Effect of Temperature on the Dielectric Relaxation in Solvent Mixtures at Microwave Frequencies

Jianfeng Lou, Anant K. Paravastu, Paul E. Laibinis,* and T. Alan Hatton*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received: August 27, 1997; In Final Form: October 2, 1997[⊗]

The dielectric relaxation behavior of organic liquids was investigated using three representative solvent mixtures between 10 and 70 °C in which the effectiveness of ideal free energy relationships for describing the process of dipolar relaxation was examined. The selected solvent mixtures (nitrobenzene−toluene, ethanol−butanol, and butanol−formamide) incorporate different specific molecular interactions. The dielectric spectra of these solvents and solvent mixtures can be fit to the Debye model to obtain dielectric relaxation times and static dielectric constants as a function of temperature and solution composition. The free energy of activation for the dipolar relaxation process, ΔG, and the Kirkwood correlation factor, g, were determined using these fitting parameters for these solvent systems at various temperatures. The results provide useful descriptions of structures and thermodynamic properties of the solvent mixtures. In particular, ΔG behaves ideally in mixing for nitrobenzene−toluene and ethanol−butanol mixtures, and exhibits nonidealities for butanol−formamide mixtures. The nonideal dielectric mixing behavior can be expressed in terms of excess free energies of activation for the dielectric relaxation process, and the excess properties can be described by activity coefficients at infinite dilution using the Margules equation.

Introduction

A knowledge of the frequency-dependent dielectric properties of solvent systems is important both in fundamental studies of solvent structure and dynamics and in practical applications of microwave-heating processes. Dielectric relaxation spectroscopy, for instance, is a powerful tool for examining the underlying physics of solvent systems,[1−3] and for exploring the molecular dynamics of liquids, which are characterized by inter- and intramolecular structures that vary rapidly with time. Historically, such studies have focused separately on long-range and short-range molecular forces.[4,5] At one extreme, long-range, nonspecific dispersion forces produce weakly bonded van der Waals complexes, while at the other, short-range, highly directional hydrogen bonding generates molecular networks. In each case, collisional and dielectric frictions contribute to the molecular dynamics of the liquid. In reaction media, these frictions can affect the pre-exponential factor of a reaction rate constant and have a major influence on reaction rates.[6−8] In reactions where the solvent is directly involved in the process (as in solvolytic reactions), the reaction rate can be markedly sensitive to the solvent structure and dynamics.[8]

In chemical processing applications, the availability of quantitative data on dielectric properties of solvent systems, or methods for their prediction, are essential for the design and implementation of microwave-heated processes. One area of particular current interest is the heating of chemical streams by microwave radiation, which appears to promise some processing advantages over conventional methods, including the possibility for remote operation, uniform temperature profiles, enhanced chemical reactivity, and product selectivity.[9,10] In applications of microwave irradiation to solution phase processing and chemical synthesis, the dielectric values of the reaction media are required for predicting heating rates and temperature profiles within a microwave-irradiated system and for performing chemical engineering analyses to optimize microwave-assisted processes.[11,12] It may also be possible to tune the microwave absorption properties of the system by using mixtures of solvents which individually do not exhibit optimal absorption properties at the industrially important frequencies of 915 MHz and 2.45 GHz, but which can be combined to yield a solvent mixture having absorption maxima at one of these two frequencies.

There have been several investigations on the dielectric behavior of solvent mixtures,[1,2,13−20] in which dielectric relaxation spectra were used to examine molecular orientations, hydrogen-bonded networks, and the microdynamics of these systems. Most of these studies have focused on the behavior of water- and alcohol-based systems, typically at room temperature. We have recently demonstrated that the frequency-dependent dielectric spectra of various solvents and solvent mixtures can be described well by three parameters: the dielectric relaxation time constant, the static dielectric constant, and the high-frequency limiting dielectric constant.[21] The three parameters for solvent mixtures can be obtained through dielectric “mixing rules” based on the solution composition and dielectric properties of pure components. In the development of this framework, we related the dielectric relaxation time constant to the free energy of activation for the dipolar relaxation and assumed that this free energy behaved ideally in mixing to generate the effective parameter for the solution. This assumption needs further examination as solvent mixtures can display strong nonidealities in thermodynamic terms and can form microscopically heterogeneous phases.

In this paper, we report the temperature-dependent dielectric relaxation of solvent mixtures at microwave frequencies. The dielectric relaxation process is related to chemical rate theory and discussed in terms of solution thermodynamics. We selected three solvent mixtures (nitrobenzene−toluene, ethanol−butanol, and butanol−formamide) to be representative of solvent mixtures with specific molecular interactions. We have measured the dielectric relaxation spectra for the solution at various compositions over a temperature range of 10−70 °C. These mixtures exhibit a principal dispersion of the Debye or near Debye type at microwave frequencies, and dielectric relaxation times and static dielectric constants could be obtained

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

S1089-5639(97)02785-0 CCC: $14.00

by fitting the spectra to the Debye model.[21] We have used the relaxation time constant to determine relevant thermodynamic parameters for the dipolar polarization process and the static dielectric constant to determine a structural parameter that characterizes the dipolar alignment within the solutions. These parameters provide useful descriptions of the structures and molecular dynamics of the solvent mixtures.

Experimental and Data Analysis

Solvents were obtained commercially and used as received. The solvents include toluene (99.9%, Mallinckrodt), nitrobenzene (min. 99%, EM Science), ethanol (dehydrated 200 proof, Pharmco), 1-butanol (99.9%, Mallinckrodt), and formamide (98%, Aldrich).

Dielectric spectra were collected using an HP 85070M dielectric measurement system with an HP 8719C network analyzer and an open-ended coaxial probe. The instrument specifications and the parameters used in measurement have been described previously.[21] In brief, the network analyzer is connected to the probe through a single transmission cable; it generates microwaves over frequencies ranging from 50 MHz to 13.5 GHz. The system was calibrated using three known standards: air, a short circuit, and 18 MΩ deionized water (Milli-Q). Separate calibrations were made at each measurement temperature to minimize the experimental error caused by contraction or expansion of the transmission cable at different temperatures. A 50 mL sample was used for each measurement, and the sample temperature was regulated using a water-jacketed glass cell connected to a recirculating water bath. A thermocouple was inserted into the sample to measure the temperature and was removed before every dielectric measurement. The dielectric spectra were collected from 10 to 70 °C in increments of 10 °C.

