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Effective Dielectric Properties of Solvent Mixtures at Microwave Frequencies

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We investigated the dielectric properties of various organic solvents and binary solvent mixtures at 21.4 °C over the frequency range of 200 MHz−13.5 GHz. These solvent mixtures—nitrobenzene−*N*,*N*-dimethylformamide, 1-butanol−formamide, nitrobenzene−toluene, ethanol−1-butanol, and nitrobenzene−chlorobenzene—as well as the pure components display a Debye or near Debye dispersion. Their frequency-dependent dielectric properties can be summarized by three parameters in the Debye equation: a static dielectric constant, a high-frequency limiting dielectric constant, and a dielectric relaxation time constant. On the basis of electrostatics, rate theory, and solution thermodynamics, we have developed dielectric "mixing rules" that describe the frequency-dependent dielectric properties of the solvent mixtures based on solution composition and the dielectric parameters for the solution components. These "mixing rules" yield good agreement between the predicted and experimental dielectric properties for the binary solvent mixtures over all solution compositions.

Introduction

Microwave dielectric heating has attracted interest in the chemical industry for its ability to provide targeted heating rapidly and uniformly and to allow the local superheating of liquids.[1−5] The application of microwave heating for local phase reactions could offer some additional advantages over conventional heating. In laboratory investigations, microwave irradiation has demonstrated improvements in rates, yields, and selectivities for various chemical reactions.[1−3] In contrast to conventional heating, microwave irradiation can be applied volumetrically and is absorbed directly throughout the medium—typical microwave penetration depths range from 3 to 40 cm for most solvents at 2.45 GHz, the operating frequency of a household microwave oven—rather than being transferred by conduction from heated surfaces. On an industrial scale, microwave heating holds the promise for increased energy efficiency, reduced equipment size, diminished downstream separations, and superior temperature control for chemical processing. To apply microwave technology to these systems, the dielectric properties of solvents and solvent mixtures at microwave frequencies are required as they are the primary components of most liquid-phase reactions and their dielectric values impact the design, implementation, and control of microwave heating systems for these applications.[6,7] These data are required for predicting heating rates and temperature profiles within irradiated chemical reactors and for performing the reaction engineering analyses needed to take full advantage of microwave heating in the chemical industry.[8−10] At a fundamental level, the frequency-dependent dielectric behavior of solvent mixtures provides information on molecular interactions and mechanisms of molecular processes.[11−14]

Despite their scientific and engineering significance, the dielectric data of pure solvents at microwave frequencies are often unavailable, let alone those of solvent mixtures.[11] In this paper, we present the dielectric spectra for various pure solvents and binary solvent mixtures at microwave frequencies and develop suitable "mixing rules" that relate the dielectric properties of the solvent mixtures to those of the parent solvents that comprise the mixture and their composition. Most available dielectric data at microwave frequencies are for heterogeneous items such as foods, geological materials, and biological samples, and these values can vary greatly due to compositional variations based on their source. In contrast, there have been few investigations reported on organic solvents despite the fact that they have standard source-independent dielectric values due to their molecular homogeneity and defined composition. This standardization and the ability to prepare homogeneous mixtures from these sources provide a useful experimental framework for establishing dielectric "mixing rules" at these frequencies. Continuous frequency-dependent dielectric spectra have been collected for certain solvents; however, these studies focused on relaxation mechanisms that produce a single (or double) Debye type dispersion, or a Cole−Cole or a Cole−Davison distribution of relaxation times.[15−18] The dielectric properties of binary mixtures of two different alcohols and alcohols with water have been studied in detail with an emphasis on the formation of hydrogen-bonded complexes and the presence of cooperative relaxation processes for different molecular clusters.[14,16,17] The characterization of the dielectric properties of solvent mixtures at microwave frequencies has both fundamental and practical utility. Beyond the control of heating, a practical application with binary solvent mixtures would be to identify their composition based on certain parameters extracted from the dielectric spectra of the pure components and the mixtures.[17] To our knowledge, no previous efforts have been made to predict the frequency-dependent dielectric properties of solutions based on those of the pure components.

We have measured the frequency-dependent complex dielectric constants ($\epsilon^* = \epsilon' - j\epsilon''$) for various solvents and five solvent pairs over the frequency range 200 MHz−13.5 GHz. The major dielectric dispersions of the solvent mixtures over this frequency range exhibit behaviors of the Debye (or near Debye) type, although the dielectric spectra over a wider frequency range may be better fit by the Cole−Cole or the Cole−Davison model. The origin of the major dispersion is suggested to be dipole reorientation under an applied external field, which is mainly responsible for the microwave heating of the solvents. We have determined that the frequency-dependent dielectric behaviors of both pure solvents and solvent mixtures over this frequency range can be described well by three parameters: a static dielectric constant, a high-frequency limiting dielectric constant,

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and a dielectric relaxation time constant that characterizes the dipolar rotational process of the molecular species. We have used these parameters to develop "mixing rules" based on solution thermodynamics and electrostatics that describe the frequency-dependent dielectric behavior of solvent mixtures. This paper describes the development of these "mixing rules" and demonstrates the effectiveness of this approach for estimating the dielectric properties of solvent mixtures at microwave frequencies.

