Zwitterions Raise the Dielectric Constant of Soft Materials

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ABSTRACT

Materials exhibiting high dielectric constants (ε_s) are critical for energy storage and actuators. A successful approach to increase ε_s by incorporating polar additives (with high ε_s) but controlling the resulting dispersion state is difficult. Here, we show that significant ε_s increases are realized by adding zwitterions, which are small molecules with a cation and an anion separated by covalent bonds. The increase in ε_s with zwitterion addition is attributed to the large molecular dipole of zwitterions, ranging from 35 to 41 Debye, as experimentally quantified, and confirmed using density functional theory. At elevated zwitterion concentration in an ethylene glycol medium, there is a non-linear increase of ε_s that eventually saturates due to the strong Coulombic interactions between zwitterions. The presented work provides a fundamental molecular understanding of why zwitterions are effective additives in boosting ε_s in soft materials.

Materials with high dielectric constants (ε_s) are critical in increasing the performance of energy-related devices such as capacitors, solid-state batteries, and biomimetic actuators.[1-3] In the case of polymer electrolytes, tough soft materials that conduct one and only one type of ion are desirable for applications such as Li batteries[4-6] and ionic actuators.[7-9] Such single-ion conductors have been extensively explored in the 21st Century but so far the ionic conductivity is always too low.[1,4,10,11] Addition of low volatility polar solvents increases the dielectric constant (softening ionic interactions), to a point (*i.e.*, cyclic carbonates, nitriles, and formamides have dipoles of ~5 Debye), and if the solvent has low glass transition temperature (T_g) the solvent also speeds up ionic motion. However, adding polar solvents leads to the loss of mechanical strength compared to the neat polymer, and high temperature applications are limited due to solvent evaporation at elevated temperatures. The combination of higher dielectric constant and lower T_g allows the conductivity to increase and seems to be the path forward but so far, the conductivity is still not high enough for practical applications.[11]

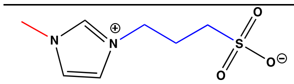
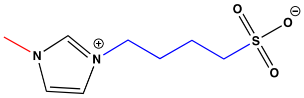
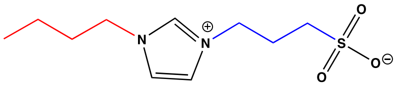
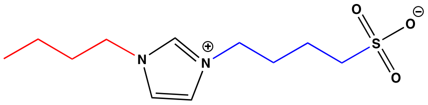
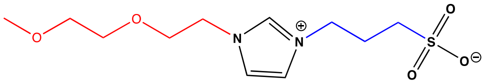
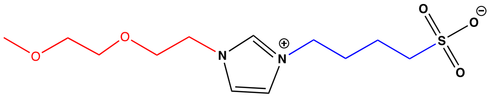
One method that shows potential for creating high-dielectric materials is through the use of zwitterionic additives.[9,12] Zwitterions are small molecules connecting a cation and an anion by covalent bonds. The molecular structure of zwitterions renders them with very large molecular dipoles, and different combinations of anion and cation are possible by different synthetic approaches.[13-17] Though zwitterion additives have shown promise, a fundamental understanding of their role as ε_s enhancers from a molecular perspective is not known. Although the ε_s of dilute zwitterion solutions to quantify the molecular dipole of zwitterions has been shown to be possible,[18,19] the ε_s of neat zwitterions as well as the zwitterion solution ε_s over the whole concentration range have not been reported. Understanding the relationship between material ε_s

with respect to zwitterion addition is critical to determine the effectiveness of zwitterions as nonvolatile extremely polar additives to increase ε_s in soft materials.