The spectra were fitted against different models using a complex nonlinear least square (CNLS) routine.[21,22] The CNLS routine minimizes an objective function (S) involving both the real and imaginary parts of the complex dielectric constant,

$$S(A) = \sum_{i=1}^{N}\{W_i'[\epsilon_m'(\omega_i;A) - \epsilon_e'(\omega_i)]^2 + W_i''[\epsilon_m''(\omega_i;A) - \epsilon_e''(\omega_i)]^2\} \quad (1)$$

where A is the parameter set used in the relaxation model, N is the number of data points, W is the weighting factor, ω is the angular frequency, ϵ_m is the value predicted by the relaxation model, and ϵ_e is the experimental value. The superscripts $'$ and $''$ denote the real and imaginary parts of the complex quantities, respectively.

Three different weighting schemes were tested on the data. In these schemes, the weighting factors were given by $W_i' = (Q_i')^{-2}$ and $W_i'' = (Q_i'')^{-2}$ with Q_i' and Q_i'' being the estimated standard deviations of the real and imaginary components, respectively, of the ith value.[23]

The three weighting schemes are unity weighting ($Q_i' = Q_i'' = 1$), proportional weighting [$Q_i' = |\epsilon_i'(\omega_i)|$ and $Q_i'' = |\epsilon_i''(\omega_i)|$], and modulus weighting [$(Q_i' = Q_i'' = [(\epsilon_i'(\omega_i))^2 + (\epsilon_i''(\omega_i))^2]^{1/2}$] for a given datum point $\epsilon_e^*(\omega_i) = \epsilon_e'(\omega_i) + j\epsilon_e''(\omega_i)$.[23] No appreciable variation was observed in the parameters estimated using these different weighting functions; unity weighting was selected for simplicity.

The general form of the relaxation model is given by the Havriliak–Nagami equation[24]

$$\epsilon^* - \epsilon_h = \frac{\epsilon_s - \epsilon_h}{[1 + (j\omega\tau)^{1-\alpha}]^{1-\beta}} \quad (2)$$

where ϵ_s is the static dielectric constant, ϵ_h is the high-frequency limiting dielectric constant, τ is the relaxation time, and α and β are empirical parameters for the distribution of relaxation times with values between zero and one. The Havriliak–Nagami equation includes three relaxation models as limiting forms. The Debye model ($\alpha = 0$; $\beta = 0$) implies a single relaxation time, while the Cole–Cole ($0 \leq \alpha < 1$; $\beta = 0$) and Cole–Davidson ($\alpha = 0$; $0 \leq \beta < 1$) models both suggest a distribution of relaxation times. The magnitudes of α and β indicate the width of the distribution function.

The CNLS fitting was performed using LEVM 6.1, a software package developed by Macdonald[22,23] and obtained from Solartron Instruments. The LEVM 6.1 program yields a standard deviation for each fitting parameter, a residual plot for both ϵ' and ϵ'', and various statistical parameters related to the quality of the fit. These outputs were used to justify the appropriate relaxation models for the solvent mixtures.

Results and Discussion

Analysis of Dielectric Relaxation Processes. A dielectric relaxation process involves rapid changes in the electric polarization $\boldsymbol{P}$, or the total electric moment per unit volume. The dielectric decay function, $\varphi(t)$, is the normalized autocorrelation function defined as

$$\varphi(t) = \frac{\langle \boldsymbol{P}(t)\cdot\boldsymbol{P}(0)\rangle}{\langle \boldsymbol{P}(0)\cdot\boldsymbol{P}(0)\rangle} \quad (3)$$

where $\langle\ \rangle$ denotes an ensemble average, $\boldsymbol{P}(0)$ and $\boldsymbol{P}(t)$ are the electric polarizations at time 0 and t, respectively, and $\cdot$ denotes the inner product of two vectors.[3] The dielectric decay functions of most liquids in the microwave region can be represented by an exponential,[3,25]

$$\varphi(t) = \exp(-t/\tau) \quad (4)$$

where τ is the dielectric relaxation time constant. This constant characterizes the process of dipolar reorientation upon application of an external electric field and contains information on the microdynamics and molecular structure of the liquids. A distribution in the relaxation time constant could occur if microheterogeneous regions exist in a system. For the solvents and solvent mixtures used in this study, we have observed that a single relaxation time constant (or the Debye relaxation model) is sufficient to describe their relaxation behavior.[21]

Figure 1 shows the frequency-dependent complex dielectric constant for butanol, formamide, and a 50/50 (v/v) butanol–formamide mixture at 10, 30, and 50 °C; the various symbols denote experimental data, and the solid lines are fitting curves for the Debye model, which describes the dielectric spectra well. Both the dielectric constant (ϵ') and loss factor (ϵ'') decrease with increasing temperature at the low-frequency end and increase with increasing temperature at the high-frequency end. (Figure 1a only shows the high-frequency regime, but the static dielectric constant for butanol does decrease with increasing temperature.) The frequency at which the loss factor is a maximum, $f_{max}(2\pi f_{max}\tau = 1)$, shifts to higher values with increasing temperature. We observed this temperature-dependent dielectric relaxation behavior for the three solvent mixtures nitrobenzene–toluene, ethanol–butanol, and butanol–formamide over the entire composition range.

Figure 2 presents the temperature-dependent behavior of the three dielectric parameters in the Debye model for butanol and

