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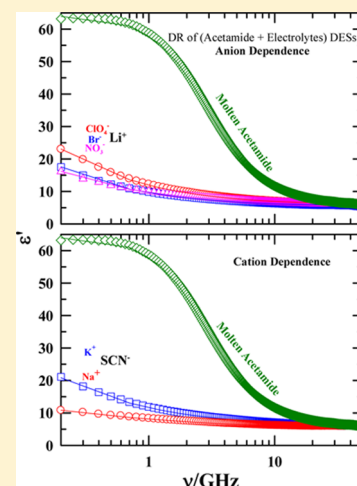
Dielectric Relaxations of (Acetamide + Electrolyte) Deep Eutectic Solvents in the Frequency Window, $0.2 \leq \nu/\text{GHz} \leq 50$: Anion and Cation Dependence

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S Supporting Information

ABSTRACT: Dielectric relaxation (DR) measurements in the frequency range $0.2 \leq \nu/\text{GHz} \leq 50$ have been carried out for neat molten acetamide and six different (acetamide + electrolyte) deep eutectic solvents (DESSs) for investigating ion effects on DR dynamics in these ionic DESSs. Electrolytes used are lithium salts of bromide (LiBr), nitrate (LiNO₃), and perchlorate (LiClO₄); sodium salts of perchlorate (NaClO₄) and thiocyanate (NaSCN); and potassium thiocyanate (KSCN). With these electrolytes acetamide forms DESSs approximately at an 80:20 mol ratio. Simultaneous fits to the measured permittivity (ϵ') and loss (ϵ'') spectra of these DESSs at ~ 293 K require a sum of four Debye (4-D) processes with relaxation times spread over picosecond to nanosecond regime. In contrast, DR spectra for neat molten acetamide (~ 354 K) depict 2-D relaxation with time constants ~ 50 ps and ~ 5 ps. For both the neat and ionic systems, the undetected dispersion, $\epsilon_\infty - n_D^2$, remains to be ~ 3 – 4 . Upon comparison, measured DR dynamics reveal pronounced anion and cation effects. Estimated static dielectric constants (ϵ_0) from fits for these DESSs cover the range $12 < \epsilon_0 < 30$ and are remarkably lower than that ($\epsilon_0 \sim 64$) measured for molten acetamide at ~ 354 K. Hydrodynamic effective rotation volumes (V_{eff}) estimated from the slowest DR relaxation time constants vary with ion identity and are much smaller than the molecular volume of acetamide. This decrease of ϵ_0 and V_{eff} is attributed respectively to the pinning of acetamide molecules by ions and orientation jumps and undetected portion to the limited frequency coverage employed in these measurements.



I. INTRODUCTION

Deep eutectic solvents (DESSs), solvents that are multi-component melts at a temperature much lower than the individual melting points of the mixture components, are increasingly finding technological as well as industrial applications.^{1–5} Many of these solvents are often biodegradable and thus offer a much cleaner alternative to the conventional organic solvents. In addition, the process of obtaining DESSs through simple mixing of components followed by gentle heating offers enormous flexibility for engineering a medium suitable to a particular chemical reaction. This, and the cost-effectiveness in producing and handling the DESSs provide the necessary economic viability for applications in electro-deposition, biocatalysis, cosmetic and pharmaceutical industries, biomass treatment and preparation of functional materials.^{1–8} Being nonaqueous, DESSs also offer a broad operational window for carrying out moisture sensitive reactions and promote green chemistry via minimizing the ecological footprint.

Solvent designing for tailoring a reaction demands a thorough understanding of medium structure and dynamics because of the proven interrelationship between reaction rate and medium effects.^{9–13} Although several earlier studies^{14–20} have suggested microheterogeneous solution structure for

several DESSs made of amide and electrolyte, sophisticated techniques such as neutron and X-ray scattering have not been employed yet to reveal the extent of spatial correlations present in such systems. A few recent fluorescence spectroscopic measurements combined with computer simulations have provided indirect evidence of spatial heterogeneity in several (amide + electrolyte) DESSs.^{21–23} However, study of dynamic (temporal) heterogeneity via direct measurements of ultrafast solution dynamics for these systems has not been performed so far, although fast fluorescence spectroscopic measurements have revealed significant decoupling between relaxation rates and medium viscosity.^{24–26} In addition, study of collective low frequency dynamics of such systems has just begun²⁷ with an aim to decipher the coupling between collective low frequency dynamics and solution heterogeneity.^{28–32} Dielectric relaxation spectroscopy (DRS) is an important experimental technique that can probe both the inherent medium dynamics and its connection to solution structure,^{33–39} and complement information accessed via time-dependent fluorescence Stokes shift (TDFSS) measurements.^{40–44} This motivates the current

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DRS measurements with the focus being placed on relaxation in the gigahertz (GHz) region where interconnection between the fast solution dynamics observed via DRS and TDFSS techniques is the most prominent.

