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Molecular and System Parameters Governing Mass and Charge Transport in Polar Liquids and Electrolytes

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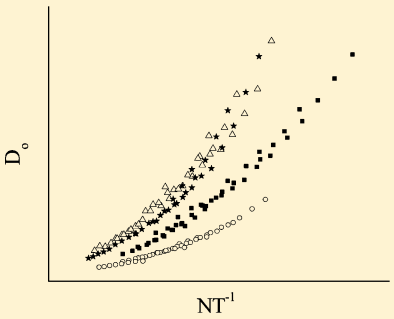
Supporting Information

ABSTRACT: Onsager's model of the dielectric constant is used to provide a molecular-level picture of how the dielectric constant affects mass and charge transport in organic liquids and organic liquid electrolytes. Specifically, the molecular and system parameters governing transport are the molecular dipole moment μ and the solvent dipole density N. The compensated Arrhenius formalism (CAF) writes the temperature-dependent ionic conductivity or diffusion coefficient as an Arrhenius-like expression that also includes a static dielectric constant (ε_s) dependence in the exponential prefactor. The temperature dependence of ε_s and therefore the temperature dependence of the exponential prefactor is due to the quantity N/T, where T is the temperature. Using the procedure described in the CAF, values of the activation energy can be obtained by scaling out the N/T dependence instead of the ε_s dependence. It has been previously shown that a plot of the prefactors versus ε_s results in a master curve, and here it is shown that a master curve also results by plotting the prefactors against N/T. Therefore, the CAF can be applied by using temperature-dependent density data instead of temperature-dependent dielectric constant data. This application is demonstrated for diffusion data of *n*-nitriles, *n*-thiols, *n*-acetates, and 2-ketones, as well as conductivity data for dilute tetrabutylammonium triflate−nitrile electrolytes.



1. INTRODUCTION

The compensated Arrhenius formalism (CAF) has been recently introduced to describe mass and charge transport in liquids and liquid electrolytes.[1−6] The CAF is based on two core postulates. First, the transport property of interest (e.g., ionic conductivity, diffusion coefficient) can be represented with an Arrhenius-like expression that includes a temperature-dependent exponential prefactor. Second, there exists a dielectric constant dependence in the prefactor and all of the temperature dependence in the prefactor is due entirely to the inherent temperature dependence of the dielectric constant. From these postulates the ionic conductivity, σ, and the diffusion coefficient, D, can be written as

$$\sigma(T, \varepsilon_s) = \sigma_o(\varepsilon_s(T)) \exp(-E_a/RT) \quad (1)$$

$$D(T, \varepsilon_s) = D_o(\varepsilon_s(T)) \exp(-E_a/RT) \quad (2)$$

where E_a is the energy of activation, ε_s is the static dielectric constant, and σ_o and D_o are the exponential prefactors for conductivity and diffusion, respectively.

The activation energy E_a is determined from a scaling procedure that cancels the dielectric constant dependence in the prefactor. The scaling process is applied to a family of solvents, where a solvent family consists of members that have the same functional group but differ in alkyl chain length. For example, in the *n*-nitrile family to be examined later, the members chosen for study are heptanenitrile, octanenitrile, nonanenitrile, decanenitrile, and dodecanenitrile. Two sets of data are required for the scaling procedure of a particular solvent family. First, the transport property of interest, e.g., σ, and ε_s are measured isothermally for each member of the solvent family. This set of isothermal conductivities is represented as σ_r. The temperature at which these measurements are made is denoted as the reference temperature T_r. When σ_r is plotted against ε_s, these isothermal data are collectively referred to as the reference curve for conductivity. Second, temperature-dependent σ measurements are collected for one particular member of the solvent family. The scaling procedure involves dividing the temperature-dependent value of σ by the reference value of σ that corresponds to the same value of the dielectric constant. This procedure is repeated for each temperature in the measurement range. A more detailed description of the scaling procedure is given elsewhere.[1,2] Exactly the same procedure can be carried out for the diffusion coefficients, D. The final result is the compensated Arrhenius equation (CAE) for conductivity (or diffusion):

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$$\ln\left(\frac{\sigma(T, \varepsilon_S)}{\sigma_r(T_r, \varepsilon_S)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \quad (3)$$

$$\ln\left(\frac{D(T, \varepsilon_S)}{D_r(T_r, \varepsilon_S)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \quad (4)$$

From eqs 3 and 4, CAF behavior is observed if a plot of the logarithm of the scaled conductivities or diffusion coefficients versus reciprocal temperature is linear. The activation energy is calculated from either the slope or intercept of the graph.

