

Research Article

Use of Electron Paramagnetic Resonance Spectroscopy to Study Dielectric Properties of Liquids

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The signal response of an EPR active species is attenuated by the medium it is in. Keeping all other parameters the same, the higher the dielectric constant of the medium, the lower the EPR signal response. This behavior is problematic in studying EPR active species in high dielectric media but can be capitalized upon to monitor changes in the dielectric constant or estimate the dielectric constant of the medium. Using a coaxial EPR cell design, the EPR signal of a stable nitroxyl radical compound (2,2,6,6-tetramethylpiperidin-1-oxyl radical) in a low dielectric constant solvent in an inner tube is attenuated by the solvent present between the inner and outer tubes (jacket medium). The attenuation increases monotonically with an increase in the dielectric constant of the jacket medium. Calibration curves can be constructed using jacket media of known dielectric constants ranging from 2 to 80 and the dielectric constant of a sample used as the jacket medium can be estimated by interpolation. This technique is applied to estimate the dielectric constants and/or composition of mixed solvents and to monitor the rate of a reaction.

1. Introduction

A static dielectric constant is a fundamental property of matter that reflects its ability to be polarized in an electric field. As such, the study of dielectric phenomena is of great importance in many areas including the study of liquid electrolytes, capacitors, phase transitions, and the effects of medium on reactivity, to name just a few [1]. We have been interested in the use of amine polymers as matrices for polymer electrolytes [2–4] and have been studying the effects of amine versus ether functional electrolyte solvents on conductivity and the speciation of dissolved salts. The dielectric constant of the solvent medium plays an important role in conductivity and it was desirable to find a rapid, low volume method for studying changes in the dielectric constant of solvent mixtures as a function of solvent composition. Measurement of the dielectric constant of a material is typically carried out using either capacitance or microwave cavity methods [5–7]. The first of these works well if the material can be conveniently fabricated to be the dielectric layer in a capacitance cell and if it does not exhibit substantial electronic or ionic conductivity. The former will short-circuit the capaci-

tance cell leading to a large D.C conductivity contribution and the latter will cause electrode polarization problems and a pronounced frequency dependence of the capacitance, necessitating specialized equipment to obtain high frequencies ($>10^6$ Hz) to measure the static (frequency-independent) dielectric constant. Commercial cells typically need several milliliters of liquid per measurement.

Microwave cavity techniques for measuring dielectric constants are relatively straightforward [7]. A resonant microwave cavity is filled with the substance of interest and the attenuation of the microwave signal is compared to that of the empty cavity and the dielectric constant is derived from the difference; the greater the attenuation, the greater the dielectric constant. Since the microwave frequency domain is already high (ca. 10^8 – 10^9 Hz) and there are no electrodes *per se*, frequency dependence and polarization phenomena are not as big a problem for ionic conductors. However, such microwave cavity equipment is often not readily available in chemistry laboratories, and special cavities are needed if corrosive or hygroscopic materials are to be measured.

Many chemistry labs have access to an electron paramagnetic resonance (EPR) spectrometer. In an EPR experiment,

a paramagnetic material is placed in a microwave cavity within a strong magnetic field. The field is changed until the energy for a resonant absorption of the microwaves by the unpaired electron species occurs. It is well known that the signal response of an EPR active species is attenuated by the medium it is in [9]. Keeping all other parameters the same, the higher the dielectric constant of the medium, the lower the EPR signal response. This behavior is problematic in studying EPR active species in high dielectric media and generally such media are avoided or special thin cells designed to minimize the attenuation are used. Although widely recognized as a problem for EPR, only a few reports exist in the literature to quantify the phenomenon, generally to outline parameters for successful use of EPR in quantitative measurements of paramagnetic species [10–12]. In principle the attenuation of the EPR signal could be capitalized upon to monitor changes in the dielectric constant of the medium, or even determine the dielectric constant, if the signal attenuation occurs regularly as a function of dielectric constant of the medium [10]. That is, the signal of a constant concentration of a paramagnetic species that does not interact with the solvent medium should decrease with an increase in the dielectric constant of the medium. If that decrease is regular, then the dielectric constant of an unknown medium could be obtained by calculation or interpolation.