We note, however, here that the present measurements are not the first DRS measurements for these systems as dielectric relaxations of a few (amide + electrolyte) DESs within the frequency window $10^{-7} \leq \nu/\text{MHz} \leq 10^2$ have already been reported.^{19,20} These relatively low frequency measurements have suggested inhomogeneous relaxation kinetics and a colossal static dielectric constant (ϵ_0). Temperature-dependent relaxation times detected in these measurements have been found to spread over half-of-a-second to a couple of nanoseconds, suggesting extremely slow relaxation originating from movements of nanosized domains formed via the interaction between amide molecules and electrolytes.^{19,20} Our frequency coverage ($0.2 \leq \nu/\text{GHz} \leq 50$) cannot probe these slow dynamics of aggregated structures, and hence we refrain from drawing any conclusion on relaxation dynamics possessing time scales longer than approximately a nanosecond. Because faster relaxation time scales are more relevant for simple chemical reactions (for example, cis–trans isomerization) as relevant reactive modes are coupled to fast density fluctuations on a barrier top,^{45–47} DRS measurements with the frequency coverage $0.2 \leq \nu/\text{GHz} \leq 50$ bridge an important information gap for dipolar density fluctuations possessing time scales between nanosecond and subhundred picoseconds. In addition, we report here the DR relaxation of neat molten acetamide and compare the data with those for several (acetamide + electrolyte) DESs to uncover differences in interaction between ions and acetamide (CH_3CONH_2) molecules in these multicomponent melts. Such a study has not been done before and constitutes the main theme of the present paper.

Electrolytes used here readily form DESs with acetamide approximately at the same mole ratio (acetamide:electrolyte::80:20) and remain as a stable liquid at ~ 293 K after melting at a relatively higher temperature and subsequent cooling.^{21–27} Six DESs with the following compositions were considered: (i) $0.78\text{CH}_3\text{CONH}_2 + 0.22\text{LiBr}$, (ii) $0.78\text{CH}_3\text{CONH}_2 + 0.22\text{LiNO}_3$, (iii) $0.75\text{CH}_3\text{CONH}_2 + 0.25\text{NaSCN}$, (iv) $0.75\text{CH}_3\text{CONH}_2 + 0.25\text{KSCN}$, (v) $0.81\text{CH}_3\text{CONH}_2 + 0.19\text{LiClO}_4$, and (vi) $0.81\text{CH}_3\text{CONH}_2 + 0.19\text{NaClO}_4$. Except for the NaClO_4 -containing DES, details regarding sample preparation for other DESs could be found elsewhere as these systems have already been studied via fluorescence^{21,22,24–26} and femtosecond Raman-induced Kerr effect spectroscopic (fs-RIKES)²⁷ techniques. $[0.81\text{CH}_3\text{CONH}_2 + 0.19\text{NaClO}_4]$ DES was obtained by following the method employed for $[0.81\text{CH}_3\text{CONH}_2 + 0.19\text{LiClO}_4]$ system. Measured glass transition temperatures (T_g 's) of these DESs are in the ~ 190 – 200 K range,²¹ and therefore, our measurement temperature is ~ 100 K above the respective T_g 's but much lower than the melting temperatures of the individual components. Note here that the current measurements and subsequent comparisons have been made among multicomponent melt systems where compositions slightly vary. This slight mismatch is deliberately allowed to ensure a qualitative comparison of the measured DR time scales with those observed earlier in either time-resolved fluorescence^{21,24,25} or fs-RIKES²⁷ measurements. This assumes importance given that the frequency window employed here is not sufficiently wide for detecting the full DR dynamics, and

relaxation parameters have been obtained via fits to model functions. In addition, these compositions correspond to approximately 25–30 electrolyte molecules per 100 acetamide molecules, and as a result, drastic variation in relaxation dynamics due to a small variation in electrolyte concentration is not expected.

II. EXPERIMENTAL DETAILS

i. Materials and Method. Acetamide ($\geq 98\%$, Merck, India), sodium thiocyanate ($\geq 99\%$, Sigma-Aldrich), potassium thiocyanate ($\geq 99\%$, Sigma-Aldrich), lithium nitrate ($\geq 99\%$, SRL, India), lithium bromide ($\geq 99\%$, Sigma-Aldrich), lithium perchlorate ($\geq 99\%$, Fluka), and sodium perchlorate ($\geq 98\%$, Alfa aesar) were vacuum-dried (~ 300 K) overnight before use. Briefly, ~ 10 g of sample was prepared for each composition by quickly transferring the required amounts of each of these compounds in a 20 mL sample vial at room temperature. Sample preparations and measurements were carried out in a tightly humidity-controlled (humidity level maintained to 37%) laboratory environment. Subsequently, the sample vials were sealed and heated slowly to ~ 350 K until it formed a uniform melt. Each of these molten samples was then allowed sufficient time to attain room temperature (293 ± 0.5 K) before any measurements. Refractive indices (n_D) were measured by using aliquots of these samples by employing an automated temperature-controlled refractometer (RUDOLPH, J357). DR measurements for neat molten acetamide were carried out after carefully melting solid acetamide by employing a heating plate (MS-H-Pro from SCIOGEX, USA) and maintaining the temperature at $T = 354 \pm 0.5$ K.

