

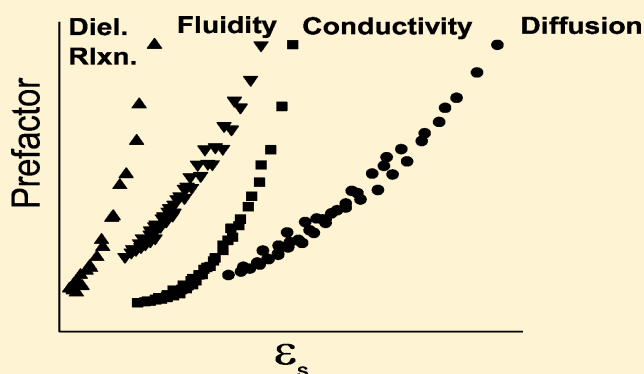
Application of the Compensated Arrhenius Formalism to Fluidity Data of Polar Organic Liquids

Matt Petrowsky, Allison M. Fleshman, and Roger Frech*

Department of Chemistry and Biochemistry, University of Oklahoma, 101 Stephenson Parkway, Norman, Oklahoma 73019, United States

Supporting Information

ABSTRACT: The temperature dependence of viscosity (the reciprocal of fluidity) in polar liquids has been studied for over a century, but the available theoretical models have serious limitations. Consequently, the viscosity is often described with empirical equations using adjustable fitting parameters that offer no insight into the molecular mechanism of transport. We have previously reported a novel approach called the compensated Arrhenius formalism (CAF) to describe ionic conductivity, self-diffusion, and dielectric relaxation in terms of molecular and system properties. Here the CAF is applied to fluidity data of pure *n*-acetates, 2-ketones, *n*-nitriles, and *n*-alcohols over the temperature range 5–85 °C. The fluidity is represented as an Arrhenius-like expression that includes a static dielectric constant dependence in the exponential prefactor. The dielectric constant dependence results from the dependence of mass and charge transport on the molecular dipole moment and the solvent dipole density. The CAF is the only self-consistent description of fluid transport in polar liquids written solely in terms of molecular and system parameters. A scaling procedure is used to calculate the activation energy for transport. We find that the activation energies for fluidity of the aprotic liquids are comparable in value, whereas a higher average E_a value is observed for the *n*-alcohol data. Finally, we contrast the molecular description of transport presented here with the conventional hydrodynamic model.



1. INTRODUCTION

Temperature-dependent viscosity studies of liquids have been performed for well over a century. Numerous empirical equations have been used to describe different kinds of liquids,^{1–10} but the adjustable fitting parameters used in these equations provide no insight into the molecular-level picture of transport. Viscosity data have also been correlated, with some success, to reduced temperature parameters.^{11–13} The viscosity of many liquids depends exponentially on temperature, and the first equation demonstrating this relationship was provided by de Guzman:¹⁴

$$\eta = Ae^{B/RT} \quad (1)$$

where η is viscosity, R is the gas constant, T is temperature, and A and B are constants. However, the most commonly used form of eq 1 is given by Andrade and includes a volume dependence in the constants A and B .^{15,16} There has also been some investigation of the temperature-dependent fluidity of liquids, where the fluidity F is defined as the reciprocal of viscosity. Equation 1 can be rewritten in terms of fluidity as¹⁷

$$F = \eta^{-1} = Ce^{-B/RT} \quad (2)$$

where C is the reciprocal of A . The temperature dependence of the viscosity has been analyzed from numerous different

viewpoints, and it would be impractical to describe all of them. However, free volume theory and transition state theory are the two most common models used to interpret these data and will therefore be briefly described.

Free volume consists of the voids that are introduced into a liquid as a result of the thermal expansion that occurs upon heating.^{18–20} 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. Free volume theory does not consider transport to be a thermally activated process.²⁰ Batschinski²¹ and Macleod²² were the first to use free volume arguments by proposing that the viscosity was inversely proportional to the specific volume. Later, Hildebrand introduced a slightly modified version of Batschinski's equation.¹⁹ However, Doolittle has presented evidence that the viscosity is an exponential function of the free volume.¹⁸ There are multiple criticisms of free volume theory. In free volume theory, the only temperature dependence is that contained in the volume; therefore, the constant volume