The CAF has been shown to very accurately describe conductivity and diffusion data for the *n*-alcohol,[1,2,4,5] *n*-acetate,[6] and 2-ketone[1,7] solvent families. In this work it will be shown that the CAF can also be applied to three additional solvent families: *n*-nitriles, *n*-acyclic carbonates, and *n*-thiols. There is a remarkable similarity in the value of the activation energy for self-diffusion for the pure aprotic polar liquids studied to date. The CAF emphasizes the role of the dielectric constant in influencing mass and charge transport in liquids, but the dielectric constant is a macroscopic solution property that does not provide insight into which molecular-level parameters affect transport. Here, Onsager's model of ε_s is utilized to provide a molecular-level picture of how transport phenomena depend on the static dielectric constant.[8] This model focuses on two properties: (1) the dipole density of the liquid and (2) the permanent dipole moment of the polar molecule. It will be shown that the dipole density provides valuable insight into the meaning of the reference curve as well as the temperature dependence of the exponential prefactor.

2. EXPERIMENTAL SECTION

All chemicals except the acyclic carbonates were obtained from either Aldrich, Alfa Aesar, or TCI America and used as received. The chemicals were stored and all samples were prepared in a glovebox (≤1 ppm H_2O) under a nitrogen atmosphere. The nitrile electrolytes were prepared at ambient glovebox temperature (approximately 27 °C) by dissolving tetrabutylammonium triflate (TbaTf) salt into solvent until the appropriate molar concentration (mol/liter) was obtained, followed by stirring for 24 h.

The capacitance and conductance were measured using a HP 4192A impedance analyzer that swept a frequency range from 1 kHz to 13 MHz. The sample holder was an Agilent 16452A liquid test fixture. The conductivity, σ, is calculated from the measured conductance, G, through the equation $\sigma = L \times G \times A^{-1}$, where L is the electrode gap and A is the electrode area. The static dielectric constant ε_s is calculated from the measured capacitance C using the equation $\varepsilon_s = \alpha \times C \times C_o^{-1}$, where α is a variable to account for stray capacitance and C_o is the atmospheric capacitance.[9] A Huber Ministat 125 bath was used to regulate the temperature from 5 to 85 °C, in increments of 10 °C. Additional details of the conductivity/dielectric constant instrumentation and method of data analysis have been previously given.[5] The density of the pure solvents was measured over the temperature range 5 to 85 °C using an Anton Paar DMA 4500 M density meter. Density measurements of 2-pentanone, 2-octanone, butyl acetate, and hexyl acetate at various temperatures in the range 5 to 85 °C were on average within 0.1% of literature values.[10]

For diffusion measurements the samples were contained in 5 mm OD and 20 cm long glass NMR tubes sealed with parafilm. The sample height in the NMR tube was constricted to 0.8 cm. Self-diffusion coefficients were measured using a Varian VNMRS-400 MHz NMR spectrometer equipped with an Auto-X-Dual Broadband 5 mm probe. The corresponding Larmor frequency for ^{1}H is 399.87 MHz. An FTS XR401 Air-Jet regulator was used to control the temperature in the measurement range from 5 to 85 °C. The gradient field strength was calibrated from literature diffusion coefficient values for ethanol.[11] The diffusion measurements were made using the Stejskal–Tanner pulsed field gradient NMR spin–echo technique.[12] For a given gradient duration and interval, the attenuation of the signal intensity was recorded as a function of the gradient field strength over the range 6 to 62 G/cm. Plotting the logarithm of intensity versus the square of the gradient field strength produced a linear relationship whose slope was used to determine the diffusion coefficient.[13]

The acyclic carbonates used in this work were synthesized in house. The following instruments were utilized for characterization of these carbonates: ^{1}H NMR spectra were obtained using a Varian Mercury-300 NMR spectrometer. GC-MS analyses were carried out using a coupled Agilent Technologies 7890A Gas Chromatograph and an Agilent Technologies 5975C inert XL EI/CI Mass Spectrometer (Agilent 19091S-433 HP-5MS Column, He carrier gas, methane chemical ionzation source).

The synthesis of the methyl alkyl carbonates (W–Z) resulted from the following procedure: A 3-neck flask was charged with 5.00 equiv of methyl chloroformate and fitted with a thermometer, pressure-equalizing funnel, and a reflux condensor with drying tube. The methyl chloroformate was cooled to ca. 5 °C using a water-ice bath, and with stirring (magnetic), 1.00 equiv of the desired primary alcohol was added to the mixture dropwise to keep the temperature below 10 °C, followed by 1.00 equiv of dry pyridine. The mixture was allowed to warm to room temperature and was then heated to 60 °C, at which point the solid pyridinium hydrochloride that formed had dissolved. The disappearance of alcohol was monitored using NMR spectroscopy. After the alcohol was consumed (24 to 60 h), the mixture was cooled to room temperature, the pyridinium hydrochloride that precipitated was removed by filtration through Celite, and the filtrate was washed with distilled water until neutral. The resulting carbonate was dried over anhydrous magnesium sulfate. IR spectroscopy showed that the samples did not contain detectable amounts of water or residual alcohol. All the samples were greater than 97% purity by ^{1}H NMR. Spot checks of compounds W and X using GC-MS (CI-methane: W [M + 1] = 161; X [M + 1] = 189) showed purities of >97 and >99%, respectively.