ii. DR Measurement Details. The complex, frequency (ν)-dependent relative permittivity, $\epsilon^*(\nu)$, is given by the following relation^{48,49}

$$\epsilon^*(\nu) = \epsilon'(\nu) - \left[i\epsilon''(\nu) + \frac{i\kappa}{2\pi\epsilon_p\nu} \right] \quad (1)$$

where κ denotes the dc conductivity of the medium and ϵ_p is the permittivity of free space. $\epsilon'(\nu)$ represents the real part of the complex permittivity whose zero frequency limit is the static dielectric constant of the medium, $\epsilon_0 = \epsilon(\nu \rightarrow 0)$. The $1/\nu$ divergence at $\nu \rightarrow 0$ limit contained in eq 1 makes an accurate determination of ϵ_0 nontrivial for conducting solutions such as the present ones. Large viscosity and slow dynamics of these DESs^{21,24,25,27} further complicate the estimation of ϵ_0 via extrapolation to the zero frequency limit of the measured frequency-dependent data. The permittivity at infinite frequency, $\epsilon_\infty = \epsilon(\nu \rightarrow \infty)$, represents the contributions from intramolecular polarizability and the intermolecular vibrations and appears at the higher frequency regime. Because the highest frequency probed by the present measurements is 50 GHz, the inaccessible portion beyond 50 GHz is contained in the measured ϵ_∞ . Note for complete measurements, $\epsilon_\infty \approx n_D^2$, where no dispersion component remains undetected. The imaginary part, $\epsilon''(\nu)$, represents the dielectric loss component and describes the dissipation of energy within the system originating from the interaction between the externally applied frequency-dependent electric field and the dipole fluctuations of the medium.

Approximately 8 mL of the thermally equilibrated molten sample (DESs and neat acetamide) was used for measurements in each case. Dielectric relaxation measurements were performed using a PNA-L network analyzer (N5230C)

combined with a probe kit (85070E) operating in the frequency range $0.2 \leq \nu/\text{GHz} \leq 50$. Air, shorting block, and water were employed as open, short, and load, respectively. dc conductivities (κ values) for DESs were measured separately, and the measured values were used in subsequent fits as initial guesses for obtaining the best possible mathematical descriptions of the experimental data. The temperature was maintained within ± 0.5 K throughout all measurements.

iii. Data Analysis. $\epsilon^*(\nu)$ so obtained for various DESs were then fitted to the Havriliak–Negami (HN) equation,⁴⁸

$$\epsilon^*(\nu) = \epsilon_\infty + \sum_{j=1}^n \frac{\Delta\epsilon_j}{[1 + (i2\pi\nu\tau_j)^{1-\alpha_j}]^{\beta_j}} \quad (2)$$

where $0 \leq \alpha_j < 1$ and $0 < \beta_j \leq 1$ and $\Delta\epsilon_j$ denotes the magnitude of the dispersion at the j th relaxation step with the time constant, τ_j . Note $\alpha_j = 0$, $\beta_j = 1$ describes relaxation via the Debye model, whereas $\alpha_j = 0$ corresponds to the Cole–Davidson (CD) and $\beta_j = 1$ to the Cole–Cole models, respectively. These relaxation parameters were determined by simultaneously fitting $\epsilon'(\nu)$ and $\epsilon''(\nu)$ by using a nonlinear least-squares routine. For adequate descriptions of the data collected over the available frequency window, fits were done at two phases. First, the data collected over a low frequency window ($0.2 \leq \nu/\text{GHz} \leq 2$) were fitted. Parameters so obtained were then used as initial guesses for fitting the data collected over the full frequency window ($0.2 \leq \nu/\text{GHz} \leq 50$). Repeat measurements were done to ensure better statistics. In addition, measurements producing equal numbers of data points for $0.2 \leq \nu/\text{GHz} \leq 2$ and $2 \leq \nu/\text{GHz} \leq 50$ frequency ranges were performed to avoid spurious weight during fit to data at the higher frequency range. The quality of the fits was determined by checking both the “goodness-of-fit” parameter (χ^2) and residual where χ^2 was defined as follows:⁵⁰

$$\chi^2 = \frac{1}{2m - l} \sum_{i=1}^m \left[\left(\frac{\delta\epsilon'_i}{\sigma(\epsilon'_i)} \right)^2 + \left(\frac{\delta\epsilon''_i}{\sigma(\epsilon''_i)} \right)^2 \right] \quad (3)$$

where m denotes the number of data triples (ν , ϵ' , ϵ''), l is the number of adjustable parameters, and $\delta\epsilon_i$ and $\sigma(\epsilon_i)$ are the residuals and standard deviations of the individual data points, respectively.

For all samples studied here, multi-Debye fits were found to be adequate. Attempts to fit using separate combinations of Debye, Cole–Cole, and Cole–Davidson processes did not yield any better descriptions of the collected data than the multi-Debye relaxations. We therefore have chosen multi-Debye fits for uniformly describing all the collected DR spectra. A total number of 201 and 501 data points within the available frequency window were recorded for each of the samples studied and a somewhat better mathematical description of the detected dynamics was obtained with the larger number of data points for a majority of these measurements. Consequently, fit parameters reported here correspond to 501 data points recorded for each sample within the frequency window employed.