Here, we show that non-volatile liquid zwitterions at room temperature exhibit the largest dielectric constant reported for soft materials (e.g., 200–270) due to the static molecular dipole that is in the range of 35–41 Debye. In their neat liquid state, zwitterions of course have many ionic interactions between neighboring molecules. However, to our surprise, their large dipoles apparently make the medium polar enough to allow the zwitterions to move in response to an applied electric field and realize enormous dielectric constants, both in their neat state and in mixtures with polar solvents. Furthermore, zwitterions in the neat liquid state exhibit collective molecular rotation under an applied electric field, which gives rise to an apparent DC conductivity similar to translational ion diffusion and the conductivity with respect to temperature is predicted using Onsager's equation. The work presented here suggests that zwitterions are alternative additives for boosting ε_s and have large implications for energy materials.

The molecular structures of the six zwitterions of this study are shown in **Table 1**, each with imidazolium cation separated from sulfonate anion by a three (propyl, P) or four (butyl, B) carbon connector. Dielectric spectroscopy was used to characterize the dielectric constant of these zwitterions in their liquid state and in anhydrous ethylene glycol solutions. Dilute solutions are the classical way to quantify the dipole of any polar molecule,[20] including zwitterions.[18,19] **Table 1** shows that the dilute solution measured dipoles (m_{dilute}) compare well with those calculated by density functional theory (DFT) methods (m_{DFT} from Gaussian09 with a polarizable continuum at 0 K). The three zwitterions with 3-carbon connectors have dipoles ~35 Debye while the other three with 4-carbon connectors have dipoles ~41 Debye. The dipole moment calculated with Gaussian is larger than the dipole moment estimated with the length of the all trans linear alkane connector, due to the larger distance between the charge centers and the polarization effect from the polarizable continuum.

Table 1. Zwitterion Dipole moment, Polarizability Volume, Volume Fraction for Polarizability Volume Overlap, and Extrapolated Estimates of the Zwitterion Dielectric Constant Compared with Measured Values at 303K.

Zwitterion Structure[a]	m_{dilute} **and** m_{DFT}[b] **(D)**	ε_s[c]	V_p (nm^3)	φ *[d]	$\varepsilon_{zw,LL}$	$\varepsilon_{zw,On}$
 MeImPS	35.0 33.5	NA	9.73	0.027	2800	376
 MeImBS	41.4 41.0	NA	13.6	0.022	3000	566
 BuImPS	35.2 34.3	230	9.84	0.027	2500	386
 BuImBS	40.0 41.5	270	12.7	0.024	2800	505
 OE$_2$ImPS	36.0 33.7	201	10.2	0.032	2800	326
 OE$_2$ImBS	41.7 41.3	250	13.8	0.025	3500	442

a. MeImPS: 4-(3-methyl-1-imidazolio)-1-propanesulfonate, MeImBS: 4-(3-methyl-1-imidazolio)-1-butanesulfonate, BuImPS: 4-(3-butyl-1-imidazolio)-1-propanesulfonate, BuImBS: 4-(3-butyl-1-imidazolio)-1-butanesulfonate, OE2ImPS: 4-(3-methoxyethoxyethyl-1-imidazolio)-1-propanesulfonate, OE2ImBS: 4-(3-methoxyethoxyethyl-1-imidazolio)-1-butanesulfonate.

b. Calculation based on B3LYP/6-31 G++(d, p) with CPCM model (solvent=1,2-ethanediol).

c. Experimentally measured ε_s at 303 K, the ε_s of BuImBS and BuImPS at 303 K is extrapolated based on the linear dependence of ε_s over $1/T$ (**Figure 1a**, dashed lines).

d. φ^* is calculated as $\varphi^* = V_m/V_p$, the ratio of zwitterion molecular volume V_{m} and polarizability volume V_{p}.