Methyl hexyl carbonate,[14] W. 83% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (t, 3H, J = 6.5 Hz); 1.27 (m, 6H); 1.1–1.4 (m, 6H); 1.5–1.7 (m, 2H); 3.70 (s, 3H); 4.06 (t, 2H, J = 6.5 Hz).

Methyl octyl carbonate,[15] X. 86% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6.5 Hz); 1.1–1.5 (m, 10H); 1.6–1.8 (m, 2H); 3.77 (s, 3H); 4.13 (t, 2H, J = 6.5 Hz). Lit.[15]: δ 0.86–0.90 (t, 3H); 1.27 (m, 10H); 1.62–1.70 (m, 2H); 3.78 (s, 3H); 4.11–4.16 (t, 2H).

Methyl decyl carbonate,[15] Y. 87% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6.5 Hz); 1.1–1.5 (m, 14H); 1.6–1.8 (m, 2H); 3.77 (s, 3H); 4.13 (t, 2H, J = 6.5 Hz). Lit.[15]: δ 0.86–0.90 (t, 3H); 1.27 (m, 14H); 1.62–1.70 (m, 2H); 3.78 (s, 3H); 4.11–4.16 (t, 2H).

Methyl dodecyl carbonate,[16] Z. 86% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 3H, J = 6.5 Hz); 1.1−1.4 (m, 18H); 1.5−1.7 (m, 2H); 3.75 (s, 3H); 4.11 (t, 2H, J = 6.5 Hz).

3. RESULTS AND DISCUSSION

3.1. *n*-Nitrile Data. The CAF is now applied to the *n*-nitrile family of solvents comprised of heptanenitrile, octanenitrile, nonanenitrile, decanenitrile, and dodecanenitrile. If the temperature-dependent conductivities of 0.0055 M TbaTf-octanenitrile over the range 5 to 85 °C are scaled to reference conductivity data at 35 °C as described in the Introduction, the activation energy calculated from eq 3 is 25.3 ± 0.4 kJ/mol from both the slope and the intercept. This procedure is then repeated for the temperature-dependent data for the other TbaTf−nitriles in this electrolyte family. The mean conductivity activation energy for the dilute nitrile electrolytes was determined by averaging the E_a values obtained from scaling temperature-dependent conductivities of octanenitrile, nonanenitrile, and decanenitrile to reference curve data at 25, 35, 45, and 55 °C. This calculated average activation energy is 26.5 ± 0.1 kJ/mol. The CAF can also be used to calculate diffusion activation energies from eq 4 by scaling temperature-dependent self-diffusion coefficients of pure nitriles to diffusion reference curve data. The average activation energy for diffusion of the nitriles was determined to be 24.1 ± 0.1 kJ/mol, which is close in value to that obtained from the conductivity data. Figure 1 demonstrates the linear behavior of compensated Arrhenius plots for the conductivity data of a dilute nitrile electrolyte and for diffusion data of a pure nitrile.

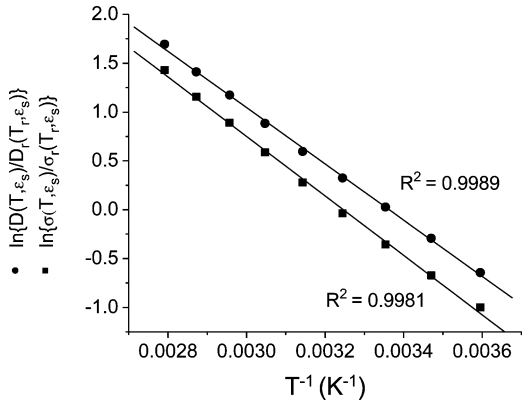

Figure 1. Compensated Arrhenius plots for 0.0055 M TbaTf−octanenitrile temperature dependent conductivity data scaled to reference conductivity data at 35 °C (squares) and temperature-dependent pure octanenitrile diffusion coefficient data scaled to reference diffusion data at 25 °C (circles).

Once the activation energy is determined from the scaling procedure, the conductivity and diffusion exponential prefactors can be calculated from eqs 1 and 2, respectively, by dividing the temperature-dependent conductivity or diffusion coefficient by the Boltzmann factor $\exp(-E_a/RT)$. The top half of Figure 2 shows that the data are divided into five separate curves when the temperature-dependent conductivities are plotted against the temperature-dependent dielectric constants for the 0.0055 M TbaTf−nitrile solutions. Each curve represents the temperature-dependent data for a particular nitrile member over the range 5 to 85 °C, in increments of 10 °C.