III. RESULTS AND DISCUSSION

i. DR of Molten Neat Acetamide. Before we investigate the ion dependence of DR in ionic DESs considered here, let us first present the results for molten neat acetamide. Figure 1 displays the real (ϵ') and imaginary (ϵ'') components of the complex dielectric spectra for acetamide measured at ~ 354 K

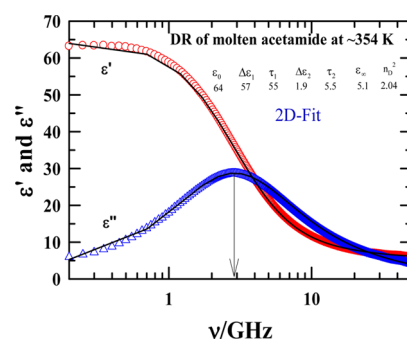


Figure 1. Dielectric relaxation of molten neat acetamide at ~ 354 K. Measured real (ϵ') and imaginary (ϵ'') components of the complex DR spectrum are shown by circles and triangles, respectively. Solid lines through these data represent simultaneous fits using 2-Debye relaxation model. Fit parameters are $\epsilon_0 = 64$, $\Delta\epsilon_1 = 57$, $\tau_1 = 55$ ps, $\Delta\epsilon_2 = 1.9$, $\tau_2 = 5.5$ ps, $\epsilon_\infty = 5.1$. The refractive index (n_D) of molten acetamide has been reported⁶² to be 1.4274 and thus $n_D^2 \approx 2.04$. Therefore, $\epsilon_\infty - n_D^2 = 3.04$, which has remained undetected in the present measurements. The arrow indicates the characteristic relaxation frequency corresponding to τ_1 .

along with the 2-D fits. Fits considering models other than 2-D relaxation (for example, Cole–Davidson) produced worse description of the measured spectra. Note the plateau in $\epsilon'(\nu)$ at the low frequency (ν) limit, which is typical for nonconducting dipolar medium.⁵⁰ In addition, $\epsilon''(\nu)$ shows a peak at $\nu_{\text{peak}} \approx 3$ GHz. Fit parameters summarized inside the figure indicate $\sim 97\%$ of the total detected relaxation is carried out by the slower ($\tau_1 = 55$ ps) of these two time scales. This matches with the characteristic relaxation time constant, $\tau_{\text{peak}} = 1/2\pi\nu_{\text{peak}} \approx 53$ ps. Interestingly, the Stokes–Einstein–Debye (SED) relation,^{52–56} $\tau_r = 3V_{\text{eff}}\eta/k_B T$, predicts a value of ~ 60 ps at ~ 354 K for single particle rotation time for acetamide if a molecular diameter (σ) of 4.5 Å and viscosity (η) of 2 cP²⁴ are used. V_{eff} , effective volume, in such a calculation is taken as molecular volume, $V_m = 2\pi\sigma^3/3$. The relationship between the single particle and the collective rotation times is, $\tau_r = [l(l + 1)/2] \times \tau$, τ denoting a time constant associated with collective orientational relaxation of rank l . For DR, $l = 1$, and therefore, $\tau_r = \tau$. This identity then suggests that the measured slowest DR time ($\tau_1 = 55$ ps) originates from, as in N,N -dimethylacetamide (DMA),⁵⁰ the isotropic rotational diffusion of acetamide molecule. This similarity between τ_1 and τ_r is somewhat perplexing given that molten acetamide is a H-bonded (two H-bonds per acetamide molecule on an average⁵⁷) liquid. Interestingly, all-atom simulation study of H-bond structural relaxation, $C_{\text{HB}}(t)$, of molten acetamide at 368 K reports a relaxation component possessing a time scale of ~ 54 ps.⁵⁸ Therefore, the close proximity between τ_1 and τ_r may be fortuitous, and the slowest relaxation in molten acetamide is dictated by, as in other H-bonded amides,⁵⁰ the waiting time for finding another H-bonding partner arriving at a suitable location with preferred orientation after breaking an already existing H-bond.

Next we comment on the possible origin of the ~ 5 ps time scale (τ_2) for molten acetamide, which contributes $\sim 3\%$ to the total detected relaxation. Such a small amplitude, however, does not suggest this fast component is unrealistic for the following reasons. First, this time scale is similar to the sub-10 ps time scale observed in the simulations of orientational relaxation for N–H bond vector and acetamide backbone in molten neat acetamide.⁵⁸ It is therefore possible that this ~ 5 ps DR

component originates from the reorientation of acetamide backbone or N–H bond vector. A hint to the involvement of H-bond breaking and re-formation with this bond vector reorientation exists in the simulated $C_{HB}(t)$, which possesses a significant component ($\sim 55\%$) that decays with a time constant of ~ 8 ps.⁵⁸ Note that fs-RIKES measurements of ionic acetamide deep eutectics considered here have detected a relaxation component with time scale in ~ 1 – 3 ps range.²⁷ In addition, previous DR studies of water and monohydroxy alcohols have detected a ~ 1 – 3 ps time scale and interpreted in terms of the flipping motion of –OH groups, and breaking and re-formation of H-bond between pairs involving center-of-mass translation.⁵⁹ All these suggest that the ~ 5 ps time scale detected in these measurements is linked to N–H bond vector reorientation coupled with H-bond relaxation of acetamide molecules.