Received: December 6, 2012

Revised: February 14, 2013

Published: February 17, 2013

viscosity should remain independent of temperature. However, multiple violations of this have been observed.^{23–26} Additionally, free volume equations cannot fit viscosity data over large temperature ranges and cannot describe hydrogen bonding liquids very well.^{21,27,28} It has been argued that any practical viscosity model cannot be based solely on volume, and that intermolecular interactions must play some role in controlling the viscosity.²⁹

Eyring applied transition state theory to liquid viscosity and derived an equation whose form is equivalent to that of eq 1.³⁰ The liquid structure is viewed as quasicrystalline,³¹ where a liquid molecule is confined to a “cage” of surrounding molecules. Transport is a thermally activated process where an energy barrier (represented by B in eq 1) must be overcome for a molecule to move from its “cage” into an adjacent “hole.” Eyring’s equation for viscosity is derived from rigorous theory and contains no adjustable fitting parameters, but it does have limitations. It often fails to account for non-Arrhenius behavior,³² which suggests that there might be some additional temperature dependence that should be included in Eyring’s model. The biggest drawback to this equation is that it is not particularly accurate;^{33,34} predicted viscosities frequently deviate by as much as 30% from experimental data.³⁵ Eyring has outlined the assumptions in his theory that may lead to the observed discrepancies,³⁶ and for these reasons it has been argued that his model should be viewed as semiempirical.³³ The limitations of the free volume and transition state models resulted in a largely empirical description of temperature-dependent viscosity that continues to this day. For example, numerous temperature-dependent viscosity studies have been performed over the past decade using various ionic liquids, and the data are fit to a variety of empirical equations that require multiple adjustable fitting parameters to achieve good fits to the data.^{37–39}

Here we will analyze the temperature dependence of liquid viscosity from a perspective that is very different from approaches in the literature to date. Our focus will be on fluidity instead of viscosity, and we begin by making three key postulates about the form of eq 2. First, the constant C (exponential prefactor) is temperature-dependent, whereas B (activation energy) has no temperature dependence. The temperature dependence of the prefactor and activation energy has been examined in many different ways in the literature,^{9,13,36,40} but there is no general consensus as to the exact functional form of this dependence. Second, we postulate that there is a static dielectric constant dependence in the exponential prefactor. Finally, we assume that all of the temperature dependence in the exponential prefactor is due to the inherent temperature dependence of the solvent static dielectric constant ϵ_s . Consequently, we can rewrite eq 2 as:

$$F(T) = F_0(\epsilon_s(T))e^{-E_a/RT} \quad (3)$$

where $F_0(\epsilon_s(T))$ is the exponential prefactor written to explicitly show the dielectric constant dependence and E_a is the temperature-independent energy of activation. We have previously shown that equations similar in form to eq 3 can be written for the ionic conductivity,^{41–43} diffusion coefficient,^{42,44} and dielectric relaxation rate constant.⁴⁵ A scaling procedure can be performed that cancels the prefactor and allows calculation of the activation energy. It will be shown that all of the fluidity data for a given solvent family lies on a single master curve when the prefactors are plotted against ϵ_s . Furthermore, the dielectric constant dependence of fluidity will

be written in terms of solvent dipole density and permanent dipole moment following the Onsager equation for ϵ_s .⁴⁶ Temperature-dependent viscosity studies have been performed for many different kinds of liquids including nonpolar molecules,^{13,16,17,36} polar molecules,^{9,16,17,36} metals,^{17,32,36,40} and molten salts.^{33,40,47,48} However, here we focus exclusively on polar organic molecules, specifically the n -acetates, 2-ketones, n -nitriles, and n -alcohols over the temperature range 5–85 °C.

2. EXPERIMENTAL SECTION

All chemicals were obtained from Aldrich, Alfa Aesar, or TCI America and used as received. The capacitance was measured using an 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 static dielectric constant ϵ_s is calculated from the measured capacitance C using the equation $\epsilon_s = \alpha \times C \times C_0^{-1}$, where α is a variable to account for stray capacitance and C_0 is the atmospheric capacitance.⁴⁹ A Huber Ministat 125 bath was used to regulate the temperature from 5 to 85 °C in increments of 10 °C.