However, if each conductivity in the top half of Figure 2 is divided by $\exp(-E_a/RT)$ to give the prefactor and these

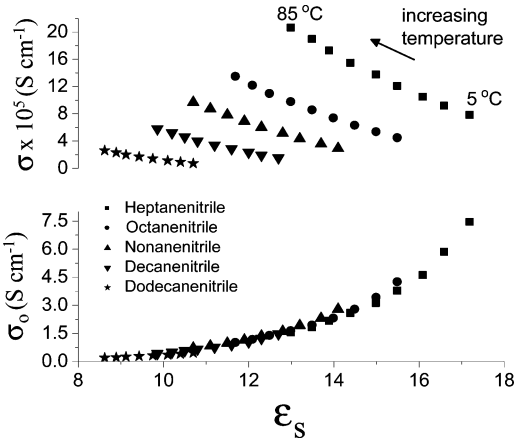

Figure 2. Top: Conductivity versus dielectric constant from 5 to 85 °C for 0.0055 M TbaTf−nitrile electrolytes (nitrile = heptanenitrile, octanenitrile, nonanenitrile, decanenitrile, dodecanenitrile). Temperatures begin at 5 °C (right-most data point for each nitrile except for dodecanenitrile which begins at 15 °C) and increase by 10 °C increments from right to left until 85 °C (left-most data point for each nitrile). Bottom: Conductivity exponential prefactor versus dielectric constant. The average E_a value of 26.5 kJ/mol was used to calculate the prefactors.

prefactors are then plotted against the same dielectric constant data, all data lie on a sharply increasing master curve as seen in the bottom half of Figure 2. The existence of a master curve supports the CAF core postulate that the exponential prefactor is a function of the static dielectric constant. Similar master curves are also observed for conductivity, diffusion, and dielectric relaxation data of other solvent families.[1−3,5,6] The nitrile diffusion data also result in a master curve, and these data will be discussed in section 3.3.

3.2. *n*-Acyclic Carbonate and *n*-Thiol Diffusion Data. The *n*-acyclic carbonate and *n*-thiol solvent families have low permittivities due to the small dipole moment of these molecules. The weak dipole moment in conjunction with the long alkyl chain length of the carbonate and thiol members studied here sufficiently hinders salt dissolution so that conductivity data could not be obtained even for dilute solutions. Only self-diffusion data of pure carbonates and thiols are presented. Figure 3 shows representative CAE plots for the diffusion data of these two solvent families. In the figure, temperature-dependent diffusion coefficient data for methyl

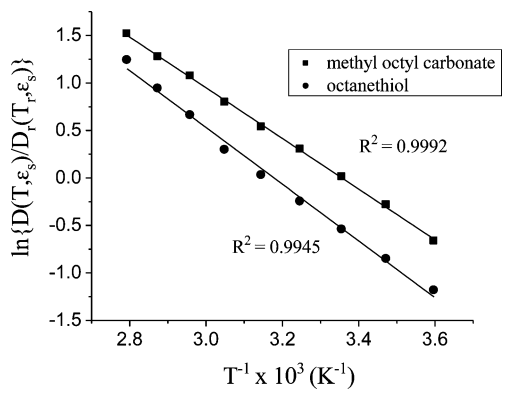

Figure 3. Compensated Arrhenius plots for diffusion data of pure methyl octyl carbonate scaled to reference data at 25 °C (squares) and pure octanethiol scaled to reference data at 45 °C (circles).

octyl carbonate over the range 5 to 85 °C were scaled to diffusion reference curve data at 25 °C that consisted of the members methyl hexyl carbonate, methyl octyl carbonate, methyl decyl carbonate, and methyl dodecyl carbonate. For the thiols, octanethiol data were scaled to reference data at 45 °C that consisted of the members hexanethiol, heptanethiol, octanethiol, and dodecanethiol.

Average CAF activation energies from diffusion data of pure liquids are given in Table 1 for the acyclic carbonate, thiol, and nitrile solvent families along with acetate[6] and ketone[7] data that have been previously reported. Despite the very different functional groups and permittivities of these solvent families, the energy barrier for mass transport is very similar in these five families of polar liquids. However, it should be noted that strongly hydrogen bonding liquids like the 1-alcohols exhibit higher E_a values for diffusion and conductivity.[1,2,5] The extent of hydrogen bonding in the thiol solvent family has been debated in the literature,[17,18] but the thiol activation energy given here from the CAF agrees very well with those for the other four aprotic solvent families in Table 1. This implies that the thiols more closely resemble non-hydrogen bonding liquids in terms of their intermolecular interactions.