DR spectra shown in Figure 1 also indicate $\epsilon_0 = 64$ for molten acetamide at ~ 354 K, which is in good agreement with earlier reports of $\epsilon_0 = 61$ at ~ 367 K.^{60,61} Moreover, the missing dispersion amplitude, $\epsilon_\infty - n_D^2 = 5.1 - 2.04 = 3.06$,⁶² reflects presence of liquid dynamics faster than detectable in the current measurements. Note such high frequency DR components in liquid amides^{63,64} and other H-bonded systems^{65–68} have been found to be critical for generating ultrafast solvent response. In addition, measurements of intermolecular collective dynamics in amides and substituted amides have reported librational response in the terahertz (1 THz = 10^{12} Hz) regime.^{69–71} Therefore, DR experiments employing a wider coverage at the high frequency regime, followed by THz measurements are required for a complete characterization of polarization dynamics of molten acetamide and acetamide-containing DESs.

ii. DR Time Scales in (Acetamide + Electrolyte) DESs: Anion Dependence. Anion dependence of dielectric relaxation of (acetamide + electrolyte) DESs is demonstrated in Figure 2 where the upper panels present the measured spectra for (acetamide + LiX) systems with $X = \text{Br}^-$, NO_3^- and ClO_4^- , and the lower panel shows those for (acetamide + NaX) systems with $X = \text{SCN}^-$ and ClO_4^- . Interestingly, neither a

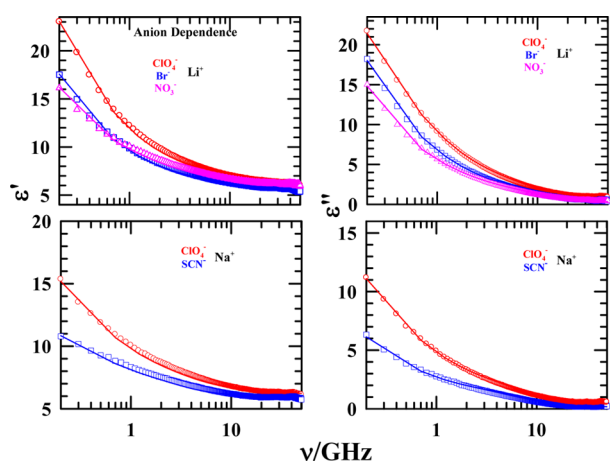


Figure 2. Anion dependence of the real (ϵ') and imaginary (ϵ'') parts of the measured DR spectra for the ionic deep eutectics, (acetamide + electrolyte) at ~ 293 K. The specific identities of the electrolytes are shown in the insets. Upper panels show real and imaginary parts for deep eutectics with lithium salts (perchlorate, bromide, and nitrate), and the lower panels present those with sodium salts (perchlorate and thiocyanate). Representations are color coded.

plateau in $\epsilon'(\nu)$ nor a peak in $\epsilon''(\nu)$ can be observed in these spectra, making estimations of ϵ_0 and characteristic relaxation time a nontrivial task. 4-Debye fits through the data are shown by the solid lines whereas the fit parameters are summarized in Table 1. Residuals shown in Figures S1 and S2 (Supporting Information) suggest that these fits, though not perfect, provide a reasonable description of both the real (ϵ') and imaginary (ϵ'') components of the dielectric spectra recorded. Note a semiquantitative description of the relaxation dynamics is only expected because the present measurements cannot access the relaxations outside the frequency window employed. All these DESs require a fast Debye relaxation component for adequately describing the measured spectra, although the amplitude associated with this component has been found to be very small (~ 1 – 3% of the total detected dispersion). We believe that this fast, sub-10 ps component is real for the following reasons: (i) DR of neat molten acetamide suggests the presence of such a fast time scale. (ii) 3-Debye fits neglecting this fast component lead to relatively poor description of the measured spectra. A comparison between residuals in Figure S3 (Supporting Information) obtained via 3-Debye and 4-Debye fits to the DR spectra measured for (acetamide + LiClO_4) system demonstrates this. Because an unconstrained 4-Debye fit to this system produced a time scale of 4 ps, fit to data for other systems were performed after fixing this fastest time constant. (iii) A considerable part of the high frequency dispersion, $\epsilon_\infty - n_D^2 \approx 4$, has remained undetected in the present measurements. Interestingly, a similar magnitude of total dispersion has also remained undetected for neat molten acetamide. All these considerations strongly suggest that this fast, sub-10 ps component is real and connected to N–H bond vector reorientation of acetamide molecule. The undetected dispersion is then attributed to the intermolecular librational and interaction-induced reorientational motions of acetamide molecules^{69–71} forming these DESs.