Experimental and Data Analysis

All solvents were obtained commercially and used as received. The solvents include nitrobenzene (NBZ, min 99%, EM Science), *N*,*N*-dimethylformamide (DMF, min 99.8%, EM Science), 1-butanol (BUT, 99.9%, Mallinckrodt), formamide (FOR, 98%, Aldrich), toluene (TOL, 99.9%, Mallinckrodt), ethanol (ETH, dehydrated 200 proof, Pharmco), and chlorobenzene (CBZ, 99.9%, Mallinckrodt). These solvents were selected based on differences in their polarity, dipole strength, and the presence of functional groups likely to form hydrogen bonds. The five solvent pairs investigated were NBZ−DMF, BUT−FOR, NBZ−TOL, ETH−BUT, and NBZ−CBZ mixtures. The solvent pairs were selected based on differences in hydrogen bonding and dipole−dipole interactions between the component molecular species.

Dielectric spectra were collected on a computer-controlled HP 85070M dielectric measurement system at 21.4 °C. The system includes an HP 8719C network analyzer with a frequency range of 50 MHz to 13.5 GHz and an open-ended coaxial probe. The probe is 19 mm in diameter and is connected to one test port of the S-parameter test set in the network analyzer through a single transmission cable. A test port power of 10 dBm and an IF bandwidth of 30 Hz in a logarithmic sweep mode were used. The system was calibrated by three known standards: air, a short circuit, and 18 MΩ deionized water (Milli-Q). A refresh calibration was performed with air to update the existing calibration before loading each sample. The probe was immersed in the solvents (50 mL) during the measurement, and the desired dielectric properties of the sample were extracted from the measured reflection coefficient.[17] The complex dielectric constants were obtained from the reflection coefficient assuming that the solvents are nonmagnetic ($\mu_r^* = 1$), homogeneous (uniform composition), and isotropic (uniform orientation). The typical accuracy with the system was ±5% for the dielectric constant (ϵ') and ±0.05 for the loss tangent (ϵ''/ϵ').

The experimental dielectric spectra were fitted to different relaxation models using a complex nonlinear least squares (CNLS) routine.[17,19] The CNLS routine minimizes an objective function (S) involving both the real and imaginary parts of the complex dielectric constant

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

where P is the parameter set used in the relaxation model, N is the number of data points, W is the weighting factor which equals $1/\sigma^2$ with σ being the estimated variance of the ith value, 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 dielectric constant. A good CNLS fit of the spectra ensures that the Kronig−Kramers relations are satisfied.[19]

The general form of the relaxation model used to fit the spectra is

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

where ϵ_s is the static dielectric constant, ϵ_h is the high-frequency limiting dielectric constant, and τ is the relaxation time. α and β are empirical parameters of the distribution of relaxation times. Three well-known models are limiting cases of this general equation; they are the Debye equation ($\alpha = 0$; $\beta = 1$), the Cole−Cole equation ($0 \le \alpha < 1$; $\beta = 1$), and the Cole−Davison equation ($\alpha = 0$; $0 < \beta \le 1$).[11,20] For the Debye equation, the real (ϵ') and imaginary (ϵ'') contributions to the dielectric behavior can be expressed by

$$\epsilon' = \epsilon_h + \frac{\epsilon_s - \epsilon_h}{1 + \omega^2\tau^2} \quad (3)$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_h)\omega\tau}{1 + \omega^2\tau^2} \quad (4)$$

Results and Discussion

Pure Solvents. Organic solvents exhibit different dielectric properties at microwave frequencies that depend on their polarity, dipole strength, and composition. We have determined the dielectric behaviors of various common organic solvents and displayed the frequency-dependent dielectric constant and loss factor as well as a plot of the loss factor versus the dielectric constant for three solvents in Figure 1. The plot in Figure 1c is commonly called a Cole−Cole plot even though the related data may not obey the Cole−Cole relaxation model. On these axes, the Cole−Cole plot displays a semicircular arc for the single Debye equation, a circular arc for the Cole−Cole equation, and a skewed arc for the Cole−Davison equation.[20]

The dielectric properties of the pure solvents are related to the molecular polarization processes that react to an externally applied electric field, each of which has a characteristic relaxation frequency or resonant frequency. Three underlying mechanisms can account for the dielectric behavior of the organic solvents: electronic (UV), atomic (IR), and dipole (MW) polarizations.[21,22] At increasing frequencies, the slower mechanisms do not contribute to the dielectric constant, and the loss factor peaks in its value over each of these characteristic frequency ranges. The decreases in ϵ' and the appearance of maxima in ϵ'' are observed in the dielectric spectra in Figure 1. The solvents display a principal dispersion at the microwave frequencies while exhibiting different values of the dielectric constant ϵ' and loss factor ϵ'' at the various frequencies as well as different frequencies (f_{max}) for the maximum in the loss factor. We observed that some solvents, such as alcohols, exhibit a major dispersion and one or more higher-frequency dispersions of much smaller amplitude over this frequency range; however, the principal dispersion is the one of interest to us here as it is mainly responsible for the dielectric heating behavior under microwave irradiation.