Based on the measured dipoles in dilute solution, Debye's polarizability volume[21-23] V_p is calculated using **Eq. 1** and is listed in **Table 1**,

$$V_p = \frac{m^2}{12\pi\varepsilon_0 k_B T} \qquad \text{(Eq. 1)}$$

where m is the molecular dipole moment and ε_0 is the vacuum permittivity. The physical significance of this volume is the region of the sample surrounding a zwitterion dipole where similar dipoles have a dipole-dipole interaction that exceeds the thermal energy k_BT. A typical contact ion pair has dipole of 15 Debye[21,24] with polarizability volume 1.8 nm^3**.** Owing to the semiflexible cation/anion molecular connectors, zwitterions have larger dipoles and since the polarizability volume grows as the square of the dipole moment, the zwitterion polarizability volumes are huge, of order 10 nm^3 for the three with propyl connectors and of order 13 nm^3 for the three with butyl connectors (**Table 1**). Also shown in **Table 1** is the volume fraction of zwitterions where their polarizability volumes start to overlap,[21,25] φ^*, which is of order 2%.

When neat single-ion conducting ionomers have their polarizability volumes of contact ion pairs start to overlap, they aggregate ions and further addition of ionic groups then lowers the dielectric constant.[21,25] In contrast with zwitterions, the dielectric constant continues to increase, albeit not as rapidly as expected by the Onsager equation (**Eq. 2**).[26]

$$\frac{p_0 m^2}{9\varepsilon_0 kT} = \frac{4\pi}{3} p_0 V_p = \frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} \cong \frac{2\varepsilon_s}{(\varepsilon_\infty + 2)^2} \text{ for large } \varepsilon_s \qquad \text{(Eq. 2)}$$

Equation 2 expects that for polar liquids, the dielectric constant ε_s is proportional to the polarizability volume and both are reciprocally related to absolute temperature due to thermal randomization of dipoles.[19] The dielectric constant should increase proportional to the number density of dipoles p_0 and the square of their dipole moment m. The temperature dependence of the dielectric constant of neat zwitterions in their liquid state is shown to be of the Onsager form of

Eq. 2 in **Figure 1a** as the open symbols. ε_∞ is the high frequency dielectric constant due to electronic polarization in the optical frequency range. The high melting temperature (T_m > 200 °C) of MeImBS and MeImPS precludes the measurement of ε_s in their liquid states, while the BuImBS and BuImPS can be measured at 150-200 °C. The oxyethylene functionalized zwitterions are supercooled liquids at ambient temperature, allowing measurement of ε_s over a wide range. The investigated zwitterions show good solubility in ethylene glycol. The polar solvent ethylene glycol also shows nearly Onsager temperature dependence (open black circles and black line in **Figure 1a**; the line is straight but does not have an intercept at 0,0). The ε_s for zwitterion/ethylene glycol solutions can be predicted based on Onsager (**Eq. 2**), and a simple additivity of dielectric constant is often assumed,[26]

$$\varepsilon_s(\varphi) = \varphi\varepsilon_{\mathrm{ZW,On}} + (1-\varphi)\varepsilon_{\mathrm{EG}} \qquad \text{(Eq. 3)}$$

for mixtures of zwitterions with dielectric constants $\varepsilon_{\mathrm{ZW,On}}$ (with volume fraction φ) and $\varepsilon_{\mathrm{EG}}$ for ethylene glycol (with volume fraction 1 - φ). The prediction based on a linear mixing rule was plotted in **Figure 1a** as solid lines for the OE2ImBS/EG solutions with $\varepsilon_{\mathrm{ZW,On}}$ = 442. Good agreement with **Eq. 3** was only found for solutions with low zwitterion content (φ < 10 vol%), while solutions with higher φ show clear deviation from the prediction of **Eq. 3**. The failure of Onsager's mixing rule is a result of intermolecular interaction between zwitterions dictated by the strong Coulombic force. Consequently, the deviation from Onsager's prediction (**Eq. 3**) is more significant at higher φ (**Figure 1a**).