Next we comment on the possible origins for the other time scales observed in the present DR measurements. First, the slowest time scale (τ_1), which is in ~ 0.5 – 1 ns range with an amplitude of ~ 50 – 70% of the total dispersion detected, is ~ 10 – 20 times slower than τ_1 for molten acetamide and indicates strong ion–acetamide interactions. In addition, this time scale does not follow the viscosity (η) trend (see Table S4 in the Supporting Information for η values).^{21,27} The fact that this time scale or the amplitude-averaged time scale considering τ_1 and τ_2 (that is, $\langle \tau_{av} \rangle = \sum_{i=1}^2 a_i \tau_i / \sum_{i=1}^2 a_i$) does not follow the viscosity trend of these DESs suggests a difference in ion–acetamide interactions upon the change in ion identity. Evidences for electrolyte-dependent interaction and dynamics have already been reflected earlier in the fluorescence and simulation studies of these ionic acetamide deep eutectics,^{21–26} and the present DR data reconfirm this general observation. Interestingly, insertion of these time scales (τ_1 or $\langle \tau_{av} \rangle$) in the SED relation,^{52–56} $V_{\text{eff}} = k_B T \tau_r / 3\eta$, not only leads to a much smaller V_{eff} for acetamide than its V_m but also predicts a wild variation of V_{eff} upon the change in electrolyte. This suggests that τ_1 does not involve either the full molecular rotation of acetamide in these ionic deep eutectics or the rotating moiety does not experience the full frictional resistance exerted by the macroscopic viscosity of the medium. A similar observation has also been made for ionic liquids while connecting the rotation volume of the dipolar ion to the slowest measured DR relaxation times.^{34,37}

Table 1. Parameters Obtained from Simultaneous Fits of Real (ϵ') and Imaginary (ϵ'') Parts of the Measured DR Spectra for (Acetamide + Electrolyte) DESs at ~ 293 K

electrolyte	ϵ_0	$\Delta\epsilon_1$	τ_1^b (ps)	$\Delta\epsilon_2$	τ_2 (ps)	$\Delta\epsilon_3$	τ_3 (ps)	$\Delta\epsilon_4$	τ_4 (ps)	ϵ_∞	χ^2	n_D^c	$\langle\tau_{av}\rangle^d$ (ps)
LiBr	23.6	13.3 (74%) ^a	715	3.0 (17%)	131	1.4 (8%)	30	0.2 (1%)	4	5.6	0.014	1.407	605
LiNO ₃	21.9	11.4 (72%)	790	2.8 (18%)	126	1.4 (9%)	29	0.1 (1%)	4	6.1	0.013	1.385	657
LiClO ₄	29.4	16.2 (69%)	630	4.4 (19%)	160	2.3 (9%)	38	0.8 (3%)	4	5.8	0.016	1.371	528
NaClO ₄	18	8 (67%)	600	2.3 (19%)	158	1.2 (10%)	41	0.4 (4%)	4	6.1	0.012	1.369	502
NaSCN	12.8	3.2 (47%)	867	2.0 (29%)	255	1.6 (23%)	54	0.06 (1%)	4	5.9	0.011	1.418	633
KSCN	25.3	13.3 (70%)	557	3.7 (19%)	120	1.8 (9%)	28	0.3 (2%)	4	6.2	0.015	1.413	463

^aNumber in parentheses indicates the dispersion amplitude of a given dispersion step in percentage. ^b τ_i ($i = 1-3$) are better within $\pm 5\%$ of the reported values (based on three to five independent measurements). ^cMeasured refractive index. ^d $\langle\tau_{av}\rangle = \sum_{i=1}^4 a_i \tau_i / \sum_{i=1}^4 a_i$ where $\sum_{i=1}^4 a_i = 1$ and $a_i = \Delta\epsilon_i / \sum_{i=1}^4 \Delta\epsilon_i$.

Note these ionic DESs are heterogeneous media,^{21–26} and therefore the hydrodynamic relation between the orientational relaxations at the collective (that is DR) and single particle limits is expected to break down. Prediction for wildly varying rotational volumes for acetamide may suggest involvement of cooperative small-amplitude motions and/or reorientational jumps.^{58,72,73} The cooperativity may arise, as discussed in earlier works,^{18,19} from the formation of H-bonded complexes between ions and acetamide molecules extended over a few-to-several molecular diameters, promoting small amplitude collective rotation at the expense of molecular rotation. In such a scenario, breaking and re-formation of H-bonds for acetamide molecules of ion–acetamide complexes can be a source for the observed slowing down. Our initial simulation results on structural H-bond fluctuations in these ionic DESs indeed suggest the presence of a slow time scale in the ~ 0.5 – 1 ns regime.

The other two DR time scales, τ_2 and τ_3 , respectively, in ~ 100 – 200 and ~ 25 – 50 ps ranges, also do not show any specific dependence on medium viscosity or electrolyte volume⁷⁴ (Table S5, Supporting Information). Note OHD-RIKES measurements of thiocyanate-ion- and lithium-ion-containing deep eutectics considered here have reported decay components with time scales in the 100 and ~ 10 – 20 ps ranges.²⁷ This suggests that the collective molecular motions that produced the above OHD-RIKES time scales also contribute to τ_2 and τ_3 in these DR measurements. This is because both OHD-RIKES and DR measurements respond to long wavelength polarization fluctuations of the system. Furthermore, dynamic Stokes shift measurements of these DES employing a limited time resolution (~ 75 ps) have reported solvation decay components with time constants in the ~ 100 ps and ~ 0.5 – 1 ns ranges along with a substantial missing faster component.^{21,24,25} All these Kerr spectroscopic and time-resolved fluorescence measurements therefore support the presence of time scales detected by the present DR measurements for these ionic DESs.