Table 1. Average CAF Activation Energies from Diffusion Data of Pure Liquids for Five Solvent Families[a]

solvent family	E_a (kJ/mol)	ε_s range
n-acetates	25.5 ± 0.3	3.43−5.46
2-ketones	23.9 ± 0.2	7.17−16.4
n-nitriles	24.1 ± 0.1	8.16−16.7
n-acyclic carbonates	22.4 ± 0.1	2.46−2.78
n-thiols	25.2 ± 0.3	3.06−4.59

[a]The dielectric constant range for each solvent family is also given.

3.3. Using Onsager's Model of ε_s to Describe Transport. The static dielectric constant ε_s plays a critical role in the CAF. In this section, ε_s is written in terms of molecular and system properties; the CAF is then utilized to discuss diffusion and conductivity in terms of these properties. Onsager's well-known expression[8] for the static dielectric constant of a polar liquid is

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{4\pi N\mu^2}{9kT} \tag{5}$$

where ε_∞ is the high frequency value of the real part of the dielectric constant, N is the dipole density of the liquid, μ is the permanent dipole moment of the polar molecule, T is temperature, and k is Boltzmann's constant. When ε_s is large compared to ε_∞, eq 5 can be written as

$$\frac{\varepsilon_s}{(\varepsilon_\infty + 2)^2} \approx \frac{2\pi N\mu^2}{9kT} \tag{6}$$

The square of the dipole moment in eq 6 is converted to SI units by dividing the right-hand side by $4\pi\varepsilon_o$ to give

$$\varepsilon_s \approx \frac{N\mu^2(\varepsilon_\infty + 2)^2}{18kT\varepsilon_o} \tag{7}$$

where ε_o is the vacuum permittivity. Equation 7 provides a theoretical explanation for the extensive observations made on a wide variety of polar liquids by Wyman[19] and is a reasonable approximation to the dielectric constant ε_s.

As an example of the application of eq 7, Table 2 shows experimentally measured temperature-dependent dielectric constants for pure nonanenitrile along with those calculated from eq 7. The dipole density N is a dipole number density and is easily determined by dividing the liquid density by its molecular weight. The high frequency permittivity is obtained from the expression $\varepsilon_\infty = \eta^2$, where η is the refractive index.[20] Only gas phase values of the molecular dipole moment μ are used for consistency, since it is well-known that solution dipole moments vary depending on the solvent and can differ from the gas phase value.[20,21] The dipole moment depends only slightly on the alkyl chain length for a given solvent family,[22,23] and here it is assumed that both μ and ε_∞ are independent of alkyl chain length and temperature. The dielectric constant data calculated from eq 7 and given in Table 2 for pure nonanenitrile were determined using the refractive index at 25 °C for hexanenitrile (1.405)[24] and the dipole moment for pentanenitrile (4.12 D).[23] The average difference between the experimental dielectric constant and the calculated value for nonanenitrile is about 20%, which supports the various assumptions made in Onsager's model.[25]

Table 2. Temperature-Dependent Static Dielectric Constants for Pure Nonanenitrile Measured Experimentally and Calculated with Eq 7

temperature (°C)	experimental ε_s	calculated ε_s
5	13.8	17.5
15	13.4	16.8
25	12.9	16.1
35	12.5	15.4
45	12	14.8
55	11.6	14.2
65	11.2	13.6
75	10.8	13.1
85	10.5	12.6

The dipole density N is a temperature-dependent property because heating a liquid results in thermal expansion that decreases the liquid density. The dipole density is observed to decrease linearly with increasing temperature over the range 5 to 85 °C for all liquids examined in this work (data not shown). From eq 7, all of the temperature dependence in the dielectric constant should be due to the quantity N/T. Therefore, a plot of ε_s vs N/T should be linear; Figure 4 shows that plots of this

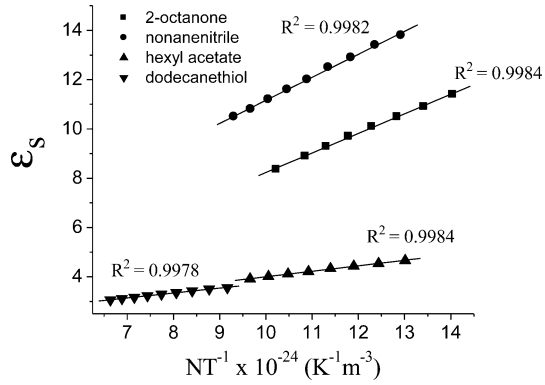

Figure 4. Static dielectric constant versus N/T over the range 5−85 °C for pure 2-octanone, nonanenitrile, hexyl acetate, and dodecanethiol.

kind are indeed linear over the temperature range 5 to 85 °C. Acyclic carbonate data are not included in Figure 4 because these plots exhibit some curvature that is not surprising, considering that eq 7 is valid for cases where ε_s is substantially greater than ε_∞. This criterion is not met with the very low permittivity acyclic carbonate data. The dielectric constants of the thiol and acetate families are relatively low, but these values are high enough so that eq 7 can describe the data.