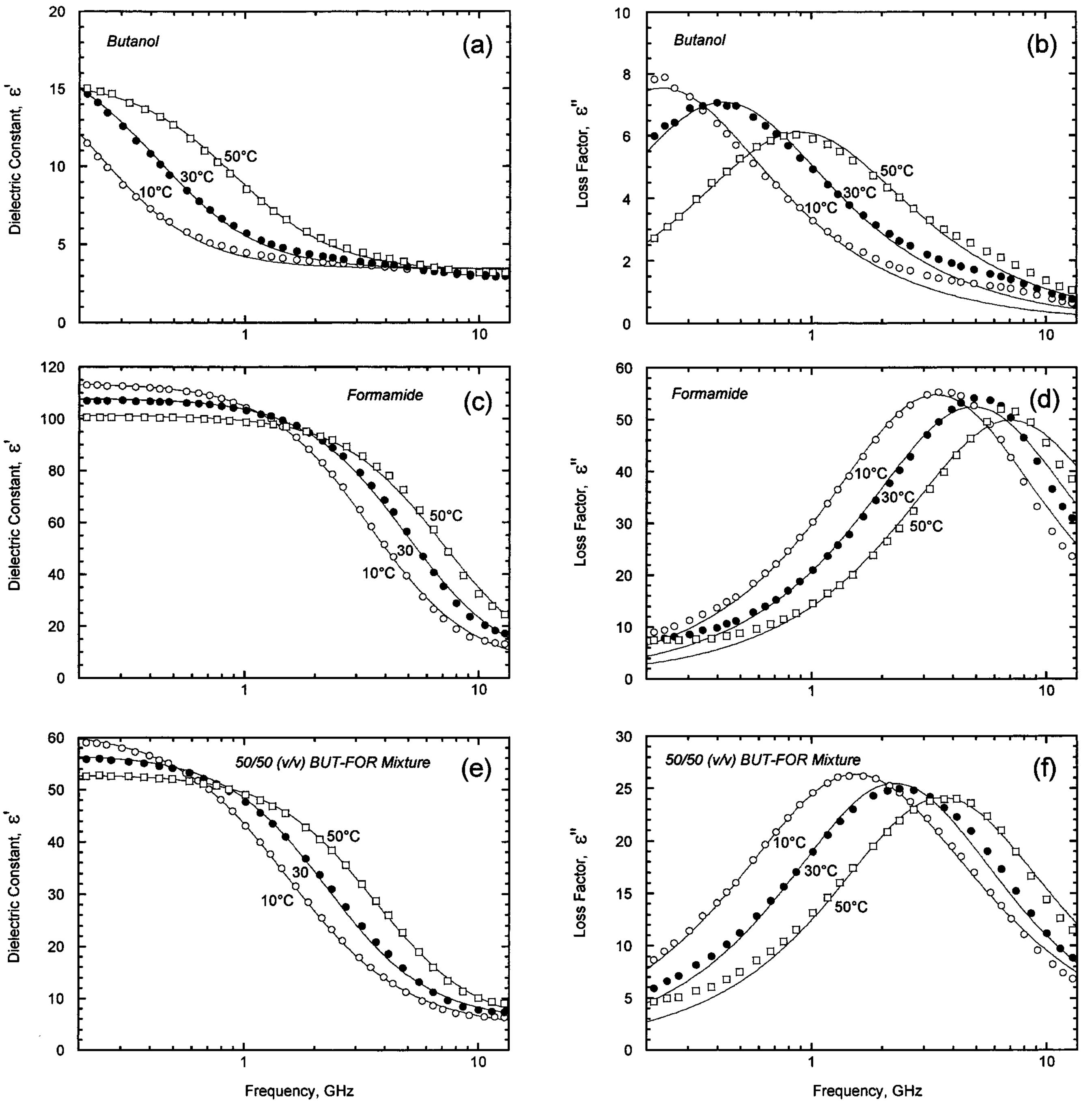

Figure 1. Measured frequency-dependent dielectric properties for butanol, formamide, and a 50/50 (v/v) butanol−formamide mixture at 10, 30, and 50 °C. Different markers denote experimental data and the solid lines represent CNLS fits to the Debye model: (a, c, and e) dielectric constant, (b, d, and f) dielectric loss factor.

formamide:[26] the dielectric relaxation time constant, τ, the static dielectric constant, ϵ_s, and the high-frequency limiting dielectric constant, ϵ_h. While ϵ_h showed essentially no variation with temperature, both τ and ϵ_s exhibited Arrhenius-type temperature dependence characteristic of energetic processes. The Arrhenius descriptions of these parameters provide a framework for estimating the frequency-dependent dielectric properties of a substance at a temperature of interest based on its dielectric spectra at two reference temperatures.[27]

The variations of $f_{\max}$ (or τ) are related to changes in the molecular interactions in the solvents and solvent mixtures. A high value of $f_{\max}$ (or a low value of τ) suggests rapid molecular motions during relaxation. Attraction to neighboring molecules could slow the relaxation process. If a solvent molecule tends to associate to form a complex, the solvent exhibits a considerably larger relaxation time than does a nonassociated solvent. An increase in temperature would allow faster molecular motions, which is consistent with the shift in $f_{\max}$ to higher values with increasing temperature in Figure 1. This shift could be due to a decreased solvent viscosity and/or a reduced effective size of molecular complexes at higher temperatures. It is worth noting the difference between the dielectric and viscous relaxation processes. The former involves only rotational motions while the latter deals with both the rotational and translational motions.[14,28]

The dielectric relaxation can be treated as a rate process involving a path over a potential barrier.[21,29] The free energy of activation for the dipole relaxation process, ΔG, can be calculated from the dielectric relaxation time[29]

$$\Delta G = RT \ln\left(\frac{k\tau T}{h}\right) \tag{5}$$

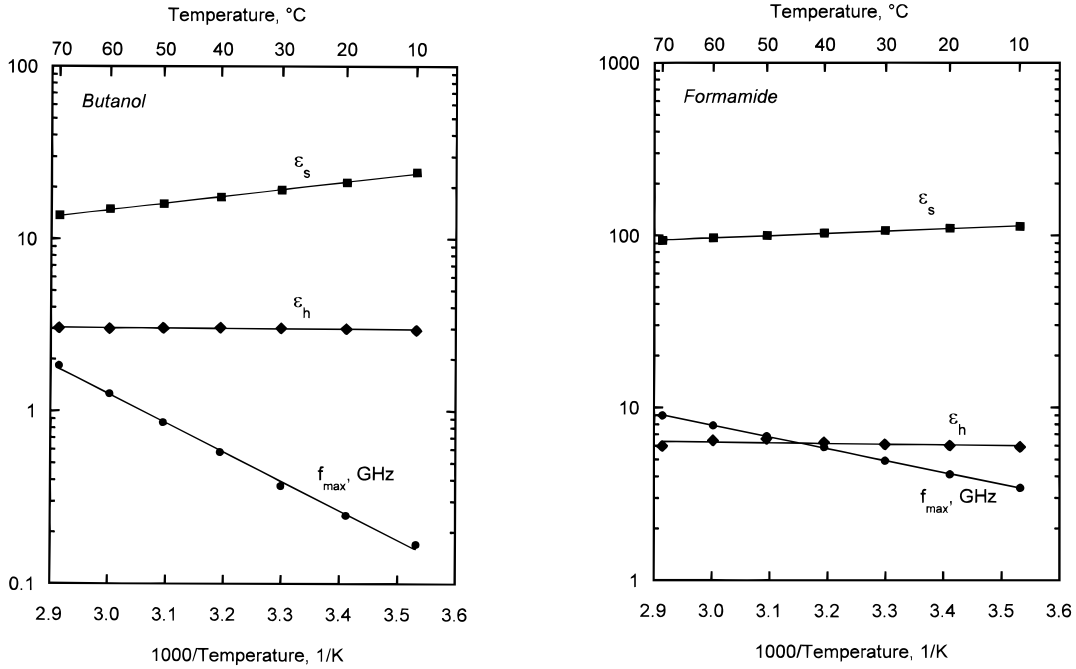

Figure 2. Dielectric parameters in the Debye model—the dielectric relaxation time constant (τ), the static dielectric constant (ϵ_s), and the high-frequency limiting dielectric constant (ϵ_h)—as a function of temperature: (a) butanol and (b) formamide.