iii. DR Time Scales: Cation Dependence. Figure 3 displays the cation dependence of the DR spectrum for (acetamide + Li/NaClO₄) and (acetamide + K/NaSCN) DESs at ~ 293 K along with the corresponding 4-D fits. Fit parameters are, as before, summarized in Table 1. Note that for both the perchlorate (ClO₄[−]) and thiocyanate (SCN[−]) DESs, τ_1 or $\langle\tau_{av}\rangle$ follows the change in η upon change in the counter metal ion of the accompanying electrolyte. However, τ_1 values for these DESs also indicate, as before for anion-dependent cases, much smaller V_{eff} and a wide variation of it with the cation identity (Li⁺/Na⁺ for ClO₄[−] DES and Na⁺/K⁺ for SCN[−] DES). The inadequacy of the SED relation is further

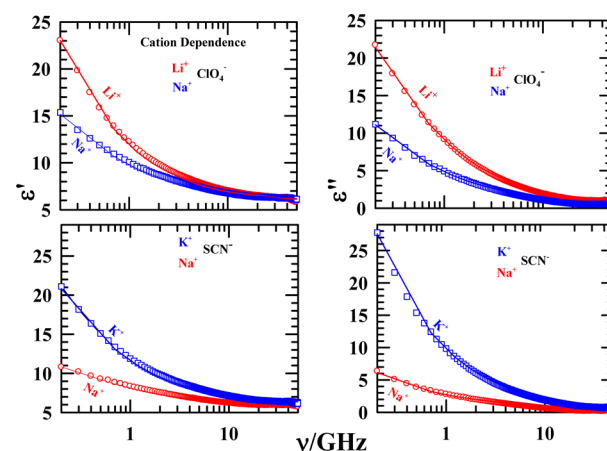


Figure 3. Cation dependence of the real (ϵ') and imaginary (ϵ'') parts of the measured DR spectra for the ionic deep eutectics, (acetamide + electrolyte) at ~ 293 K. Upper panels show spectra for perchlorate salts of lithium and sodium, and lower panels present thiocyanate salts of sodium and potassium. Representations are color coded.

highlighted in larger τ_1 values for (acetamide + NaSCN) DES than for the (acetamide + LiBr) system although the former is less viscous than the latter. It is therefore evident that the detected reorientational dynamics in these systems cannot be interpreted in terms of isotropic molecular rotation of acetamide, and nonhydrodynamic modes such as jumps may be involved. We also mention here that electrolytes in these DESs may produce ion pairs and other higher order complex species that might contribute to the relaxation process by adding, due to larger sizes, further slower relaxation time scales.⁷⁵ More complete measurements using a wider frequency window are therefore required to capture the full DR dynamics of these complex molten systems.

iv. Static Dielectric Constant, ϵ_0 , from Fit: Anion and Cation Dependence. Data in Table 1 indicate that ϵ_0 values from fits vary in the range ~ 13 – 30 and exhibit a dependence on both cation and anion identity. Note this range of ϵ_0 may involve a large uncertainty because the lowest frequency accessed is 200 MHz, and dipolar relaxation at $\nu < 200$ MHz, if any, has remained completely unaccounted for during fits. Such a possibility may exist as a characteristic plateau of $\epsilon'(\nu)$ in the limit of lower frequencies is absent in the DR spectra recorded for all these ionic deep eutectics. Analyses of multiple data sets for a given system recorded in the employed frequency window suggest an overall error bar of ± 2.5 for these estimated ϵ_0 values. This large error bar notwithstanding, such a range of ϵ_0 for these DESs is striking because it reflects a drastic decrease from the value ($\epsilon_0 = 64$) measured for molten neat acetamide at

~354 K. This decrease appears even more dramatic if one considers that the measurements for molten acetamide were done at a temperature ~61 K higher than that for these DESs, and that a rise in solution temperature decreases ϵ_0 via reducing long-ranged orientational spatial correlations.^{34,48} The observed decrease for these DESs may, however, take place if formation of an ion–acetamide complex quenches, partially or fully, the rotational degrees of freedom of the surrounding acetamide molecules. Formation of such “irrotationally bound” solvent molecules via ion–solvent electrostatic interactions has been proposed before while explaining the marked decrease in static dielectric constant upon addition of electrolyte in aqueous and nonaqueous media at ambient condition.^{76–78} Note dilution of dipole density upon addition of electrolyte also contributes to the observed reduction in ϵ_0 but is likely to be overwhelmed by the reduction due to freezing of surrounding dipolar acetamide molecules ($\mu_{\text{acetamide}} = 3.7$ D)⁶⁰ via the ion–acetamide interaction. Kinetic polarization deficiency arising from a coupling between the rotation of the acetamide (dipolar) molecules and the translation of the ions may also contribute to the observed reduction of ϵ_0 values.^{79,80} Note calculated dynamic Stokes shift magnitudes for a dipolar solvation probe in these ionic DESs (except in the presence of NaClO_4) assuming $\epsilon_0 \sim 30$ were found to be in reasonable agreement with experimental values.^{21,24,25} This provides support for the ϵ_0 range observed in the present DR measurements. Ion solvation by acetamide leading to quenching of acetamide rotation coupled with electrolyte-induced breakdown of the H-bond network,^{76–78} and kinetic depolarization effects,^{79,80} may therefore, be the reasons for the observed reduction in ϵ_0 for these ionic DESs.