The dipole moment of the liquid can be calculated from the slope of the lines in Figure 4. The calculated dipole moments of nonanenitrile, 2-octanone, hexyl acetate, and dodecanethiol are summarized in Table 3 and compared with literature values, with reasonable agreement between the two sets of data. It was not possible to find literature values of the dipole moment for the four compounds in Figure 4. However, as noted earlier, the magnitude of the dipole moment varies only slightly with the length of the alkyl chain. Therefore, the comparisons in Table 3 are appropriate.

Table 3. Comparison between Dipole Moments (Debyes) Calculated Using Eq 7 and Appropriate Literature Values[a]

compound	$\mu(D)$ calcd	literature	$\mu(D)$ lit.
nonanenitrile	3.42	pentanenitrile[23]	4.12
2-octanone	3.17	2-butanone[26]	2.78
hexyl acetate	1.69	ethyl acetate[23]	1.78
dodecanethiol	1.55	ethanethiol[27]	1.60

[a]Refractive indices used to calculate the high frequency permittivity for the nitriles, ketones, acetates, and thiols are 1.405 (hexanenitrile), 1.395 (2-hexanone), 1.392 (butyl acetate), and 1.440 (butanethiol), respectively. These values were obtained from ref 24.

The top half of Figure 5 shows that expected trends[2,28] based on alkyl chain length and temperature are observed when diffusion coefficients are plotted against the dielectric constant for five different solvent families, but there is no collective grouping of the data. The scatter in the data between members of the carbonate family is similar to that for the other four families, although this trend is difficult to observe due to the dielectric constant scale used in the figure.

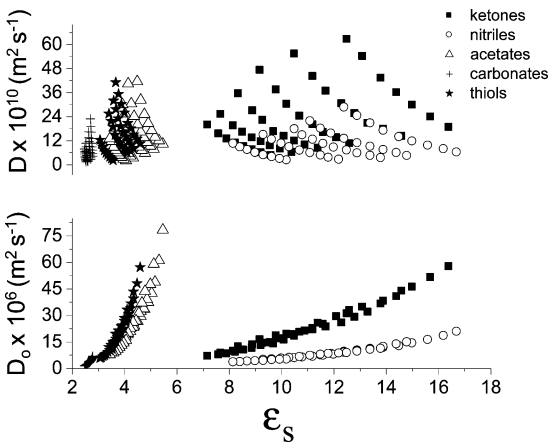

Figure 5. Top: Temperature-dependent diffusion coefficients versus temperature-dependent dielectric constants over the range 5 to 85 °C for five different families of pure solvents: ketones (squares), nitriles (circles), acetates (triangles), acyclic carbonates (crosses), and thiols (stars). Bottom: Temperature-dependent diffusion exponential prefactors (calculated from the data shown in the top half of Figure 5) versus temperature-dependent dielectric constants. The E_a values used to calculate the prefactors for each solvent family are given in Table 1.

Dividing each temperature-dependent diffusion coefficient in the top half of Figure 5 by $\exp(-E_a/RT)$ yields the exponential prefactor D_o (eq 2). A plot of the resulting prefactors against the dielectric constants results in a master curve for each solvent family as shown in the bottom half of Figure 5. The acetate and thiol master curves are closely spaced to each other because these two solvent families have similar dipole moments. Conversely, the ketone and nitrile master curves are shifted to the right of the acetate/thiol data because of their much higher dipole moments.

If the entire temperature dependence of the dielectric constant is contained in the quantity N/T as expressed by eq 7, it should be possible to use the CAF written in terms of N/T rather than ε_s. The "compensation" in the compensated Arrhenius formalism accounts for the temperature dependence in the exponential prefactor. In principle, the quantity $N(T)/T$ can be substituted into eqs 1 and 2 in place of the static dielectric constant $\varepsilon_s(T)$, resulting in

$$\sigma(T) = \sigma_o(N(T)/T)\exp(-E_a/RT) \tag{8}$$

$$D(T) = D_o(N(T)/T)\exp(-E_a/RT) \tag{9}$$

Writing $N(T)$ emphasizes the implicit temperature dependence of the dipole density. The compensated Arrhenius equations for conductivity and diffusion (eqs 3 and 4) written in terms of dipole density then become

$$\ln\left(\frac{\sigma(T, N(T)/T)}{\sigma_r(T_r, N(T_r)/T_r)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \tag{10}$$

$$\ln\left(\frac{D(T, N(T)/T)}{D_r(T_r, N(T_r)/T_r)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \tag{11}$$

To check the validity of eqs 8−11, density data were collected for the families of pure ketones, nitriles, acetates, and thiols described earlier in this paper. Two isothermal reference curves, at 25 and 45 °C, were formed for the ketones, nitriles, and thiols by plotting the values of D (previously measured and discussed earlier) against N/T_r in place of ε_s; two similar reference curves at 30 and 50 °C were prepared for the acetates. Temperature-dependent diffusion coefficients were then scaled to the reference diffusion coefficient with the same value of N/T, thereby canceling the two prefactors. This is identical to the procedure described earlier using ε_s. The resulting CAE plots were very linear and activation energies obtained from both slope and intercept were essentially identical (within 6%) to those obtained from the scaling procedure using the static dielectric constant (Table 1). A plot of the diffusion exponential prefactors against N/T results in the series of master curves shown in Figure 6 for each of the ketone, nitrile, acetate, and thiol solvent families.