where T is the absolute temperature, and k, h, and R are Boltzmann's constant, Planck's constant, and the molar gas constant, respectively. A plot of ΔG versus T ($\Delta G = \Delta H - T\Delta S$) can yield the enthalpy ΔH and the entropy ΔS of activation for the dielectric relaxation process. These thermodynamic parameters characterize the molecular interactions and dynamics of the solvents and solvent mixtures.

The static dielectric constant, ϵ_s, provides additional information about the molecular configuration of neighboring dipoles through a correlation parameter, g, in the Kirkwood equation,[21]

$$\frac{(\epsilon_s - 1)(2\epsilon_s + 1)}{9\epsilon_s}\frac{M}{d} = P_{e+a} + \frac{4}{9}\pi\frac{N_A g\mu^2}{kT} \tag{6}$$

where P_{e+a} is the molar electronic and atomic polarization, μ is the permanent molecular dipole moment in the liquid, M is the molecular weight, d is the density, and N_A is Avogadro's number. P_{e+a} is related to the refractive index, n, through the equation[25,30]

$$P_{e+a} = \frac{(1.1n^2 - 1)M}{(1.1n^2 + 2)d} \tag{7}$$

and μ can be calculated from the gas phase dipole moment,[31] μ_g, using the Onsager relationship[32]

$$\mu = \frac{(2\epsilon_s + 1)(n^2 + 2)}{3(2\epsilon_s + n^2)}\mu_g \tag{8}$$

The correlation factor, g, can be calculated from the measured static dielectric constant through eqs 6–8.[33] The g values are generally intermediate between 0 and 5.[32] A value of g greater than 1 suggests a parallel alignment of neighboring dipoles, and a value of g less than 1 implies an antiparallel arrangement. A nonpolarizable solvent or a solvent without specific interactions would yield a g value close to 1. The g value approaches unity at high temperatures, as expected from destruction of the alignment of neighboring dipoles. An association of solvent molecules through specific molecular interactions, such as hydrogen bonding, tends to yield a high value of g.[21]

Nitrobenzene–Toluene Mixtures. Figure 3a shows that ΔG of the nitrobenzene–toluene mixtures is a linear function of temperature over the range of 10–70 °C for all compositions. The values of ΔH and ΔS are obtained from the slopes and intercepts, respectively, of the lines for different solution compositions. Figures 3b and 4 present plots of ΔG, ΔH, and ΔS as functions of the solution composition, with the plots of ΔG at seven temperatures. All three parameters are observed to be linear functions of the composition, consistent with the ideal dielectric mixing behavior that might be expected on the basis of the nature of these solvent mixtures. Nitrobenzene and toluene are polar and nonpolar solvents, respectively, and they do not associate with each other or with like molecules; the Kirkwood correlation parameters of these solvents are close to 1. Despite their difference in polarity, nitrobenzene and toluene are completely miscible over all compositions and no specific interactions are anticipated between the two molecules. The value of ΔG for nitrobenzene is much higher than that for toluene, suggesting a higher energy barrier for the rotation of nitrobenzene dipoles. As the molecular sizes of nitrobenzene and toluene are similar, the higher energy barrier for nitrobenzene can be attributed to the frictional force experienced by the nitrobenzene molecule during its rotational motion, which could be produced by the polarization effect of the NO_2 group on neighboring molecules. The linear relationships presented in Figures 3 and 4 suggest that a single microscopically homogeneous phase prevails over the entire composition range for the nitrobenzene–toluene mixtures between 10 and 70 °C. The addition of toluene to nitrobenzene can be considered to be a simple dilution of nitrobenzene dipoles.

Ethanol–Butanol Mixtures. Parts a and b of Figure 5 show ΔG of the ethanol–butanol mixtures as a function of temperature at different solution compositions and as a function of solution composition at different temperatures, respectively. Over the temperature range of 10–60 °C, ΔG varies linearly with the mole fraction of butanol except for large deviations with pure butanol at 10 and 20 °C, while its dependence on

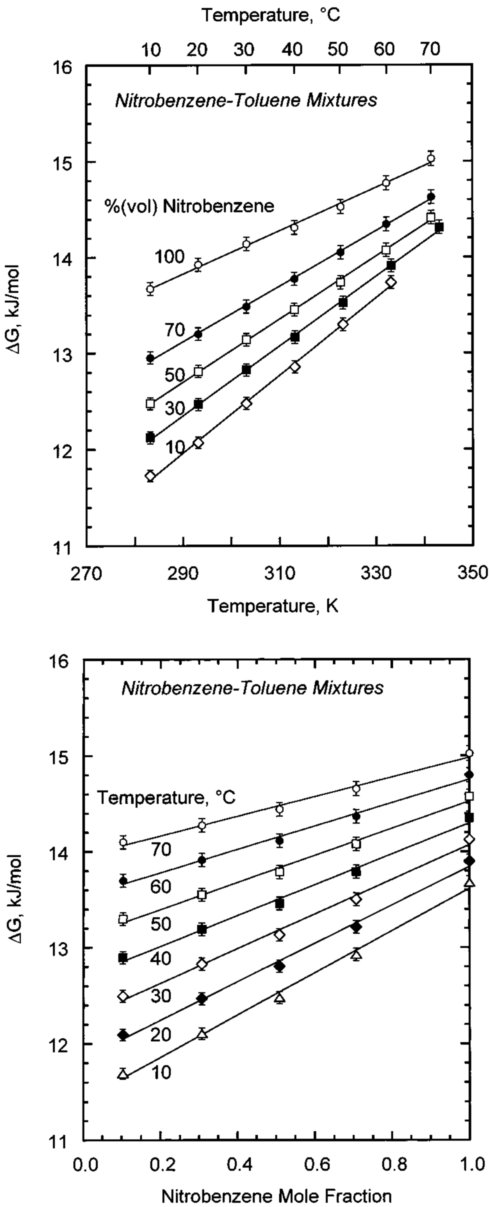

Figure 3. The free energy of activation for the dipolar relaxation process, ΔG, for nitrobenzene–toluene mixtures as functions of (a) temperature and (b) solution composition. The markers denote experimental data, and the lines are their linear fits.

temperature deviates from linearity at temperatures below ~30 °C for most solution compositions.