Data in Table 1 also reveal that among the (acetamide + LiX) systems, ClO_4^- -containing DES possesses the largest ϵ_0 . The same is also true when we compare ϵ_0 between (acetamide + NaX) DESs. For the SCN^- -containing DESs, ϵ_0 in the presence of Na^+ is found to be nearly half of that found for the corresponding K^+ -containing one. A comparison between (acetamide + Na/LiClO_4^-) deep eutectics also reveals that ϵ_0 for the Na^+ -containing deep eutectic system is ~1.6 times lower than that for the corresponding Li^+ -containing system. Considering the chemistry of these systems one can suggest that cation solvation and the reduction of the Kirkwood factor due to the electrolyte-induced breakdown of the H-bond network of the liquid acetamide are probably among the dominant reasons^{76–78} for the observed decrease of ϵ_0 . A simulation study probing the ion dependences for both the kinetic depolarization effects^{79,80} and lifetime of the acetamide–ion complexes can examine this proposition.

Note here that, as the current measurements cover only a part of the total relaxation, finding the “true” fit model is somewhat problematic. Consequently, the observed adequacy of multi-Debye fits for DESs spectra may be fortuitous. Fortunately, collected DR spectra for molten neat acetamide provide semiquantitatively correct estimates for ϵ_0 and the slowest relaxation time scale. These form the basis for a discussion on ion effects on DR of these ionic DESs. Comparison with relaxation time scales from time-resolved fluorescence^{21,24,25} and Kerr spectroscopic²⁷ measurements provide additional fidelity to the DR time scales obtained via 4-D fits. The general applicability of 4-D description for the detected part of the relaxation in these DESs is shown representatively in Figure S6 and Figure S7 along with the relevant fit parameters summarized in Table S8 (Supporting

Information). It is evident from these figures and the table that 4-D fits provide a uniform general description of the measured spectra for these DESs, without strictly assigning any specific mechanism to the relaxation modes. Interestingly, adoption of such a generalized description can be found in earlier works investigating the effects of molecular solvents on DR of ionic liquids.^{34,81,82}

IV. CONCLUDING REMARKS

In summary, the present DR measurements of neat molten acetamide and six different (acetamide + MX) deep eutectics in the frequency window $0.2 \leq \nu/\text{GHz} \leq 50$ have revealed marked dependence of relaxation parameters on the identity of the electrolytes. A drastic decrease of ϵ_0 has been found for each of the six systems studied, and the range $12 < \epsilon_0 < 30$ resembles that reported for various types of ionic liquids.^{34–39,83} Multi-Debye fits have been found to describe the detected relaxation dynamics, with the fastest time constant appearing to be connected to N–H bond vector relaxation. The slowest subnanosecond relaxation time scales for these DESs deviate strongly from hydrodynamic predictions and suggest involvement of either collective small amplitude rotation or orientational jump followed by structural H-bond relaxation. Although the present measurements have missed relaxation dynamics at both the low frequency ($\nu < 0.2$ GHz) and high frequency ($\nu > 50$ GHz) wings, fit parameters describing the measured DR spectra corroborates well with dynamic Stokes shift results from experiments and calculations.^{21,24–26} In addition, several features of DR dynamics of these ionic deep eutectics resemble those observed for room temperature ionic liquids and electrolyte solutions.

Because DR measurements of these conducting media involve the nontrivial problem of dealing with conductivity divergence at $\nu \rightarrow 0$, care must be exercised to protect estimated ϵ_0 values for such solutions from turning anything between erroneous to completely wrong. Our confidence for the reported range of ϵ_0 for these ionic deep eutectics arises from correctly reproducing the reported ϵ_0 values and slowest DR time constants for neat water, several nonaqueous media and their electrolyte solutions at ambient condition. This is exemplified in Table S9 (Supporting Information), which provides a comparison between DR fit parameters from our measurements and those available in the literature^{84–86} for aqueous solutions of sodium chloride (NaCl) and potassium chloride (KCl) at a few electrolyte concentrations. Representative fits along with residuals are provided in Figure S10 and Figure S11 (Supporting Information). In addition, when (acetamide + urea) deep eutectics⁸⁷ have been subjected to DR measurements, we find $\epsilon_0 \approx 69$ at ~333 K, which, as observed earlier for aqueous urea solutions,⁸⁸ increases with urea concentration. Temperature-dependent DR measurements of these ionic and nonionic DESs and their simulation interpretations will constitute our future works. Further, one needs to investigate the interplay between H-bond frustration⁸⁹ and locally preferred structures⁹⁰ for a molecular level understanding of the interconnection between the depression of freezing point and heterogeneity for these and other deep eutectics.

■ ASSOCIATED CONTENT

Supporting Information

Residuals of fits of the real and imaginary parts of the DR and dielectric spectra. Tables of viscosity coefficients, conductivities,

ion volumes and radii, and fitting parameters. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b01502.

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Notes

The authors declare no competing financial interest.

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