The viscosity was measured with a Cambridge VISCOLab 4000. The temperature was regulated over the range 5–85 °C in increments of 10 °C using a Huber Ministat 240 bath. Viscosities of butyl acetate, pentyl acetate, hexyl acetate, 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol over the temperature range 5–85 °C were on average within 6% of literature values.⁵⁰

The density of the pure solvents was measured over the temperature range 5–85 °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 5–85 °C were on average within 0.1% of literature values.⁵⁰

3. RESULTS AND DISCUSSION

3.1. Scaling Procedure. A scaling procedure must be used to calculate the activation energy in eq 3. This procedure is based on the idea that there are two different ways in which the dielectric constant can be varied. First, the dielectric constant changes with temperature, and the temperature-dependent expression for the fluidity (eq 3) incorporates this dependence into the prefactor. Second, the dielectric constant can be varied isothermally by changing the alkyl chain length for a family of solvents. A solvent family consists of a group of liquids that all have the same functional group but differ in the length of the alkyl chain attached to the functional group. For example, the n -alcohol family studied in this work includes decanol, nonanol, octanol, heptanol, and hexanol. Isothermal fluidities that result from changing the alkyl chain length of a solvent family are defined as reference fluidities and are symbolized by F_r . The temperature at which these data are collected is denoted as the reference temperature T_r . An isothermal plot of fluidity versus dielectric constant is termed the reference curve at temperature T_r . The fluidity reference curve at 55 °C is depicted in the bottom half of Figure 1 for the 1-alcohol family. The fluidity increases as the dielectric constant increases for a particular reference curve. This trend is expected because a liquid is usually more fluid, or less viscous, as the alkyl chain length is decreased. Equation 3 can be rewritten as follows to describe reference fluidities:

$$F_r(T_r) = F_0(\epsilon_s(T_r))e^{-E_a/RT_r} \quad (4)$$

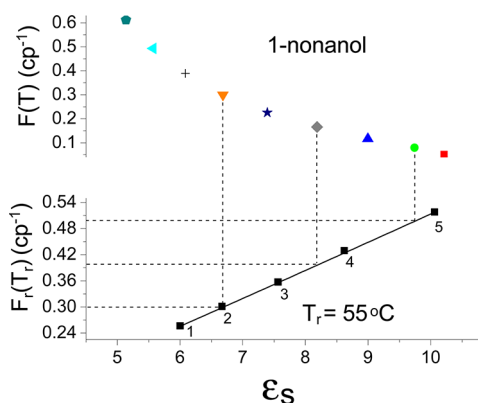


Figure 1. Top: Temperature-dependent fluidity versus temperature-dependent dielectric constant for 1-nonanol at 5 (square), 15 (circle), 25 (upward facing triangle), 35 (diamond), 45 (star), 55 (downward facing triangle), 65 (cross), 75 (leftward facing triangle), and 85 °C (pentagon). Bottom: Isothermal fluidity versus isothermal dielectric constant at 55 °C for the 1-alcohol solvent family. The family members are labeled as follows: (1) decanol, (2) nonanol, (3) octanol, (4) heptanol, and (5) hexanol.

The scaling proceeds by dividing each temperature-dependent fluidity by the reference fluidity that corresponds to the same value of ϵ_s . The determination of the reference fluidity for a given temperature-dependent fluidity is demonstrated schematically in Figure 1 for nonanol at 15, 35, and 55 °C using the reference curve at 55 °C. The scaling is described mathematically by dividing eq 3 by eq 4:

$$\frac{F(T)}{F_r(T_r)} = \frac{F_0(\epsilon_s) e^{-E_a/RT}}{F_0(\epsilon_s) e^{-E_a/RT_r}} \quad (5)$$

The exponential prefactors cancel because they are assumed to be functions of ϵ_s only. Taking the natural logarithm of both sides of eq 5 leads to the final expression:

$$\ln\left(\frac{F(T)}{F_r(T_r)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \quad (6)$$

Equation 6 is called the compensated Arrhenius equation (CAE) for fluidity, and if CAE behavior is observed, then a plot of $\ln[F(T)/F_r(T_r)]$ versus T^{-1} is linear and the activation energy can be determined from either the slope or the intercept. Equations 3–6 and the postulates therein are collectively referred to as the compensated Arrhenius formalism (CAF). The CAF has successfully been applied to other transport phenomena including ionic conductivity,^{41–43,51} self-diffusion,^{42,44} and dielectric relaxation.⁴⁵

Figure 2 shows CAE plots that result from scaling temperature-dependent fluidities for hexyl acetate (0–80 °C), octanenitrile (5–85 °C), and nonanol (5–85 °C) to their reference fluidities at 40, 25, and 55 °C, respectively. These plots are very linear, as demonstrated by their correlation coefficients. The activation energies from the slope and intercept of Figure 2 for hexyl acetate, octanenitrile, and nonanol are given in Table 1.