The carbonate data are excluded from Figure 6 because, as previously mentioned, eq 7 does not describe these data very well due to the extremely low permittivities of these compounds. To summarize, the compensated Arrhenius formalism can be performed for a solvent family without any dielectric constant data. Instead, temperature-dependent density data can be used to determine an E_a value and hence the corresponding Boltzmann factor. A simple calculation leads to the exponential prefactors and, if the underlying assumptions

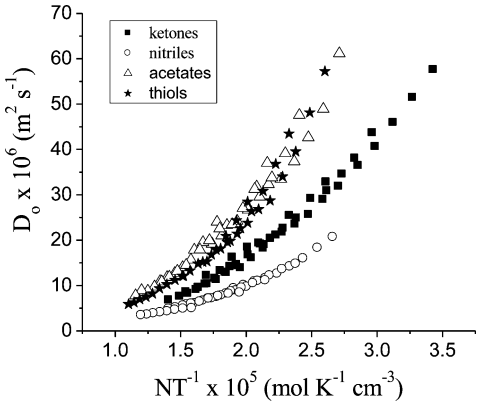

Figure 6. Diffusion exponential prefactors versus N/T over the range 5 to 85 °C for four families of pure solvents: ketones (squares), nitriles (circles), acetates (triangles), and thiols (stars). The E_a values used to calculate the prefactors are given in Table 1.

are correct, the formation of a master curve when the prefactors are plotted as a function of N/T as illustrated by Figure 6.

A comparison of the bottom half of Figure 5 with Figure 6 is informative. The basic difference between the two plots is that the factor μ^2 is missing in the abscissa of Figure 6. In other words, the data of Figure 6 are normalized to a permanent dipole moment of unity. In the discussion following Figure 5, we noted that the acetate data and thiol data were grouped together at lower values of ε_s, separated from the ketone and nitrile data similarly grouped at higher values of ε_s. The difference in the dipole moments of the two groups is responsible for the separation of the two sets of curves. Removal of the dependence on μ in Figure 6 shifts the curves so that the curves begin at about the same point on the abscissa (although the ketone data begin at slightly larger values).

We now consider the molecular basis for the reference curve by examining conductivity data for dilute TbaTf–nitrile solutions. For example, the conductivity reference curve at 35 °C is designated in Figure 7 by solid circles and is formed by plotting conductivities of each member of the nitrile family measured at 35 °C against the value of ε_s also measured at 35 °C for each member. The conductivity increases fairly sharply

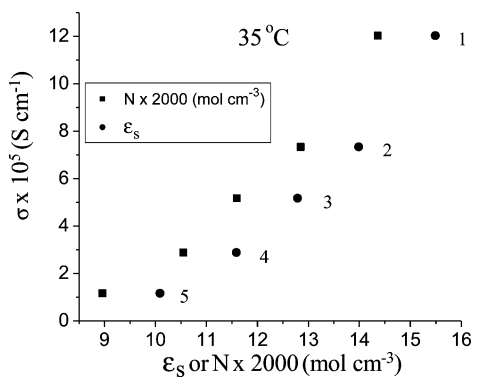

Figure 7. Conductivity versus dielectric constant (circles) and conductivity versus dipole density (squares) at 35 °C for 0.0055 M TbaTf–nitriles: (1) heptanenitrile, (2) octanenitrile, (3) nonanenitrile, (4) decanenitrile, and (5) dodecanenitrile. The dipole densities are multiplied by a factor of 2000 so that both curves can be shown on the same abscissa scale.

as the alkyl chain length of the nitrile decreases, which is similar to behavior observed for other solvent families.[1,6]

The conductivities in Figure 7 are also plotted against the nitrile dipole density N, which was also measured at the reference temperature of 35 °C. Since μ and ε_∞ are approximately constant from member to member in a solvent family and all measurements in Figure 7 are at 35 °C, eq 7 states that ε_s differs between members of the nitrile family only due to the change in dipole density. The direct proportionality between dielectric constant and dipole density[20] means that an isothermal plot of σ vs N should have an almost identical shape to a plot of σ vs ε_s, as is observed in the figure above. Since the CAF E_a value is constant for a particular solvent family, the reference curve simply states that the isothermal conductivity or diffusion coefficient is higher for a short alkyl chain member compared to a long alkyl chain member because the short alkyl chain member has a higher density of dipoles.