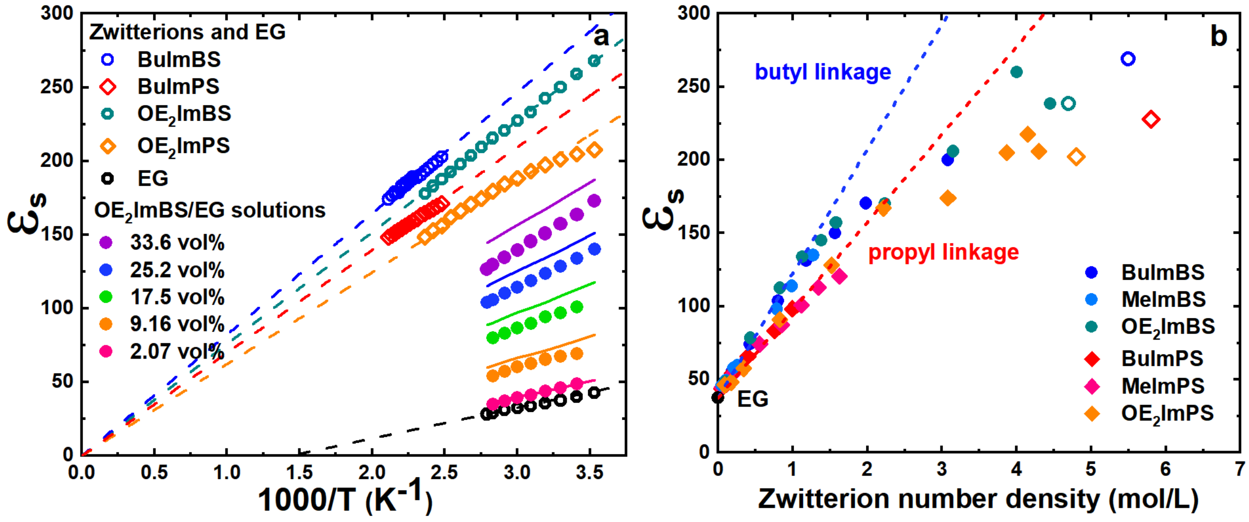


Figure 1. Dielectric constant $\varepsilon_{s,}$ of neat zwitterionic liquids (open-colored symbols), ethylene glycol (open black), and OE2ImBS/EG mixtures (filled colored). (a) Neat zwitterion ε_s were fitted with the Onsager Equation (**Eq. 2**) shown as dashed lines with zero intercept. Solid color lines are the prediction of zwitterion/EG solution ε_s based on Onsager Equation (**Eq. 2**) using the linear mixing rule (**Eq. 3**) with the ε_s for neat EG and expected zwitterion dielectric constant $\varepsilon_{\mathrm{ZW,On}}$ = 442. The black dashed line represents the linear fitting of measured ε_s for neat EG. (b) Zwitterion number density dependence of dielectric constant in ethylene glycol solutions at 30 °C. Dashed lines are the dilute solution fits to **Eq. 3** that determine $\varepsilon_{\mathrm{ZW,On}}$ listed in **Table 1**. Open symbols represent the neat zwitterions in the liquid state.

Figure 1b further shows that the proportionality between dielectric constant and number density of zwitterions expected by **Eqs. 2** and **3** is valid at low enough concentrations in ethylene glycol solutions. The dashed lines have slopes of 85 L/mol for the butyl connectors and 60 L/mol for the propyl connectors in dilute solutions. At the concentration of neat zwitterionic liquids, the dashed lines would predict the dielectric constant of neat zwitterion liquids $\varepsilon_{\mathrm{ZW,On}}$ based on the solution ε_s with low zwitterion φ. The $\varepsilon_{\mathrm{ZW,On}}$ is ~ 350 for zwitterions with propyl connector and ~ 500 for zwitterions with butyl connector, which are both significantly higher than the actual value of the measured ε_s of neat zwitterions, shown as the open symbols in **Figure 1b**. The deviation from the linear mixing rule of **Eq. 3** is more significant at higher φ. The neat zwitterion ε_s (open symbols) are only ~ 1/3 of their extrapolated $\varepsilon_{ZW,On}$ values based on **Eq. 3** fit to the dilute data.