We fitted the experimental dielectric spectra to the three different relaxation models by the CNLS routine and determined that the Debye relaxation model is sufficient to describe the major dispersion of the various solvents over this frequency range. Table 1 lists the three parameters that are required to describe the frequency-dependent dielectric properties for these solvents through the Debye equation (eqs 3 and 4). The frequency where the loss factor is a maximum, f_{max}, is related

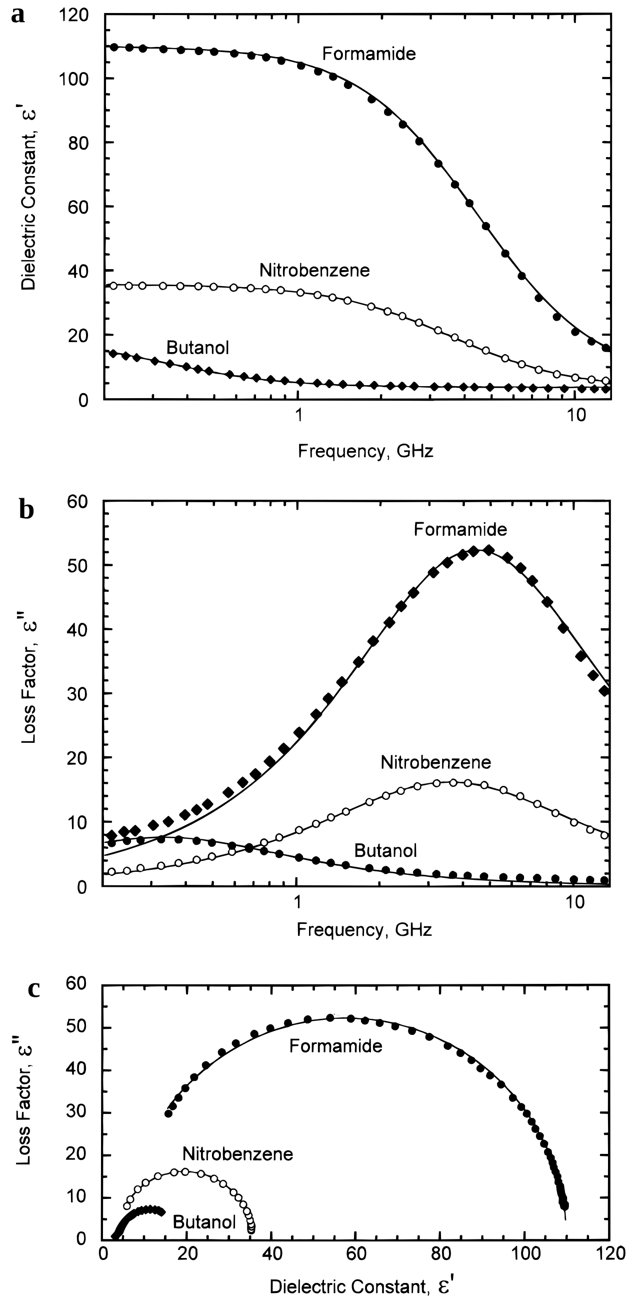

Figure 1. Measured frequency-dependent dielectric properties for three organic solvents at 21.4 °C. The markers denote experimental data, and the solid lines represent CNLS fits to the Debye equation (eqs 3 and 4). (a) Dielectric constant, (b) Dielectric loss factor, and (c) Cole–Cole plot.

TABLE 1: Debye Relaxation Parameters of Various Solvents at 21.4 °C

solvents	ϵ_s	ϵ_h	f_{max}
toluene	2.7	2.3	9.18
chlorobenzene	6.2	3.3	9.46
butanol	19.0	3.8	0.33
ethanol	25.4	4.9	0.95
nitrobenzene	35.7	3.3	3.58
dimethylformamide	38.5	10	10.9
formamide	110.0	5.3	4.43

to the relaxation time, τ, by[21]

$$2\pi f_{max}\tau = 1 \qquad (5)$$

From Table 1, the static dielectric constants and relaxation times vary significantly for typical organic solvents, while the high-frequency limiting dielectric constants are quite similar in value. The broad differences in ϵ_s and f_{max} for these solvents provide a useful set of parameters for tailoring the dielectric absorption characteristics of a reaction mixture by choice of solvent, or frequency, or use of solvent mixtures.