The activation energies obtained from the slope in a CAE plot have always been found to be very similar to those from the intercept in our studies of conductivity,^{41–43} diffusion,^{42,44} and dielectric relaxation.⁴⁵ Furthermore, the E_a values are largely independent of the reference temperature or family member used in the scaling process. Table 2 lists the mean E_a

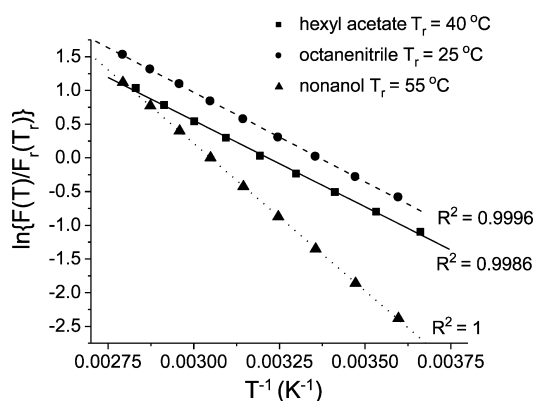


Figure 2. CAE plots for hexyl acetate scaled to 40 °C, octanenitrile scaled to 25 °C, and nonanol scaled to 55 °C, respectively.

Table 1. CAE Fluidity Activation Energies from the Slope and Intercept of Figure 2 for Pure Hexyl Acetate, Octanenitrile, and Nonanol

solvent	E_a (slope) (kJ/mol)	E_a (intercept) (kJ/mol)
hexyl acetate	21.3 ± 0.3	21.4 ± 0.3
octanenitrile	22.0 ± 0.2	22.1 ± 0.1
nonanol	36.4 ± 0.1	36.4 ± 0.1

Table 2. Average CAE Activation Energies from Fluidity Data for the *n*-Acetate, 2-Ketone, *n*-Nitrile, and *n*-Alcohol Solvent Families

solvent	E_a (kJ/mol)
<i>n</i> -acetates	21.5 ± 0.4
2-ketones	18.4 ± 0.3
<i>n</i> -nitriles	22.6 ± 0.1
<i>n</i> -alcohols	36.9 ± 0.2

value for each solvent family obtained by averaging the E_a values from CAE plots for multiple family members scaled to several different reference temperatures. The fluidity activation energies for the aprotic liquids are within a few kilojoules per mole of each other, but the alcohol E_a value is substantially higher. The E_a values are also very similar between the 2-ketones, *n*-acetates, *n*-nitriles, *n*-thiols, and *n*-acyclic carbonates when the CAF is applied to diffusion data, whereas the diffusion activation energy for the 1-alcohol family is higher than those of the aprotic liquids.^{44,52} Furthermore, fluidity activation energies are slightly lower than but comparable to those for diffusion in a given pure solvent family.

3.2. Fluidity Prefactor. The exponential prefactors for fluidity can be calculated after the activation energy is determined from the scaling process. The prefactor is determined from eq 3 by dividing the fluidity (measured at each temperature T) by the Boltzmann factor $\exp(-E_a/RT)$. The top half of Figure 3 plots temperature-dependent fluidities versus temperature-dependent dielectric constants for five pure 1-alcohols. The fluidity increases and the dielectric constant decreases with increasing temperature for each alcohol member as expected. The data are divided into five distinct curves with each curve representing the temperature-dependent data for a particular alcohol member. However, the bottom half of Figure 3 shows that plotting the fluidity prefactors versus dielectric constant places all of the data on a single master curve. The existence of a master curve supports the CAF postulate that the

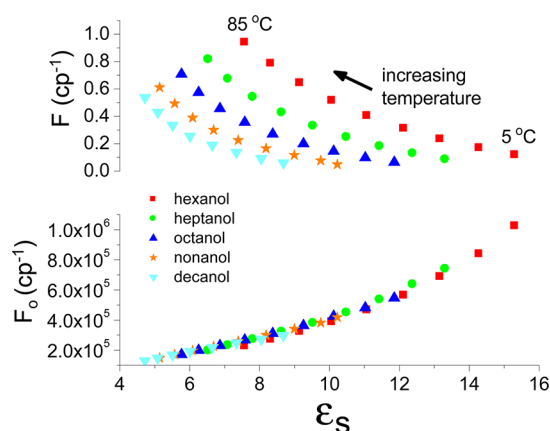


Figure 3. Top: Temperature-dependent fluidities versus temperature-dependent dielectric constant for 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol. For each alcohol member, the left-most data point represents 85 °C, and each consecutive data point to the right represents a temperature that is 10 °C lower. Bottom: temperature-dependent exponential prefactors versus temperature-dependent dielectric constant. The prefactors are obtained by dividing the fluidities in the top half of the Figure by $\exp(-E_a/RT)$ with $E_a = 36.9$ kJ/mol.