The main motivation of determining the $\varepsilon_{ZW,On}$ from dilute solution measurements is to predict the solution ε_s. As shown in **Figure 1b**, a linear mixing rule with the neat zwitterion ε_s would underestimate the solution ε_s at low φ. Additionally, the measurement of neat zwitterion ε_s in their liquid state remains challenging, as most zwitterions reported so far show T_m over 200 °C. $\varepsilon_{ZW,On}$ can be used to compare the capability of different zwitterions to increase the dielectric constant of any polar medium they are soluble in, and provides reasonable prediction of the solution ε_s for different solvents with a simple linear mixing rule (**Eq. 3**) up to about 10 vol%. At very high φ, the measured ε_s reaches a plateau for OE2ImPS and OE2ImBS that coincides with ε_s of the neat zwitterions. For the other four crystalline zwitterions, such a high concentration cannot be reached near 30 °C.

The concept of polarizability volume overlap is demonstrated to be useful in **Figure 2a**, as the polarizability volume overlap parameter φ/φ^* nicely reduces all data for the six different zwitterions in ethylene glycol solutions. There seems to be a linear dependence of dielectric constant on φ/φ^* that decreases in slope by a factor of 0.6 once the polarizability volumes start to overlap. The continued linear increase of dielectric constant makes zwitterions quite different from contact ion pairs (which start to show ε_s decrease for $\varphi/\varphi^* > 1$), indicating that zwitterion mixtures can realize extremely large dielectric constants with potential uses in boosting the dielectric constant of single-ion conductors and other energy materials. The macroscopic ε_s of mixtures can also be predicted with a 1/3 mixing rule derived by Landau and Lifshitz[27] and used extensively for binary mixtures of polar solvents by Looyenga.[28]

$$[\varepsilon_s(\varphi)]^{1/3} = \varphi\varepsilon_{\mathrm{zw,LL}}^{1/3} + (1-\varphi)\varepsilon_{\mathrm{EG}}^{1/3} \tag{Eq. 4}$$