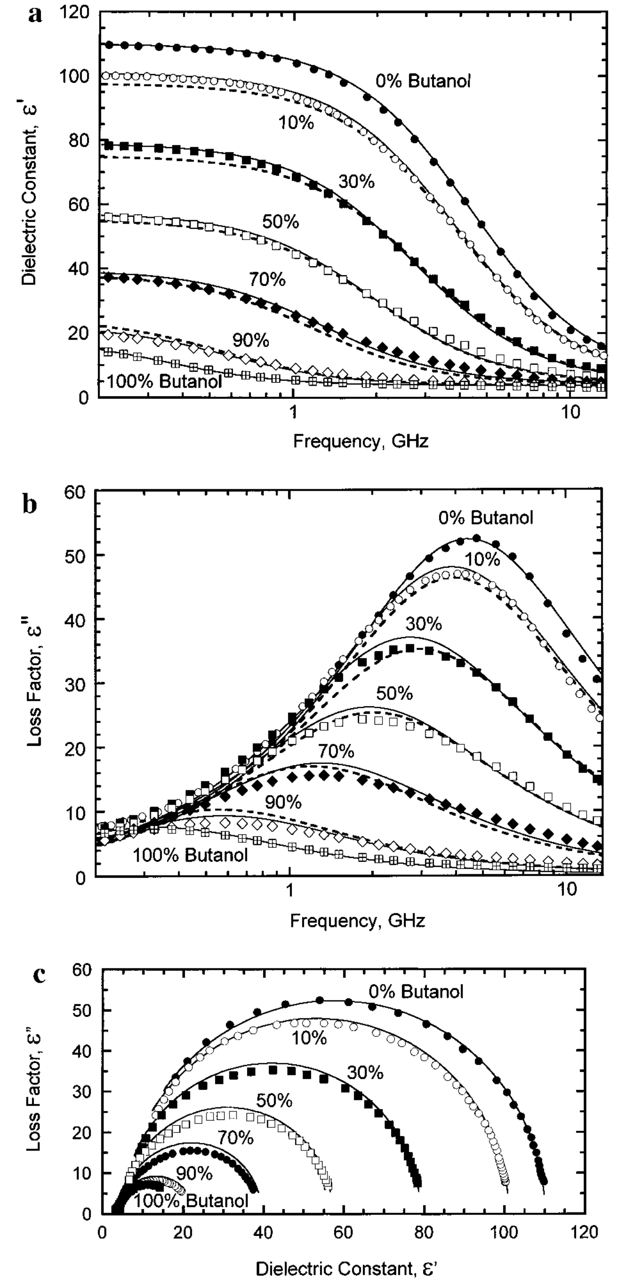

Figure 2. Measured frequency-dependent dielectric properties for butanol–formamide mixtures over the entire composition range at 21.4 °C. The markers denote experimental data and the solid lines represent CNLS fits to the Debye equation (eqs 3 and 4). (a) Dielectric constant, (b) Dielectric loss factor, and (c) Cole–Cole plot. The dashed lines in (a) and (b) are the predicted results through dielectric “mixing rules” (see text).

Solvent Mixtures. We measured the dielectric spectra of five solvent pairs—NBZ–DMF, BUT–FOR, NBZ–TOL, ETH–BUT, and NBZ–CBZ—and observed the dielectric properties of the binary solvent mixture to be intermediate between those of the two pure solvents that comprise the mixture. Figure 2 shows the dielectric behaviors of BUT–FOR mixtures and demonstrates that they can be modulated by solvent composition, where the dielectric constant, the loss factor, and the loss peak change consistently with composition. Each of the five solvent mixtures exhibits similar dielectric relaxation behaviors to those of the component pure solvents with the principal dispersion of the solvent mixtures being described well by the Debye equation regardless of any complex interactions between the solution components. Values of the three dielectric parameters needed to describe the data by the Debye equation were determined by the CNLS algorithm for the various solvent mixtures, and the results are presented in Table S-1 (Supporting Information). In contrast to the case for pure solvents, it would be impractical to establish a standard library for solvent mixtures due to the large number of possible solvent combinations and solvent compositions. The challenging question arises, therefore, as to how to estimate the composition-dependent dielectric properties of the solvent mixtures based on those of the pure solvents.

Dielectric "Mixing Rules". The Debye equation requires three parameters to describe the frequency-dependent dielectric relaxation behavior of solvents and solvent mixtures. Our goal was to relate the three parameters for the solvent mixtures to those of the pure solvents through appropriate dielectric "mixing rules". We derived these composition-based "mixing rules" based on electrostatics, rate theory, and solution thermodynamics.