temperature dependence in the prefactor is given by the temperature dependence of ϵ_s . Figure 4 shows that fluidity and

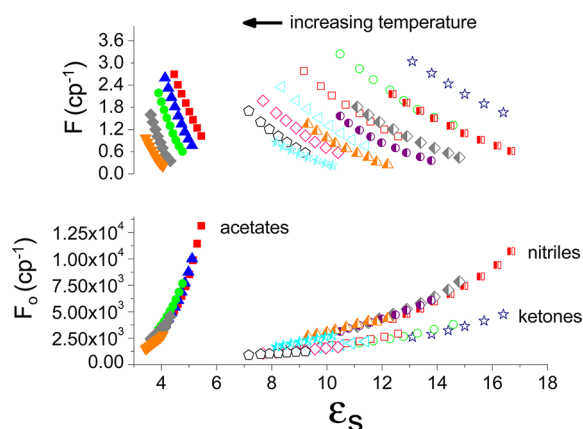


Figure 4. Top: Temperature-dependent fluidities versus temperature-dependent dielectric constant for three aprotic solvent families. The n -alkyl acetates are represented by filled symbols: butyl acetate (square), pentyl acetate (triangle), hexyl acetate (circle), octyl acetate (diamond), and decyl acetate (upside down triangle). The 2-ketones are represented by open symbols: pentanone (star), hexanone (circle), heptanone (square), octanone (sideways triangle), nonanone (diamond), and decanone (pentagon). The n -alkyl nitriles are represented by half-filled symbols: heptanenitrile (square), octanenitrile (diamond), nonanenitrile (circle), decanenitrile (triangle), and dodecanenitrile (star). Bottom: temperature-dependent exponential prefactors versus temperature-dependent dielectric constant. The E_a value used to calculate the prefactors for each solvent family is given in Table 2.

prefactor trends for three aprotic solvent families are qualitatively similar to those observed for the alcohols in Figure 3. However, the magnitude of the prefactors for the alcohols is about two orders of magnitude higher than that for the aprotic liquids.

3.3. Comparing CAE and Simple Arrhenius Behavior. Simple Arrhenius plots have frequently been used to describe

temperature-dependent viscosity or fluidity data of liquids.^{17,36,53} A simple Arrhenius graph results from plotting the logarithm of either the viscosity or fluidity against reciprocal temperature; a linear relationship allows the activation energy to be calculated from the slope. Figure 5 displays simple

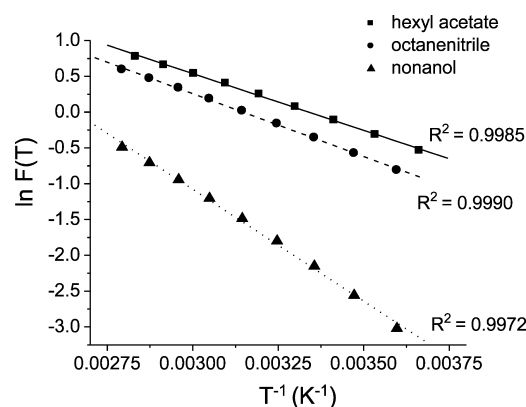


Figure 5. Simple Arrhenius plots for n -hexyl acetate, n -octanenitrile, and n -nonanol.

Arrhenius plots of fluidity data for n -hexyl acetate, n -octanenitrile, and n -nonanol over the temperature range 5–85 °C. These plots are linear with resulting activation energies of 13.2 ± 0.2 , 14.6 ± 0.2 , and 26.0 ± 0.5 kJ/mol for hexyl acetate, octanenitrile, and nonanol, respectively. It is informative to compare the simple Arrhenius plots of Figure 5 with CAE plots for the same members (Figure 2). Whereas both simple Arrhenius and CAE plots are linear, CAE activation energies for a given solvent family (Table 2) are always higher than those obtained from simple Arrhenius plots of that family. Similar results are observed for conductivity and diffusion data; these differences in E_a value originate in the difference of the ordinate scale between CAE and simple Arrhenius plots.⁴⁴ Although the difference in value between CAE and simple Arrhenius activation energies can be <10 kJ/mol, the exponential prefactors are affected to a much greater extent. Figure 6 shows that no master curve results for the nitrile family if the fluidity prefactors are calculated using the E_a value obtained from the simple Arrhenius plot for octanenitrile. There is a narrow range of E_a values that produces a master