The values of ΔG for butanol and ethanol are 2–8 kJ/mol greater than those for toluene and nitrobenzene. This difference is attributed to the formation of hydrogen-bonded networks for ethanol and butanol that tend to increase the effective size of a rotating dipole and the dielectric frictional force between the rotating dipole and its neighboring molecules. We also observed that the ΔG values of butanol are 2–3 kJ/mol higher than those of ethanol over the temperature range of 10–60 °C; this difference is consistent with previous findings.[25] Generally, alcohols exhibit one major dispersion in the microwave region and one or more minor dispersions at higher frequencies. The relaxation time constant for the major dispersion increases with increasing chain lengths for *n*-alcohols and tends to disperse since microheterogeneous regions result from hydrophobic interactions for the long-chain alcohols. In the case of butanol, the Cole–Cole model generally yields better fits to the dielectric spectra than does the Debye model; nevertheless, the latter is sufficient to describe the principal dispersion at microwave frequencies, and both models give the same value for the relaxation time constant and the static dielectric constant.

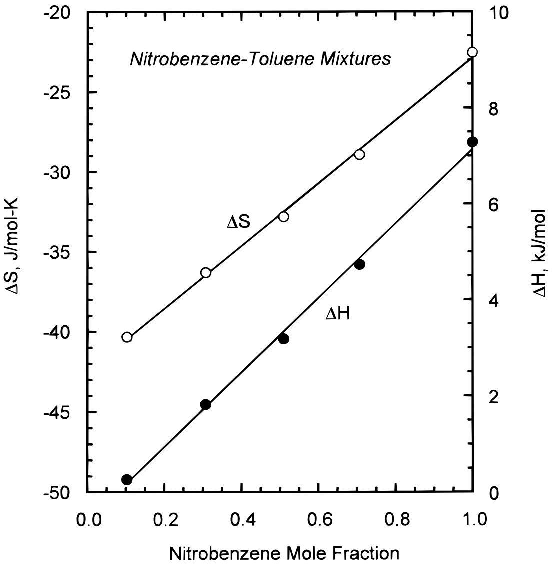

Figure 4. Thermodynamic parameters ΔH and ΔS of the dipole relaxation process for nitrobenzene–toluene mixtures as a function of nitrobenzene mole fraction. The lines are linear fits.

Hydrogen-bonded structures can also form between ethanol and butanol molecules in an ethanol–butanol mixture. Despite the distinctly different ΔG values of ethanol and butanol and the presence of hydrogen bonding between ethanol and butanol molecules, there is a linear relationship of ΔG versus butanol composition in Figure 5b which suggests that the ethanol and butanol molecules in the mixture react to the external field in a strongly cooperative way rather than individually over the temperature range of 10–60 °C. Pure alcohol molecules are believed to form a cyclic chain cluster through hydrogen bonding, and the hydrogen-bonded linkages are constantly being formed, broken, and reformed.[1,16] In the ethanol–butanol mixtures, the two different molecules are suggested to behave interchangeably in forming the cyclic molecular clusters, yielding a microscopically homogeneous liquid phase and a pure Debye-type dielectric dispersion. The primary relaxation in these mixtures is attributed to the cooperative process of the cyclic clusters, with the clusters having an increased dipole moment relative to individual molecules.

In Figure 5a, the relationship between ΔG and temperature deviates from linearity below ~30 °C; this deviation implies that the ethanol–butanol mixtures follow different dielectric relaxation mechanisms in the temperature region of 10–60 °C. This finding is supported by the Kirkwood correlation factor, *g*, obtained from the static dielectric constant. Figure 6 shows the *g* factor as a function of temperature for the ethanol–butanol mixtures. For most compositions, the value of the *g* factor achieves a maximum at ~30 °C, suggesting a change in the dipolar alignment around this temperature. This dynamic transition region (~30 °C) is almost independent of the solution composition. The varying relaxation behavior over the temperature range of 10–60 °C may be caused by changes in the hydrogen-bonding ability that produce different structures of cyclic clusters. Factors such as changes in the angle between the neighboring dipoles or in the average number of molecules in each cluster could yield different cluster structures.

Despite a cooperative rotation under the external field, the ethanol–butanol mixtures exhibit a relationship between ΔG and temperature (Figure 5a) similar to that of pure ethanol, suggesting that ethanol molecules dominate the dielectric relaxation behavior for these mixtures. This observation is

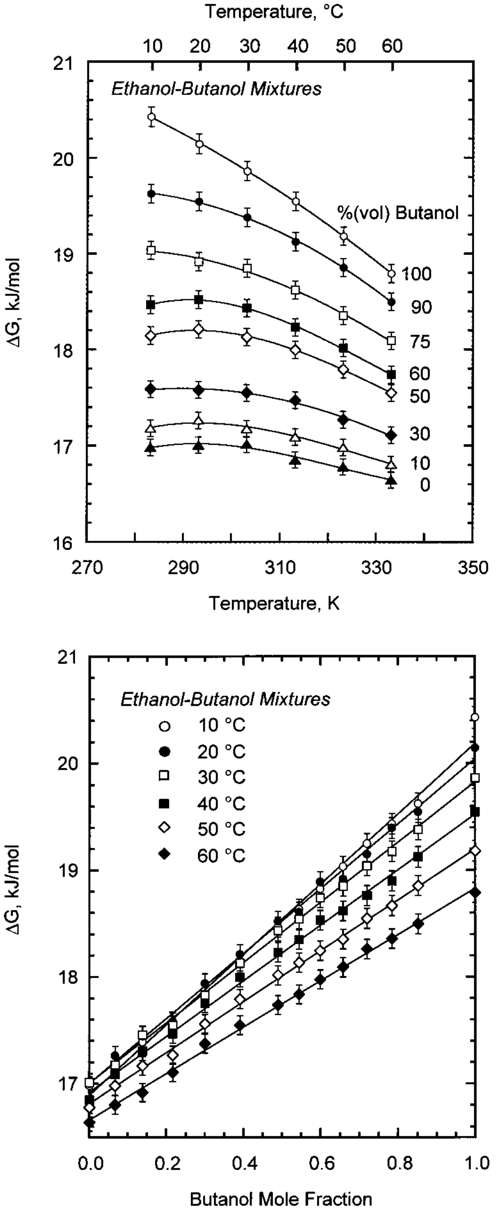

Figure 5. ΔG for ethanol−butanol mixtures (a) as a function of temperature at different solution compositions and (b) as a function of solution composition at different temperatures. The lines in a are guides to the eye, and the lines in b are linear fits.