I. Dielectric Relaxation Time Constant. Dielectric relaxation is described as an exponential decay of polarization with time upon the removal of an externally applied electric field.[23] The relaxation time may be defined as the time required for the polarization to decay to 1/e of its initial value, with e being the natural logarithmic base. Dipole polarization dominates the dielectric relaxation in the microwave region and is responsible for the frequency-dependent behavior of ϵ' and ϵ''. Eyring et al. have applied the theory of rate processes to molecular dipole relaxation by the equation[24]

$$\tau = \left(\frac{h}{kT}\right) \exp\left(\frac{\Delta G}{RT}\right) \tag{6}$$

where ΔG is the free energy of activation for the dipole relaxation, T is the absolute temperature, and k, h, and R are Boltzmann's constant, Planck's constant, and the molar gas constant, respectively. By applying eq 6 to both pure solvents and solvent mixtures and assuming that ΔG is ideal in mixing, i.e.,

$$\Delta G_{\text{mix}} = \sum_i x_i \Delta G_i \tag{7}$$

we obtain a mixing formula for the relaxation time at a constant temperature

$$\ln \tau_{\text{mix}} = \sum_i x_i \ln \tau_i \tag{8}$$

where x is mole fraction, and the subscripts mix and i represent the solvent mixture and pure solvent components, respectively.[25] We used eq 8 to calculate the relaxation time constants for the five solvent mixtures at different compositions and compared them to those measured by experiments. The experimental and predicted relaxation time constants, as well as the relative error for the calculated values, are tabulated in Table 2 for the BUT−FOR mixtures; related results for the NBZ−DMF, NBZ−TOL, ETH−BUT, and NBZ−CBZ mixtures are presented in Table S-2 (Supporting Information). In general, eq 8 predicts the experimentally determined relaxation times for the mixtures with a precision better than ±10%.

II. Static Dielectric Constant. The static dielectric constant for a mixed system has long been a subject of theoretical investigation.[11,20,26,27] While these efforts have yielded equations that relate the static dielectric constant to the structural parameters for a pure liquid and produced various mixing formulas that provide estimates of the effective dielectric constant for heterogeneous or dispersed-continuous systems, little attention has focused on estimating the effective dielectric properties for solvent mixtures.

TABLE 2: Experimental and Theoretical Results for the Dielectric Relaxation Times of Butanol−Formamide Mixtures at 21.4 °C

BUT vol. fraction, %	τ_{exp}, ps	τ_{mod}, ps[a]	relative error, %
0	35.9	35.9	0.0
10	41.1	40.5	−1.6
30	58.3	54.0	−7.4
50	82.0	78.8	−3.9
70	122.4	132.7	8.4
90	274.4	284.1	3.5
100	482.3	482.3	0.0

[a] Calculated from eq 8.

The Onsager and Kirkwood equations are frequently used to relate the static dielectric constant of a polar solvent to its dipole strength.[23,26−28] The Onsager equation was derived via a macroscopic approach which considered a point dipole within a cavity and treated the environment around the dipole as a continuum.[29] This model allows for the effect of the polarization of the dipole on its environment (reaction field), but it does not account for specific dipole interactions. The Kirkwood equation was developed based on statistical mechanics, and, in principle, permits an exact evaluation of the specific dipole interactions from molecular parameters.[30−32] The Kirkwood equation can be expressed as a generalized form of the Onsager equation by incorporating a correlation parameter which measures the molecular configuration of neighboring dipoles due to short-range intermolecular interactions

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

where $P_{\text{e+a}}$ is the molar electronic and atomic polarization, μ is the permanent molecular dipole moment in the liquid as enhanced by the reaction field, g is the correlation parameter, M is the molecular weight, d is the density, and N_A is Avogadro's number. Equation 9 reduces to the Onsager equation when g equals unity. Rigorous calculation of the correlation factor is usually impractical due to insufficient knowledge of the liquid's structure. A parallel alignment of neighboring dipoles will yield a value of g greater than one, and an antiparallel arrangement will result in a value of g less than one. $P_{\text{e+a}}$ is related to the refractive index through the equation[23,28]

$$P_{\text{e+a}} = \frac{(1.1n^2 - 1)\,M}{(1.1n^2 + 2)\,d} \tag{10}$$

where n is the refractive index. μ can be calculated using the Onsager relationship[26]

$$\mu = \frac{(2\epsilon_s + 1)(n^2 + 2)}{3(2\epsilon_s + n^2)}\mu_g \tag{11}$$

where μ_g is the gas-phase dipole moment.[33] The Kirkwood equation produces values for the correlation factor that deviate from unity by different amounts, indicating structural differences between the solvents (Table 3). The data suggest that intermolecular interactions that produce molecular association, such

TABLE 3: Dipole Moment and Kirkwood Correlation Factor of Various Pure Solvents at 21.4 °C

	ϵ_s	μ_g,[a] D	μ,[b] D	g[c]
chlorobenzene	6.2	1.69	2.22	0.91
butanol	19.0	1.66	2.13	3.72
ethanol	25.4	1.69	2.13	3.30
nitrobenzene	35.7	4.22	6.08	1.01
DMF	38.5	3.82	5.07	1.19
formamide	110.0	3.73	5.06	1.80

[a] Values taken from ref 32. [b] Calculated from eq 11. [c] Calculated from eq 9.

as hydrogen bonding in ethanol and butanol, will contribute to larger deviations in the value of g from unity.

