion at ~1.2 GHz.

A more comprehensive investigation is underway, covering the high frequency part of the dielectric spectrum (>20 GHz), which is needed for a more detailed analysis of the mixtures and the pure IL.

Notes and references

† The system is based on a Hewlett-Packard Model 85070 M Dielectric Probe system connected to a HP 8720D Vector Network Analyzer (VNA). Procedures for calibrating the instrument and recording the spectra are described in detail elsewhere.[13,14] All spectra were measured at least twice using separate calibrations. Sample temperature was controlled with a Hetofrig (Denmark) thermostat-circulator to ± 0.02 °C with an accuracy of ~0.05 °C. $p_{1,2}$dca was prepared, purified and characterized following procedures published previously.[15] Solutions in DCM were prepared by mass under dry conditions using solvent of analytical quality. Molar concentrations were derived from the densities of the components (determined by vibrating tube densitometry) assuming ideal mixing.

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