consistent with the linear relationships observed between ΔG and butanol mole fraction in Figure 5b, where only pure butanol exhibits large deviations from linearity at 10 and 20 °C. The domination effect by ethanol molecules on the dielectric behavior of the mixtures could be due to the presence of cyclic clusters in the ethanol−butanol mixtures in which the structure is controlled by the ethanol molecules. At high temperatures, ethanol and butanol form similar cyclic cluster structures as implied by the linear relationships between ΔG and the mole fraction of butanol over the whole composition range. These molecules, however, adopt different cluster structures at low temperatures; the relationships between ΔG and the mole fraction of butanol still show good linearity with the exception of pure butanol since ethanol seems to dominate the dielectric relaxation behavior of the ethanol−butanol mixtures.

Butanol-Formamide Mixtures. Parts a and b of Figure 7 display plots of ΔG as functions of temperature and solution composition, respectively, for the butanol−formamide mixtures. Figure 8 shows the *g* factor as a function of solution composition between 10 and 70 °C for these mixtures. Unlike the ethanol−butanol mixtures, the butanol−formamide mixtures as well as their pure components do not exhibit a convincing transition temperature; both ΔG and the *g* values do not show appreciable change with temperature except at very high butanol concentrations (Figures 7a and 8). ΔG displays a nonlinear dependence on butanol mole fraction between 10 and 70 °C (Figure 7b). The *g* factor has a value of approximately 2 (±10%) at butanol mole fractions below ~0.6, above which it increases rapidly.

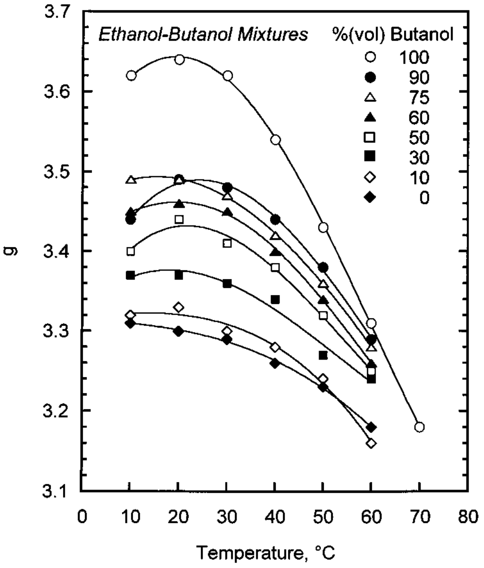

Figure 6. The Kirkwood correlation factor, *g*, as a function of temperature for ethanol−butanol mixtures. The lines are guides to the eye.

Formamide is a protic solvent and the formamide molecules are capable of forming hydrogen bonds with one another. The Kirkwood correlation parameter, *g*, increases from 1.78 to 1.88 (~5%) for formamide over 10 to 70 °C, suggesting a certain degree of association by means of a parallel orientation of the neighboring dipoles due to hydrogen bonding. This negligible temperature dependence of the *g* values for formamide implies that formamide molecules show very little change with temperature in their hydrogen-bonding ability. In contrast, as has already been noted, butanol molecules form cyclic clusters and the structure of these clusters is sensitive to temperature. In a butanol−formamide mixture, the two kinds of molecules can associate through hydrogen bonding. With a small amount of butanol in formamide, butanol molecules will form aggregates with formamide molecules, but it is unlikely to form the cyclic clusters observed in pure butanol. The structure of these aggregates (e.g., size and shape) does not show appreciable changes until the butanol mole fraction is above ~0.6. Beyond this mole fraction of butanol, the addition of butanol tends to increase the size of the aggregates, as suggested by the significant increase in the *g* value as shown in Figure 8. In this region, there probably exist some cyclic chain clusters similar to those for butanol molecules. Figures 7b and 8 present this nonideal dielectric mixing behavior; the butanol mole fraction of ~0.6 is a transition region below which the cyclic cluster structures may not form. When butanol−formamide mixtures contain the cyclic structures, they display composition-dependent relaxation mechanisms as indicated by the strongly nonlinear behavior of *g* and ΔG, as shown in Figures 7a and 8. As observed with pure formamide, the butanol−formamide mixtures do not exhibit significant changes in the values of ΔG and *g* with temperature except at very high butanol contents, suggesting that the relaxation of these mixtures is dominated by formamide.

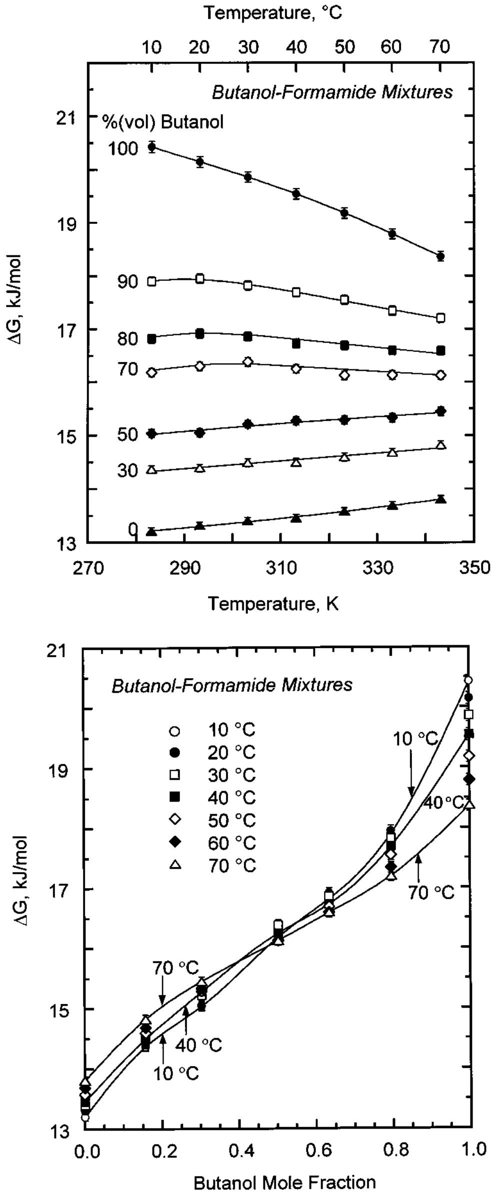

Figure 7. ΔG for butanol−formamide mixtures (a) as a function of temperature at different solution compositions and (b) as a function of solution composition at different temperatures. The lines are guides to the eye.