A solvent mixture can be considered to be a heterogeneous system at the molecular level, and, for a binary solvent mixture, one component can be treated as the dispersed phase and the other as the continuum. Many attempts have been made to investigate theoretically the dielectric properties of composite systems such as coarse dispersions, colloidal dispersions, and molecular dispersions.[20,34] The dielectric constant of a dilute dispersion of spherical inclusions (particles) has been developed based on electrostatics[35−37]

$$\frac{\epsilon_{s,mix} - \epsilon_{s,m}}{\epsilon_{s,mix} + 2\epsilon_{s,m}} = \varphi_d \frac{\epsilon_{s,d} - \epsilon_{s,m}}{\epsilon_{s,d} + 2\epsilon_{s,m}} \tag{12}$$

where the subscripts d and m denote the dispersed and continuous phases, respectively, and φ_d is the volume fraction of the dispersed phase. In the derivation of eq 12, all interparticle interactions are neglected, and the particle dimensions are assumed to be much less than the incident wavelength so that scattering effects can be ignored. Equation 12 was extended to describe mixtures with highly dispersed volume fractions by Bruggeman via a differential procedure[38,39]

$$\frac{\epsilon_{s,mix} - \epsilon_{s,d}}{\epsilon_{s,m} - \epsilon_{s,d}} \left(\frac{\epsilon_{s,m}}{\epsilon_{s,mix}} \right)^{1/3} = 1 - \varphi_d \tag{13}$$

Bruggeman proposed an effective medium theory in deriving eq 13 where he suggested that the apparent dielectric constant surrounding an individual particle is $\epsilon_{s,eff}$, not $\epsilon_{s,m}$. Equation 13 is usually called the Bruggeman equation, and it allows for long-range particle interactions. Another notable mixing formula based on the effective medium theory is the Bottcher equation[40]

$$\frac{\epsilon_{s,mix} - \epsilon_{s,m}}{3\epsilon_{s,mix}} = \frac{\epsilon_{s,d} - \epsilon_{s,m}}{\epsilon_{s,d} + 2\epsilon_{s,mix}} \varphi_d \tag{14}$$

Bottcher treated the dispersed system as a close aggregate of two types of spherical globules and assumed that the polarization of the whole system is the sum of both kinds of the spheres. Despite the same underlying effective medium theory, the Bruggeman equation is asymmetric (matrix-inclusion type) and the Bottcher equation is symmetric (statistical mixture type).[41,42]

We applied the above mixing formulas to calculate the static dielectric constants of binary solvent mixtures. For the Kirkwood equation, the molar volume M/d, molar polarization P_{e+a}, gas-phase moment μ_g, refractive index n, and correlation parameter g were calculated on a mole-weighted basis. For the Bruggeman equation, we also examined the effect of phase inversion, where we denote the Bruggeman O/W equation when the less polar component is chosen to be the dispersed phase and the Bruggeman W/O equation when the more polar component is the dispersed phase. Figure 3 compares the predicted values from these different mixing formulas to the experimental data for the BUT−FOR mixture. The Bruggeman O/W equation yielded the best prediction among the mixing formulas. The Kirkwood equation significantly overpredicted the dielectric constants of the BUT−FOR mixture. The Bruggeman O/W and W/O equations predicted distinctly different dielectric results between which lie the calculated values from the Bottcher equation. The results for the BUT−FOR mixture are also listed in Table 4 with calculated values from the Kirkwood and Bruggeman O/W equations, along with the relative errors associated with the use of each formula. Similar results are supplied in Table S-3 for the NBZ−DMF, NBZ−TOL, ETH−BUT, and NBZ−CBZ mixtures (Supporting Information). In general, we observed that the Bruggeman O/W equation predicted the static dielectric constant well for the five solvent mixtures, typically within ±10%. The underlying physics for the validity of the Bruggeman O/W equation is still under investigation. The Kirkwood equation yielded good predictions for the NBZ−DMF and ETH−BUT mixtures but produced large discrepancies between the predicted and measured values for the BUT−FOR, NBZ−TOL, and NBZ−CBZ mixtures. This difference is probably caused by the oversimplified assumptions inherent in the use of the correlation factor g, where the ideal mixing behavior only applies when the dipole moments of the two components are approximately the same and the structural changes (e.g., molecular complexing due to H-bonding) upon mixing are small. In general, the calculation of g for the solvent mixture is very difficult (or even impossible) owing to the complex interaction between the components,