Using a coaxial EPR cell design to eliminate any problems due to paramagnetic species differentially interacting with the medium being measured, we have shown that the EPR signal of a stable nitroxyl radical compound (2,2,6,6-tetramethyl-piperidin-1-oxyl radical) in a low dielectric constant solvent in an inner tube is attenuated by the solvent present between the inner and outer tubes (jacket medium). The attenuation increases monotonically with an increase in the dielectric constant of the jacket medium. We report here initial studies of the use of this EPR technique to measure changes in dielectric constants of solvent mixtures, to measure solvent mixture compositions, to monitor reactions, and to determine dielectric constants.

2. Experimental

2.1. General. All solvents used were reagent grade from commercial sources and were used as received. Distilled or deionized water was used when appropriate. The stable radical 2,2,6,6-tetramethyl-piperidin-1-oxyl was purchased from Sigma-Aldrich. Standard thin wall 3, 4, and 5 mm diameter NMR tubes were purchased from Wilmad Lab Glass. Literature values for all solvents and solvent mixtures used here are assumed to reflect those of the samples used [13, 14].

2.2. Cell Fabrication and Use. Coaxial cells (Figure 1) were constructed and used as follows: solutions of 2,2,6,6-tetramethyl-piperidin-1-oxyl in hexane were made up in 3 and 4 mm NMR tubes at concentrations high enough that their EPR spectra gave strong, exchange-coupled singlet signals. These reference sample NMR tubes were then flame sealed using standard techniques. For use, a few drops of a desired solvent/solution was placed in an NMR tube of a larger

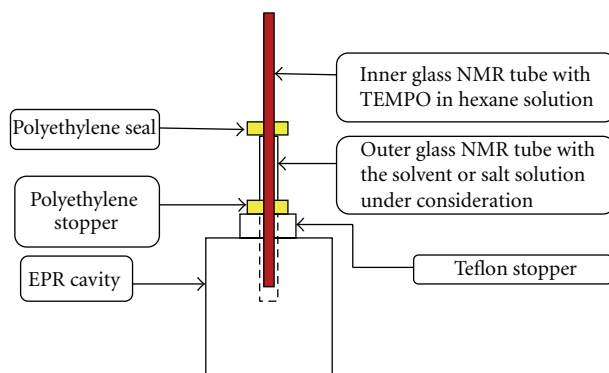


FIGURE 1: Schematic diagram of the coaxial EPR cell assembly.

diameter than the reference sample and that had been cut to be a few centimeters shorter than the reference sample tube. The reference sample tube was placed in the larger diameter tube and sliding a tapered polyethylene sheath down the reference tube sealed the solvent cell. The sheath both centered the inner tube in the outer tube and prevented the solvent from evaporating. The cell was then ready to be placed in the EPR spectrometer cavity.

2.3. EPR Measurements. All measurements were carried using a Bruker EMX EPR spectrometer operating at the X band with a Bruker 048T Microwave Bridge and Bruker ER073 Magnet. A standard rectangular cavity operating in TE 102 mode (Bruker 4102 ST cavity) was used. The signal channel was kept constant at a magnetic field modulation frequency of 100 kHz. The microwave frequency was held constant at 9.725 GHz and the microwave power was held constant at 0.201 mW for all the measurements. A securely fitting poly(ethylene) stopper was put around the lower part of the jacket tube to assure the insertion of the coaxial assembly to the same cavity depth for every measurement. Marks on the reference tube, the jacket tube, and the cavity were aligned before every measurement. Central alignment of the coaxial assembly in the cavity was maintained using a standard Teflon sample holder located at the top of the Bruker 4102 ST cavity. The spectrometer was housed in a temperature-controlled room. A thermocouple was attached to the microwave cavity and the change in the temperature was measured at every 30 minutes for 7.5 hours under standard operating conditions, with measurements of a sample being taken every 30 minutes during this period. The temperature was measured to be $21.7 \pm 0.5^\circ\text{C}$.