4. CONCLUSIONS

Mass transport in liquids has been studied for over a century. The temperature dependence of mass transport, and specifically viscosity and diffusion, has largely been described from two different perspectives although other models have been recently introduced.[29,30] First, Eyring's transition state theory describes transport as a thermally activated process.[31] Here the liquid is assumed to have a quasicrystalline structure where a liquid molecule is confined in a "cage" of surrounding molecules. An energy barrier must be surmounted in order for a molecule to move from its "cage" into an adjacent "hole." The molecule traverses a distance roughly equivalent to the molecular diameter during this transition. While transition state theory explains the experimentally observed exponential temperature dependence of the viscosity and diffusion coefficient, it has been the subject of criticism. Transition state theory cannot explain the non-Arrhenius transport behavior exhibited by many liquids.[32] Furthermore, the relatively small activation energies obtained from liquid viscosity and diffusion data using transition state theory imply that a large fraction of the molecules (commonly 20%) are in the transition state at any given time.[33] It is known that the energy of activation must be sufficiently large in order for equilibrium statistics to apply.[31] Additionally, there is also skepticism that the movement of a molecule from its "cage" to a "hole" could occur over distances as large as the molecular diameter.[33]

Free volume theory has also been used to characterize temperature-dependent mass transport. Free volume consists of the voids that are introduced into a liquid as a result of the thermal expansion that occurs upon heating.[34−36] There is no explicit temperature dependence in free volume theory; the temperature dependence of mass transport is due to the implicit temperature dependence contained in the liquid volume. Cohen and Turnbull have described temperature-dependent diffusion in liquids using free volume theory.[37] Here, a solvent molecule is confined to a "cage" composed of surrounding solvent molecules. Density fluctuations in the liquid will occasionally open a void within the "cage" that is large enough to allow translational movement of the solvent molecule. Diffusion results from the translational motion of a molecule across the void within its cage. Unlike transition state theory, free volume theory does not consider transport to be a thermally activated process. Instead, diffusion is due to the redistribution of free volume within the liquid. Free volume theory predicts that the temperature dependence of a transport

property results from the temperature-dependent volume change and therefore the transport property should not change with temperature if the volume is held constant. However, many exceptions to this statement are known.[32,37]

Macedo and Litovitz have pointed out that both Eyring's transition state theory and free volume theory describe certain aspects of mass transport well, but that a combination of both theories is required to satisfactorily describe transport.[32] The compensated Arrhenius formalism also utilizes both a volume component and an activation component. We postulate that both the ionic conductivity and diffusion coefficient have an Arrhenius-like form that also includes a dielectric constant dependence in the exponential prefactor (eqs 1 and 2). We consider transport to be a thermally activated process as evidenced by the inclusion of the Boltzmann factor $\exp(-E_a/RT)$ in eqs 1 and 2. The volume dependence of the CAF is more subtle. The temperature dependence of the exponential prefactor is due entirely to the temperature dependence of the dielectric constant, but Onsager has shown that the temperature dependence of the dielectric constant is proportional to the quantity N/T. Besides the explicit temperature dependence given in the denominator, the dielectric constant is temperature-dependent due to the inherent temperature dependence of the dipole density N. The dipole density decreases with increasing temperature as a result of the thermal volume expansion that occurs upon heating of the liquid. The CAF accounts for non-Arrhenius transport behavior by canceling out the temperature dependence in the prefactor that is due to the dielectric constant,[1,5,38] or equivalently as shown here, due to N/T. Furthermore, the CAF activation energy is substantially higher than that obtained from transition state theory. For a representative CAF activation energy of 25 kJ/mol, the fraction of molecules in the transition state at room temperature is 0.004%. This fraction is still only 0.02% for the highest temperature at which data were collected (85 °C).

It is well-known that conventional transport theories often predict results that are not in agreement with experimental data.[39−41] Hildebrand has pointed out that too much emphasis has been placed on mathematical models instead of experimental data, and especially temperature-dependent data.[35] We have approached this problem from the opposite point of view. The CAF very accurately describes copious amounts of temperature-dependent data for ketones, acetates, alcohols, nitriles, carbonates, and thiols. The CAF has been shown to describe the temperature dependence of conductivity, diffusion, and dielectric relaxation data, and studies are currently underway to extend the CAF to viscosity in liquids. This work shows that adjustable fitting parameters are not required to explain mass and charge transport in liquids. Instead, transport can be described very well using simple molecular and system parameters, i.e., the molecular dipole moment and the dipole density.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of ionic conductivity (0.0055 M TbaTf), static dielectric constant, diffusion coefficient, and density data as a function of temperature for the nitriles, ketones, acetates, acyclic carbonates, and thiols. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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