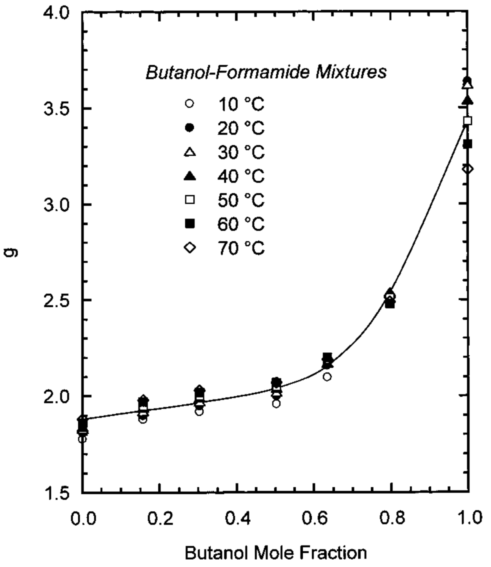

Figure 8. The Kirkwood correlation factor, g, as a function of solution composition for butanol−formamide mixtures at different temperatures. The line is a guide to the eye.

The excess free energy of activation for the relaxation process, ΔG^{EX}($\Delta G^{EX} = \Delta G_{mix} - \sum x_i \Delta G_i$, where x is mole fraction, and subscripts mix and i denote solvent mixtures and pure solvent components, respectively[34]), is used to quantify the nonideal mixing terms of ΔG for the butanol−formamide mixtures.[35] Figure 9a shows plots of $\Delta G^{EX}/(RTx_1x_2)$ against butanol mole fraction, where $\Delta G^{EX}/(RTx_1x_2)$ appears to be a linear function of the mole fraction of butanol at different temperatures. As an important concept in solution thermodynamics, the excess Gibbs energy, G^{EX}, can be correlated with various empirical and theoretical models for predicting vapor−liquid equilibrium data. A commonly used empirical model for binary mixtures is the Margules equation

$$\frac{G^{EX}}{x_1 x_2 RT} = A_{21}x_1 + A_{12}x_2 \qquad (9)$$

where A_{21} and A_{12} are constants and are the natural logarithms of the activity coefficients at infinite dilution. The linear relationship presented in Figure 9a is a form analogous to the Margules model in vapor−liquid equilibrium thermodynamics. The activity coefficients at infinite dilution are obtained from these lines for butanol (γ_1^∞) and formamide (γ_2^∞) and shown in Figure 9b, where γ_1^∞ and γ_2^∞ show a positive and a negative deviation, respectively, from unity. The positive deviation for γ_1^∞ suggests that butanol interacts more strongly with formamide than does formamide with its like molecules, and the negative deviation for γ_2^∞ implies that butanol interacts less strongly with formamide than does butanol with its like molecules. Over the temperature range of 10−70 °C,γ_1^∞ does not show any significant changes while γ_2^∞ decreases exponentially with inverse temperature. This framework provides a useful basis for incorporating nonidealities into the estimation of ΔG for solvent mixtures.

Conclusions

The temperature-dependent dielectric relaxation behavior at microwave frequencies was investigated for three binary solutions including nitrobenzene−toluene, ethanol−butanol, and butanol−formamide mixtures. These solutions exhibit differences in their molecular structures and relaxation dynamics as revealed from an analysis of the relaxation time constants and the static dielectric constants obtained from their dielectric spectra. The nitrobenzene−toluene mixture displays ideal dielectric mixing behavior, with ΔG, ΔH, and ΔS, the thermodynamic parameters of the dipolar relaxation, being linear functions of solution composition. The ethanol and butanol molecules behave interchangeably in forming circular molecular clusters and rotate in a cooperative way, and their mixture exhibits a microscopically homogeneous phase and a linear dependence of ΔG on the solution composition. The ethanol−butanol mixtures show a change in the relaxation mechanism with temperature at ~30 °C. In contrast with the other two solutions, the butanol−formamide mixtures display a nonlinear dependence of ΔG on solution composition. Below a butanol mole fraction of ~0.6, the butanol−formamide mixtures roughly follow a temperature-independent relaxation mechanism that is dominated by contributions from the formamide molecules; it is unlikely that these solutions contain cyclic chain clusters. At high butanol mole fractions, g and ΔG exhibit a strongly