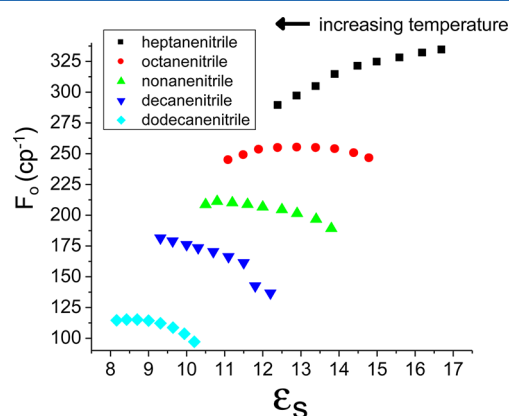


Figure 6. Temperature-dependent exponential prefactors versus temperature-dependent dielectric constant for the nitrile family where the prefactors are calculated using the simple Arrhenius E_a value from octanenitrile (14.6 kJ/mol).

curve. A nitrile master curve is only observed for activation energies in the range from 20.5 to 24 kJ/mol. Similar results occur for fluidity data of the acetates, ketones, and alcohols; the CAE gives activation energies within the narrow range required to produce a master curve, whereas simple Arrhenius activation energies yield no master curve. This behavior has also been reported for 1-alcohol diffusion and conductivity data^{43,44} as well as for diffusion and conductivity data of the acetate family.⁴²

3.4. Molecular and System Properties Controlling Fluidity. We have shown that fluidity data for the acetates, ketones, nitriles, and alcohols over the temperature range 5–85 °C can very accurately be described with eq 3, but we have not described the origin of the dielectric constant dependence in the fluidity prefactor. We have previously shown⁵² that Onsager's model of ϵ_s ⁴⁶ can be used to explain mass/charge transport in terms of the solvent dipole density N and permanent molecular dipole moment μ . A concise approximation to Onsager's equation can be written as

$$\epsilon_s \approx \frac{N\mu^2(\epsilon_\infty + 2)^2}{18kT\epsilon_0} \quad (7)$$

where ϵ_∞ is the high-frequency value of the real part of the dielectric constant, T is temperature, k is Boltzmann's constant, and ϵ_0 is the vacuum permittivity. Equation 7 states that the temperature dependence of the dielectric constant is due to the quantity N/T . The dipole density N is determined by dividing the liquid density by its molecular weight; therefore, all of the temperature dependence in N is due to the temperature-dependent density. It then follows that the exponential prefactor from eq 3 can approximately be written as $F_0(N(T)/T)$ instead of $F_0(\epsilon_s(T))$ because it is the temperature dependence of ϵ_s that is important in the CAF rather than the magnitude of ϵ_s . Figure 7 demonstrates that master curves

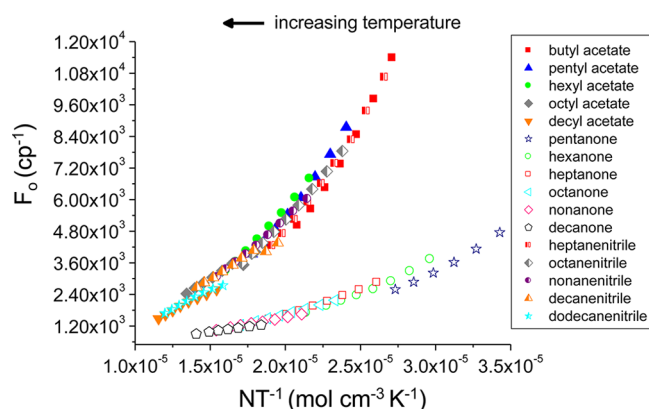


Figure 7. Temperature-dependent exponential prefactors of Figure 4 plotted against NT^{-1} .

result when the fluidity prefactors are plotted against NT^{-1} instead of ϵ_s . Hence, the CAF can be applied using temperature-dependent density data instead of temperature-dependent dielectric constant data. The acetate data in Figure 7 are not horizontally shifted from the remaining data as in Figure 4 because plotting against NT^{-1} rather than μ^2NT^{-1} normalizes the data to unit dipole moment.