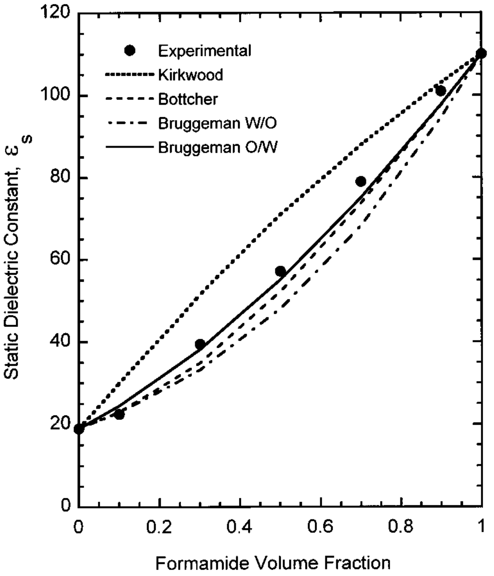

Figure 3. Comparison of predicted static dielectric constants from various mixing formulas and experimental results for butanol−formamide mixtures at 21.4 °C. Solid symbols denote experimental data, and the lines are the predicted results from the mixing formulas.

TABLE 4: Experimental and Theoretical Results for the Static Dielectric Constants of Butanol−Formamide Mixtures at 21.4 °C

BUT vol. fraction, %	$\epsilon_{s,exp}$	$\epsilon_{s,mod}$[a] Kirkwood	relative error, %	$\epsilon_{s,mod}$[d] Bruggeman O/W	relative error, %
0	110.0	110.0	0.0	110.0	0.0
10	101.0	103.1	2.1	97.7	−3.3
30	79.0	88.0	11.4	75.1	−4.9
50	57.2	71.0	24.1	55.1	−3.7
70	39.5	51.6	30.6	38.2	−3.3
90	22.5	30.0	33.5	24.5	8.9
100	19.0	19.0	0.0	19.0	0.0

[a] Calculated from eq 9. [b] Calculated from eq 13.

TABLE 5: Experimental and Theoretical Results for the High-Frequency Limiting Dielectric Constants of Butanol−Formamide Mixtures at 21.4 °C

BUT vol. fraction, %	$\epsilon_{h,exp}$	$\epsilon_{s,mod}$[a]	relative error, %
0	5.3	5.3	0.0
10	5.0	5.1	2.0
30	4.9	4.7	−3.3
50	4.8	4.4	−7.8
70	4.5	4.2	−7.7
90	3.8	3.9	2.9
100	3.8	3.8	0.0

[a] Calculated from eq 15.

which limits the application of the Kirkwood equation to particular solvent mixtures.

III. High-Frequency Limiting Dielectric Constant. The dielectric constant of a chemical species at "infinite" frequency is often defined as the sum of the electronic and the atomic polarizations, where the electronic polarization equals the square of the internal refractive index of the solvent, and the atomic polarization typically corresponds to approximately 10% of the electronic polarization.[43] The high-frequency limiting dielectric constant ϵ_h, however, can still include contributions from dipole polarization of much smaller amplitude than the principal dispersion. The ϵ_h of solvent mixtures can be calculated based on theoretical models as well as many empirical formulas,[26] and these formulas yield only slight differences between them because the ϵ_h values are usually close. For our investigation, a simple capacitor-in-series model (eq 15) proved sufficient to calculate the value of ϵ_h for the solvent mixtures[27]

$$\frac{1}{\epsilon_{h,mix}} = \sum_i \varphi_i \frac{1}{\epsilon_{h,i}} \qquad (15)$$

Equation 15 yielded good predictions for all the five solvent pairs as shown in Table 5 for the BUT−FOR mixtures and in Table S-4 (Supporting Information) for the other four solvent mixtures.

IV. Evaluation of Mixing Formulas. We used the logarithmic mixing formula (eq 8), the Bruggeman O/W equation (eq 13), and the capacitor-in-series model (eq 15) to calculate the three dielectric parameters of the solvent mixtures ($\epsilon_{s,mix}$, $\epsilon_{h,mix}$, and τ_{mix}) for use in the Debye relaxation model. The three parameters, computed using the dielectric properties of the pure component solvents and the solution composition, were inserted into the Debye model (eqs 3 and 4) to predict the frequency-dependent dielectric behaviors of the solvent mixtures. The predicted dielectric values matched the measured results well for the five solvent mixtures for all solution compositions as shown by the examples in Figures 2 and 4. Figure 2a,b presents the experimental and predicted dielectric properties of the BUT−FOR mixtures for all solution compositions, and Figure 4a,b shows those of 50/50 (v/v) mixtures for the five solvent pairs. It is important to note that the 50/50 (v/v) mixtures generally exhibit the largest discrepancies between the experimental and theoretical results; nevertheless, in all the comparisons presented in Figure 4, the discrepancies are rather small over the whole frequency range.