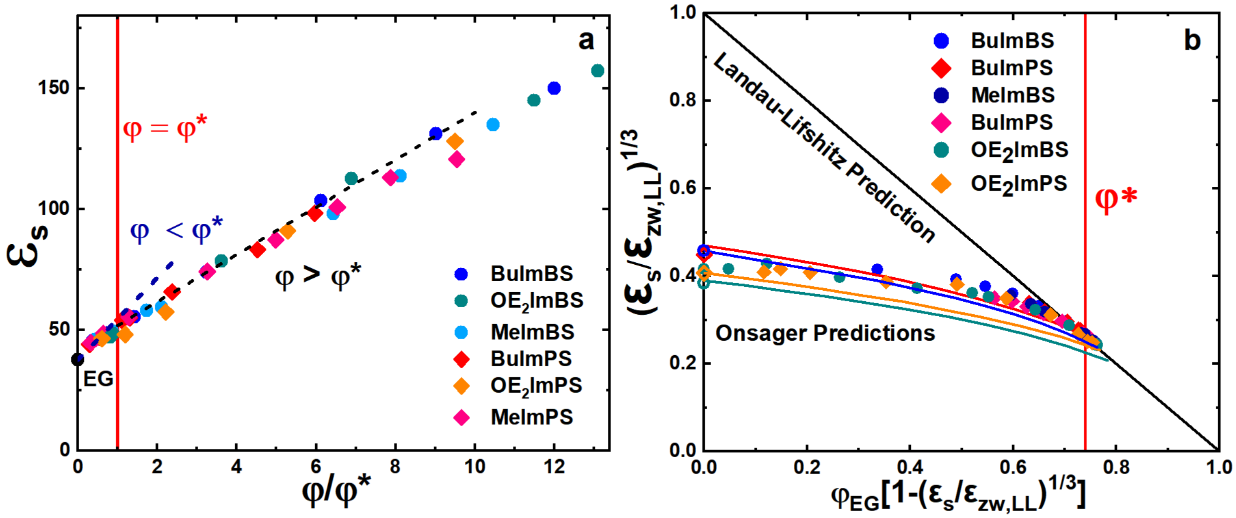


Figure 2. Dielectric constant ε_s replotted over reduced concentration and linearized Landau-Lifshitz mixing equation. (a) Data from **Figure 1b** replotted as a function of polarizability volume overlap parameter, reducing all data and showing two different slopes above and below the polarizability volume overlap concentration, φ^*. (b) Data replotted in the form that the Landau and Lifshitz Equation (**Eq. 4**) expects to be linear (black line), which is only observed below the polarizability volume overlap, denoted by the vertical red line. The expected neat zwitterion dielectric constants $\varepsilon_{\mathrm{zw,LL}}$ listed in **Table 1** are based on fitting the Landau and Lifshitz Equation (**Eq. 4**) to each data set with $\varphi < \varphi^*$. Colored lines are Onsager predictions based on the measured neat zwitterion dielectric constants at 30 °C (open symbols) with the values for neat BuImPS and BuImBS extrapolated using the Onsager temperature dependence from **Figure 1a**.

Equation 4 applies to many mixtures of polar small molecules and to mixtures of single-ion conducting ionomers and polar additives.[29,30] The linearized form[10] of **Eq. 4** is plotted in **Figure 2b**, shown as the black line. The dilute data with $\varphi < \varphi^*$ (beyond the vertical red line) do obey **Eq. 4** and are fit to obtain $\varepsilon_{\mathrm{ZW,LL}}$ listed in **Table 1** and used to construct **Figure 2b**. The other data at higher zwitterion concentrations are below the black line, indicating that these mixtures with overlapping polarizability volumes have lower dielectric constants, owing to interactions. The colored lines are Onsager's prediction with the ε_{s} measured for each neat zwitterionic liquid.

The giant zwitterion molecular dipoles also demonstrate themselves by showing a conductivity plateau in their $\sigma'(\omega)$ spectra shown in **Figure 3a**. The observed apparent DC conductivity is hypothesized to be caused by zwitterion rotation under the alternating AC field. When the external field changes direction at low enough frequency, the zwitterions rotate somewhat to follow that field, which leads to an effective charge displacement similar to translational ion diffusion. The AC field for $\omega < 1/\tau_{\sigma}$ (shown in **Figure 3a**) biases the thermally randomized distribution of zwitterion dipoles to preferentially point towards the positively charged electrode. The biasing makes the zwitterionic liquid polarizable, reflected in a large ε_{s} but also contributes to an apparent conductivity σ from the same rotational biasing.

$$\sigma = \frac{vm^2}{\tau_{\sigma}kT} = \frac{9\varepsilon_0(\varepsilon_s-\varepsilon_\infty)(2\varepsilon_s+\varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty+2)^2}\frac{1}{\tau_\sigma} \qquad \text{(Eq. 5)}$$

v is the number density of zwitterion molecules. The final form of **Eq. 5** was obtained using **Eq. 2**, and the calculated conductivity is plotted as dashed curves shown in **Figure 3b** with the measured apparent zwitterion conductivities shown as symbols, with remarkable agreement. This false apparent DC conductivity reinforces the notion that conductivity is not the right metric for ion conducting electrolytes.[25] The enormous dipoles of zwitterions make this false conductivity visible, it really should be present in any system with rotatable dipoles but orders of magnitude smaller for normal dipoles.

Equation 5 is derived based on two assumptions: 1) the time scale of the collective zwitterion rotation is the onset of the DC plateau (τ_σ, see **Figure 3a**) and 2) the rotation occurs on the length scale of the zwitterion's molecular dipole (m/e). At lower frequencies than the $\sigma'(\omega)$ and $\varepsilon'(\omega)$ plateaus, **Figure 3a** even shows the usual macroscopic polarization effect caused by the apparent σ. The agreement between the calculated σ and the measured σ in **Figure 3b** suggests that zwitterion partial rotation accounts for the measured apparent conductivity (~10^{-8} S/cm at 300 K in **Figure 3a**).