Whereas eq 7 describes the temperature dependence of the dielectric constant fairly well for aprotic liquids, it is widely known that Onsager's equation for ϵ_s cannot accurately predict

permittivities for hydrogen bonding solvents.⁵⁴ This point is further demonstrated in Figure 8, where fluidity prefactors for

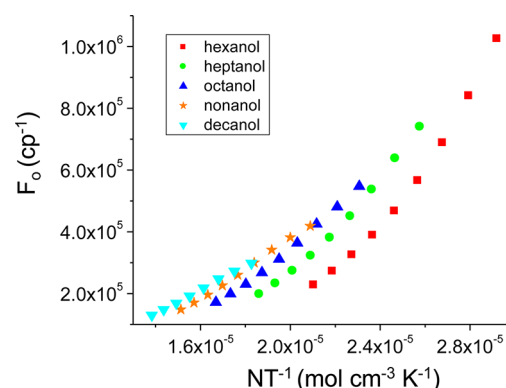


Figure 8. Temperature-dependent exponential prefactors of Figure 3 plotted against NT^{-1} for the 1-alcohol family.

the alcohols are plotted against NT^{-1} . No master curve results in Figure 8, even though a master curve is observed when the alcohol prefactors are plotted against the experimentally measured dielectric constant (Figure 3). Clearly, experimental values of ϵ_s for associated liquids contain a temperature dependence in addition to NT^{-1} that is not accounted for in Onsager's equation. Kirkwood developed a model for protic liquids that accounts for this additional temperature dependence through a structural parameter called the g factor.^{55,56} This factor estimates the extent by which dipolar rotation is hindered by short-range intermolecular interactions. A typical aprotic liquid has a g value close to one, implying that Onsager's equation is applicable. The g factor cannot be precisely calculated on an ab initio basis due to insufficient information about the structure of the liquid; therefore, g values are often determined experimentally.

4. CONCLUSIONS

In the Introduction, free volume theory and transition state theory were described because they are the models most commonly used to explain temperature-dependent liquid viscosities. Both theories have had some degree of success in describing transport but also have limitations. It has been argued that a combination of free volume theory and transition state theory is required to sufficiently explain transport phenomena.³² The CAF includes both a volume component and an activation component. The fluidity is identified as a thermally activated process due to the Boltzmann factor in eq 3. The volume dependence of the CAF originates in the exponential prefactor by way of the static dielectric constant because the quantity N in eq 7 is a dipole density. The dipole density changes with temperature due to the thermal volume expansion of a liquid that occurs while heating.

Fluidities are often used to describe diffusion coefficients and ionic conductivities in solution;^{57,58} therefore, it is useful to examine these correlations for the organic liquids studied here. The top half of Figure 9 shows that the data are strongly correlated when diffusion coefficients are plotted against fluidities for the ketone family of solvents. However, the bottom half of Figure 9 shows that there is substantial scatter in the data when conductivities of dilute ketone electrolytes are plotted against the electrolyte fluidity. It should be noted that from hydrodynamic theory it is more appropriate to plot the

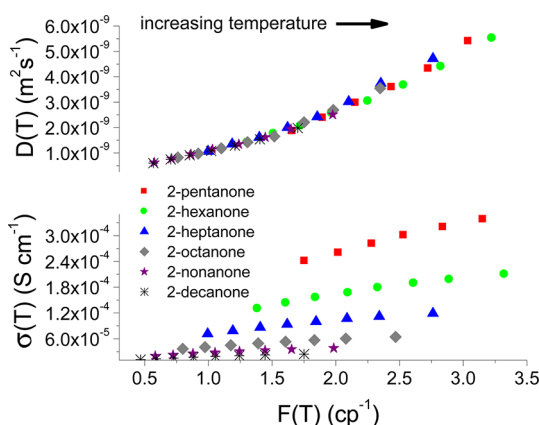


Figure 9. Top: temperature-dependent self-diffusion coefficients versus temperature-dependent fluidities for six pure ketones. Bottom: temperature-dependent conductivities versus temperature-dependent fluidities for six 0.0055 M TbaTf-ketone electrolytes. The data were measured from 5 to 65 °C, in increments of 10 °C, as well as at 80 °C. The 2-pentanone data cover a more limited temperature range from 5 to 55 °C.