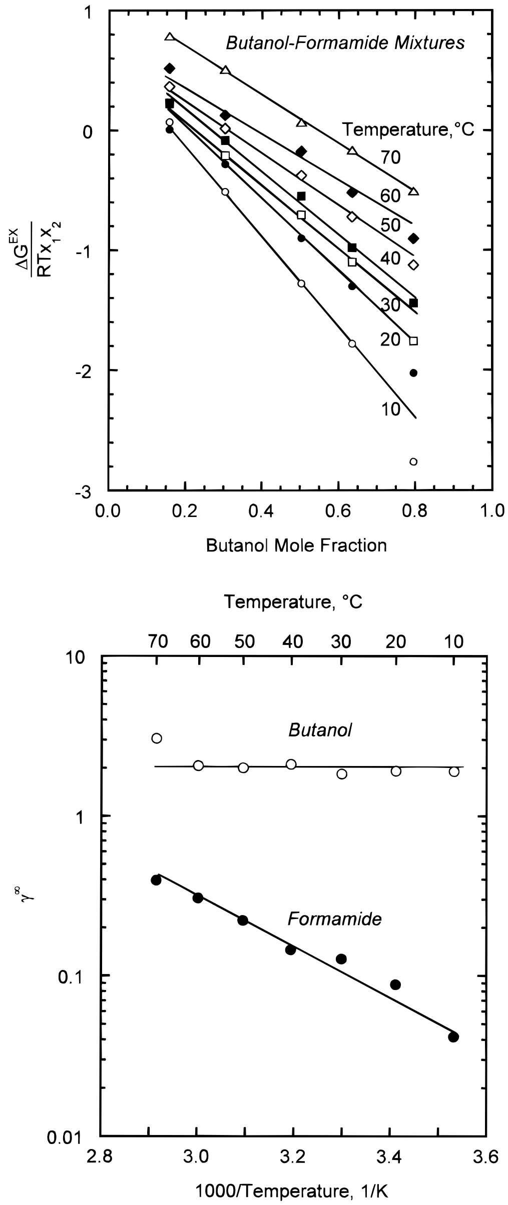

Figure 9. The excess free energy of activation for the dipolar relaxation process, ΔG^{EX}, for butanol−formamide mixtures and activity coefficients of butanol and formamide at infinite dilution obtained from the excess properties: (a) $\Delta G^{EX}/(RTx_1x_2)$ as a function of solution composition at different temperatures and (b) the activity coefficients at infinite dilution, γ^{∞}, as a function of temperature. The lines in a are linear fits of data points between butanol mole fractions of 0.2 and 0.7, and the lines in b are guides to the eye.

nonlinear behavior that implies a composition-dependent relaxation mechanism for the butanol−formamide mixtures.

In summary, the free energy of activation for the dipolar relaxation process, ΔG, is ideal in mixing for the nitrobenzene−toluene and ethanol−butanol mixtures and nonideal for the butanol−formamide mixtures. To accommodate these nonidealities, a framework using excess properties and the Margules equation is applicable. As a good approximation, however, a logarithmic mixing rule[21] is well-suited for estimating the relaxation time constants for these solvent mixtures over the temperature range of 10−70 °C.

Acknowledgment. A.P. participated in this project under the support of the MIT Undergraduate Research Opportunities Program. We thank Solartron Instruments for providing the LEVM Version 6.1 CNLS fitting program. This project was funded by the Electric Power Research Institute and the National Science Foundation under Grant Number CTS-9413894.

References and Notes

(1) Crossley, J. *Adv. Mol. Relax. Processes* **1970**, *2*, 69−99.

(2) Kaatze, U. *J. Mol. Liq.* **1993**, *56*, 95−115.

(3) Kaatze, U. *Radiat. Phys. Chem.* **1995**, *45*, 549−566.

(4) Murrell, J. N.; Jenkins, A. D. *Properties of Liquids and Solutions*, 2nd ed.; Wiley: New York, 1994.

(5) Israelachvili, J. *Intermolecular & Surface Forces*, 2nd ed.; Academic Press: London, 1991.

(6) Barthel, J.; Bachhuber, K.; Buchner, R.; Gill, J. B.; Kleebauer, M. *Chem. Phys. Lett.* **1990**, *167*, 62−66.

(7) Barthel, J.; Bachhuber, K.; Buchner, R.; Hetzenauer, H. *Chem. Phys. Lett.* **1990**, *165*, 369−373.

(8) Wijnen, J. W.; Engberts, J. B. F. N.; Blandamer, M. J. *J. Chem. Soc. Perkin Trans. 2* **1993**, 363−367.

(9) Abramovitch, R. A. *Org. Prep. Proced. Int.* **1991**, *23*, 685−711.

(10) Mingos, D. M. P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991**, *20*, 1−47.

(11) Ayappa, K. G.; Davis, H. T.; Davis, E. A.; Gordon, J. *AIChE J.* **1992**, *38*, 1577−1592.

(12) Ayappa, K. G.; Brandon, S.; Derby, J. J.; Davis, H. T.; Davis, E. A. *AIChE J.* **1994**, *40*, 1268−1272.

(13) Firman, P.; Marchetti, A.; Xu, M.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1991**, *95*, 7055−7061.

(14) Suryavanshi, B. M.; Mehrotra, S. C. *Indian J. Pure Appl. Phys.* **1991**, *29*, 482−487.

(15) Kaatze, U.; Lonnecke-Gabel, V. *J. Mol. Liq.* **1991**, *48*, 45−60.

(16) Bao, J.-Z.; Swicord, M. L.; Davis, C. C. *J. Chem. Phys.* **1996**, *104*, 4441−4450.

(17) Mashimo, S.; Kuwabara, S.; Yagihara, S.; Higasi, K. *J. Chem. Phys.* **1989**, *90*, 3292−3294.

(18) Kaatze, U.; Menzel, K.; Pottel, R. *J. Phys. Chem.* **1991**, *95*, 324−331.

(19) Kaatze, U.; Pottel, R.; Schafer, M. *J. Phys. Chem.* **1989**, *93*, 5623−5627.

(20) Chelliah, N.; Sabesan, R. *Indian J. Pure Appl. Phys.* **1994**, *32*, 425−429.

(21) Lou, J.; Hatton, T. A.; Laibinis, P. E. *J. Phys. Chem.* A **1997**, *101*, 5262−5268.

(22) Macdonald, J. R. In *Impedance Spectroscopy*; Macdonald, J. R., Ed.; Wiley: New York, 1987.

(23) Macdonald, J. R.; L. D. Potter, J. *Solid State Ionics* **1987**, *23*, 61−79.

(24) Havriliak, S.; Negami, S. *J. Polym. Sci.* **1966**, *C14*, 99.

(25) Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill: New York, 1955.

(26) The three dielectric parameters for ethanol show similar temperature-dependent behavior to that in Figure 2a for butanol; however, the three parameters for toluene do not show a temperature dependence within experimental errors.

(27) Lou, J.; Hatton, T. A.; Laibinis, P. E. In *Microwaves: Theory and Application in Materials Processing IV*; Clark, D. E., Sutton, W. H., Lewis, D. A., Eds.; *Ceramics Trans.* **1997**, *80*, 115−122.

(28) Srivastava, G. P.; Mathur, P. C.; Tripathi, K. N. *Indian J. Pure Appl. Phys.* **1968**, *6*, 561−563.

(29) Glasstone, S.; Laidle, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

(30) Michnick, R. B. *Ph.D. Thesis*, Massachusetts Institute of Technology, 1995.

(31) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1990.

(32) Bottcher, C. J. F. *Theory of Electric Polarization*; Elsevier Scientific: Amsterdam, 1973; Vol. 1.

(33) Mole-based averages of the molar volume, M/d; molar polarization, P_{e+a}; gas phase moment,μ_g; and refractive index, n are used in calculating the g factor for solvent mixtures.

(34) The subscript mix for ΔG is omitted elsewhere in the text for simplicity.

(35) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*, 5th ed.; McGraw-Hill: New York, 1996.