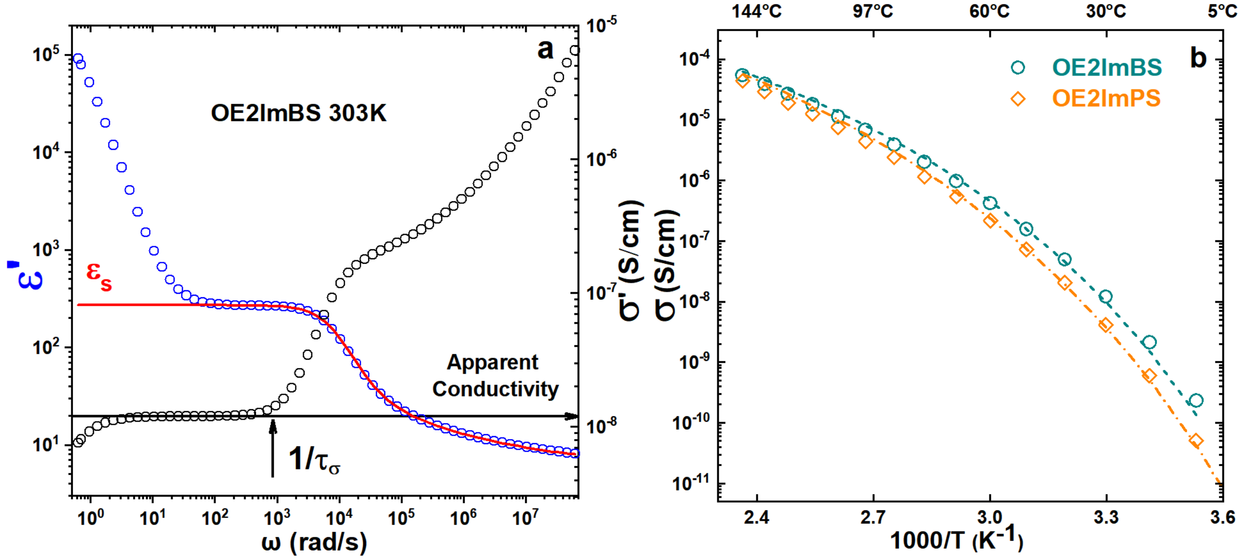


Figure 3. Apparent DC conductivity for the pure zwitterion OE2ImBS. (a) Real parts of conductivity $\sigma'(\omega)$ and permittivity $\varepsilon'(\omega)$ spectra for OE2ImBS at 303 K. The red line indicates the determination of ε_S, the black line indicates the determination of σ, and the black arrow indicates the reciprocal time scale $1/\tau_\sigma$. (b) The zwitterion conductivity predicted with **Eq. 5** is plotted as the dashed curves and compared with the measured temperature dependence of apparent

zwitterion conductivity, shown as the open symbols. The true DC conductivity of these zwitterions is unmeasurably tiny.

In summary, we study the dielectric constants of zwitterions in their neat state and in their mixtures with ethylene glycol. Using the dielectric constant of dilute solutions, the dipole moment of the zwitterion can be determined and is found to agree with simple DFT calculations. Since the zwitterion dipoles are 7-8 times larger than the dipoles of the most polar organic solvents and the dipole gets squared when calculating the dielectric constant, these zwitterions are powerful dielectricizers. As the concentration of zwitterion is increased beyond the polarizability volume overlap, zwitterions begin to interact with each other, and this makes the dielectric constant of the mixture lower than expected by simple mixing rules. However, the enabling observation is that the dielectric constant of zwitterion mixtures continues to increase with zwitterion content, and this suggests they may be very useful as polar additives (i.e., dielectricizers) for all sorts of energy materials, including single-ion conductors. Initial studies of such have begun and show promise for ionic actuators.[9]

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Competing Interests

The authors declare no competing interests.

Additional Information

Supplemental information

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