molar conductivity against the fluidity, but a plot like this shows identical behavior to that observed in the bottom of Figure 9 (data not shown). The diffusion and conductivity trends observed in Figure 9 also occur for the nitriles, acetates, and alcohols. It is not entirely clear why the fluidity is more closely correlated with diffusion data than with conductivity data, but it is probably related to the fact that both diffusion and fluidity transport phenomena of a pure liquid are governed by the same dipolar interactions. Solvent dipolar interactions also play a crucial role in the conductivity but so do ion–ion and ion–solvent interactions that are not accounted for by the fluidity. It must be remembered that the fluidity is a macroscopic solution transport property, and we have shown here that it can be described satisfactorily in polar organic liquids by using the dipole density and dipole moment of the solvent (via the dielectric constant). Therefore, correlating conductivities or diffusion coefficients to fluidity is an indirect way of characterizing transport; fluidities depend on the same molecular and system parameters, that is, dipole density and dipole moment, that also control conductivity and diffusion. Figure 10 shows that both the diffusion and conductivity data for the ketones can be described very well by plotting the prefactors against N/T .

Finally, it is useful to contrast the CAF with hydrodynamic theory to explicitly describe how our interpretation of transport differs from conventional models. As an example, consider self-diffusion in a pure polar liquid. Why is the diffusion coefficient of 2-pentanone larger than that for 2-decanone for a given temperature? Hydrodynamic theory answers this question by stating that the much larger 2-decanone molecule experiences a greater resistive drag (as evidenced by a higher viscosity) compared with 2-pentanone. Therefore, a 2-decanone molecule has a lower mobility than a 2-pentanone molecule. From an alternate viewpoint, the CAF shows that the family of ketones has similar intermolecular interactions (as evidenced by similar E_a values for each member) because each member has the same functional group. Because the intermolecular interactions coupling a collection of 2-pentanone molecules are similar to those coupling a collection of 2-decanone molecules, 2-pentanone molecules do not “move faster” than 2-decanone

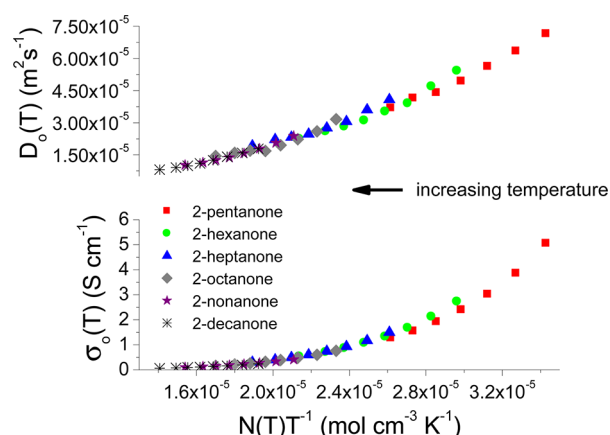


Figure 10. Top: temperature-dependent diffusion prefactors plotted against N/T for the pure ketone family. Bottom: temperature-dependent conductivity prefactors (0.0055 M TbaTf) plotted against N/T for the ketone family. The temperature range of these data is given in the caption of Figure 9.

molecules. The diffusion coefficient of 2-pentanone is larger because 2-pentanone has a greater number of dipoles compared with 2-decanone for a given volume of liquid (as evidenced by the higher dielectric constant for 2-pentanone). Simply put, the diffusion coefficient is higher for 2-pentanone because more molecules are available for transport. The preceding explanation is essentially a verbal description of the CAF expression for the diffusion coefficient: $D(T) = D_0(\epsilon_s(T)) \exp(-E_a/RT)$. 2-Pentanone and 2-decanone experience similar interactions; therefore, the Boltzmann factor $\exp(-E_a/RT)$ is the same for both ketones. However, the higher dipole density and therefore dielectric constant for 2-pentanone leads to a larger exponential prefactor for 2-pentanone compared with 2-decanone.

■ ASSOCIATED CONTENT

Supporting Information

Viscosity, static dielectric constant, and density data are given as a function of temperature for the nitriles, ketones, acetates, and alcohols. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rfrsch@ou.edu. Tel: (405) 325 3831. Fax: (405) 325 6111.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We wish to thank Army Research Office for support of this work through grant no. W911NF-10-1-0437. We are grateful to Dr. Susan Nimmo for her guidance with the NMR diffusion measurements and acknowledge the National Science Foundation for its financial support of the NMR equipment (grant no.: CHE#0639199). We thank the Johnson research group in the OU Physics Department, and especially Jeremy Jernigen, for their help with glovebox modifications. We appreciate the expertise of Chris Crowe in software development for the HP 4192A.

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