3. Results and Discussion

3.1. Use of EPR to Evaluate Dielectric Properties of Solvent Mixtures: Nonpolar Solvents. In studying the behavior of lithium salts in mixed amine/ether solvents it became important to show that the dielectric constant of mixtures of N,N,N',N'-tetramethylethylenediamine (TMEDA, $\epsilon = 2.8$) and 1,2-dimethoxyethane (glyme, $\epsilon = 7.2$) changes is a continuous, monotonic fashion. As a test of the EPR technique described

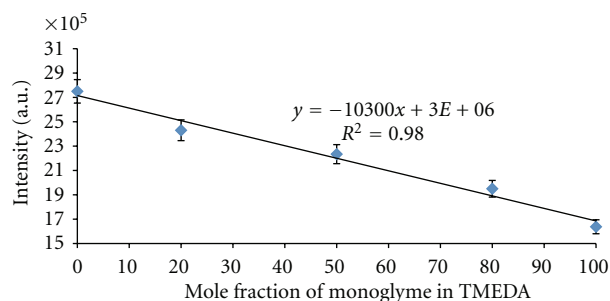


FIGURE 2: TEMPO reference EPR signal intensity (arbitrary units) as a function of mole fraction glyme in TMEDA. The 4/5 mm coaxial tube assembly was used. Error bars of 3.5% are shown as discussed in the text.

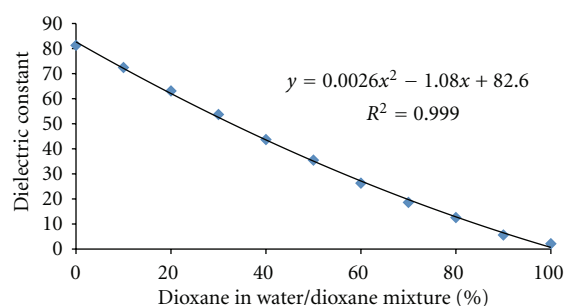


FIGURE 3: Plot of dielectric constant as a function of dioxane/water composition (w/w) at 25°C [8].

here, the EPR signal intensities of a TEMPO sample were measured using 4/5 mm coaxial tubes as described in the experimental section, and using TMEDA, glyme, and a series of TMEDA-glyme solutions of varying composition as the jacket media. The results are plotted in Figure 2 for EPR signal intensity in arbitrary units (a.u.) as a function of mole fraction of glyme in TMEDA. As shown in Figure 2, the signal intensity changes in an apparently linear fashion and, as expected, decreases with increasing dielectric constant. The 3.5% error bars shown in Figure 2 reflect measurement of systemic errors (*vide infra*). These measurements verified that EPR could be used to study changes in the dielectric constant of liquids.

3.2. Use of EPR to Evaluate Dielectric Properties of Solvent Mixtures: NonPolar/polar Solvents. The nonpolar solvents, TMEDA and glyme, described above do not cover a very wide range of dielectric constants ($\epsilon = 2.8\text{--}7.2$). In order to investigate a solvent pair with a broader range of dielectric constants, 1,4-dioxane/water was chosen as these common solvents cover a very broad range of dielectric constants ($\epsilon = 2.2\text{--}78$), the dielectric constants for a wide range of dioxane/water compositions are available in the literature [8], and 1,4-dioxane is miscible with water in all proportions. Figure 3 shows the dielectric constants for 1,4-dioxane/water mixtures at 25°C as a function of percent dioxane by weight from data taken from [8]. From the plot it can be seen