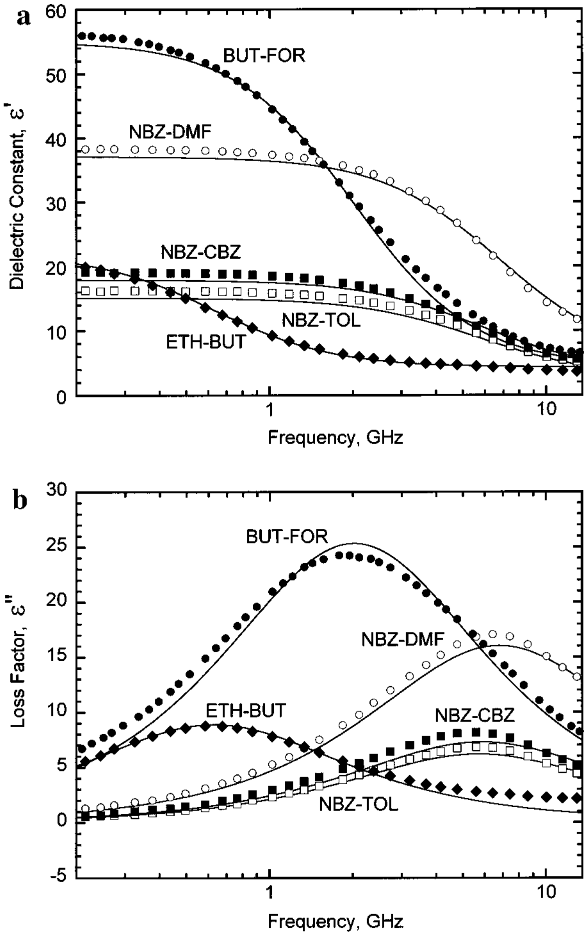

Figure 4. Experimental and theoretical dielectric spectra of 50/50 (v/v) mixtures of the five solvent pairs at 21.4 °C. The markers denote experimental data, and the solid lines are the predicted results from the dielectric "mixing rules". (a) Dielectric constant and (b) Dielectric loss factor.

The accuracy of the model for estimating the effective dielectric properties for a solvent mixture depends differently on the errors for the three calculated parameters used in the Debye model. Despite the greater relative error associated with ϵ_h, its effect on the predicted dielectric properties for the mixture is negligible as its absolute value is small relative to ϵ_s. The relaxation time constant and static dielectric constant have more significant effects on the dielectric spectra of the mixture at these frequencies. The former is estimated well (±10%) from eq 7 using the assumption of ideal mixing behaviors. Further refinements may be possible by incorporating nonideal mixing terms into ΔG_{mix}; however, we expect the agreement between the calculated and experimental dielectric spectra to improve only modestly for most systems by their addition. We expect greater agreement if the error in ϵ_s could be reduced. In general, the plateau in ϵ' at high frequency and the frequency for the inflection point are predicted well (Figures 2a and 4a) by the model; the greatest disagreements occur at the lowest frequencies for ϵ' (Figures 2a and 4a) and in the maximum value of ϵ'' (Figures 2b,c and 4b). These disagreements in ϵ' at low frequencies ($\epsilon' \approx \epsilon_s$ at low frequencies) and in the maximum value of $\epsilon''(\epsilon''_{max} = [\epsilon_s - \epsilon_h]/2)$ result from the error in estimating $\epsilon_{s,mix}$. Of the errors associated with $\epsilon_{s,mix}$, $\epsilon_{h,mix}$, and τ_{mix}, the error in $\epsilon_{s,mix}$ impacts the level of agreement the most. Estimates of the frequency-dependent dielectric properties of simple liquid-phase mixtures by this model would most improve by the availability of better abilities to predict the parameter $\epsilon_{s,mix}$.[44]

Conclusions

The frequency-dependent dielectric behaviors of various organic solvents and solvent mixtures at microwave frequencies are described well by the Debye equation and can be summarized by three parameters.[45] We have developed dielectric "mixing rules" based on electrostatics, rate theory, and solution thermodynamics, from which these three parameters can be readily calculated for solvent mixtures using those of the pure solvents that comprise the mixture. The composition-dependent expressions successfully predict the frequency-dependent dielectric properties for various binary solvent mixtures over all solution compositions.

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Supporting Information Available: Tables listing the dielectric relaxation parameters for the five solvent mixtures—NBZ−DMF, BUT−FOR, NBZ−TOL, ETH−BUT, and NBZ−CBZ—that were obtained from the CNLS fitting of measured dielectric spectra to the Debye equation, and the experimental and theoretical results for dielectric relaxation time constants, static dielectric constants, and high-frequency limiting dielectric constants, respectively, of NBZ−DMF, NBZ−TOL, ETH−BUT, and NBZ−CBZ mixtures (9 pages). Ordering information is given on any current masthead page.

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(44) Of the parameters for the mixture, $\epsilon_{\mathrm{s,mix}}$ is the one most relevant to other areas of research and application; the difficulty in obtaining good estimates from theory was unexpected.

(45) We note that the dielectric relaxation behaviors of some solvents (such as acetone, tetrahydrofuran, and glycerol) do not obey the Debye equation. The dielectric mixing behavior of these solvents is under investigation.