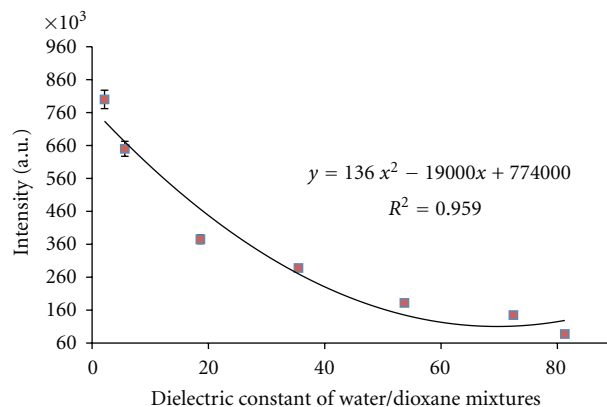


FIGURE 4: TEMPO reference EPR signal intensity (arbitrary units) as a function of dielectric constant for various dioxane ($\epsilon = 2.14$)/water ($\epsilon = 81.3$) mixtures [8]. The 4/5 mm coaxial tube assembly was used. Error bars of 3.5% are shown as discussed in the text.

that there is a curvature to the data and it fits better by a polynomial function ($R^2 = 0.999$) than a linear one ($R^2 = 0.991$). This is likely related to nonlinear changes with solvent composition due to hydrogen bonding [15].

The 4/5 mm coaxial assembly was used to measure EPR signal intensities for several different dioxane/water mixtures of known dielectric constants [8]. The results are shown in Figure 4. From Figure 4 it can be seen that a wide range of dielectric constants can be covered with the 4/5 mm assembly with the water-dioxane mixtures. The calibration curve fits best with a polynomial fit as seen earlier in Figure 3.

Mixtures of 80% water/20% dioxane (w/w) and 40% water/60% dioxane were prepared and treated like unknowns. EPR signal intensities were measured for the samples and dielectric constants determined from the calibration curve were found to be 61.3 and 28.7, respectively. Literature values for the dielectric constants of 80% water/20% dioxane (w/w) and 40% water/60% dioxane are 63.1 and 26.3, respectively. Absolute errors of approximately 2 were seen for dielectric constants for both the unknowns. Correlating the measured dielectric constants with % water/% dioxane values from the literature [8] gave 79.2% water/20.8% dioxane and 42.0% water/58% dioxane. There was an absolute error of ca. 2% water content for both samples. The above results show that the 4/5 mm assembly can be used to measure the % water in solvent mixtures. It should be noted that the data is fit to a parabolic curve (polynomial of degree 2). According to the fit, the intensity starts to go higher again at the higher water concentrations (high dielectric constant), implying that the dielectric constant decreases, which is not possible. Measurements made at the higher end of the dielectric constant axis will therefore likely have greater errors. The use of different fits or visual interpolation may improve the results.

The 3/4 mm coaxial assembly was also used to measure different mixtures (w/w) of water and dioxane. Figure 5 shows a plot of dielectric constant of dioxane-water mixtures versus the EPR signal intensity. Similar to the 4/5 mm

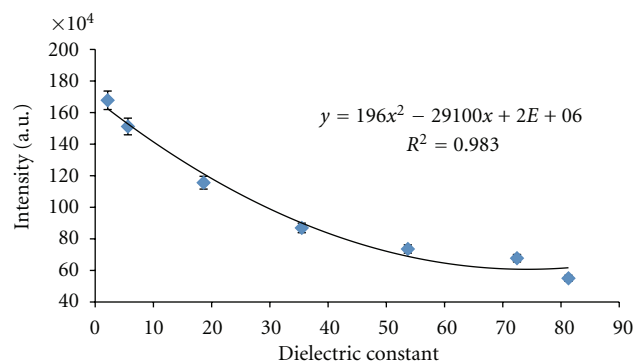


FIGURE 5: TEMPO reference EPR signal intensity (arbitrary units) as a function of dielectric constant for various dioxane ($\epsilon = 2.14$)/water ($\epsilon = 81.3$) mixtures [8]. The 3/4 mm coaxial tube assembly was used. Error bars of 3.5% are shown as discussed in the text.

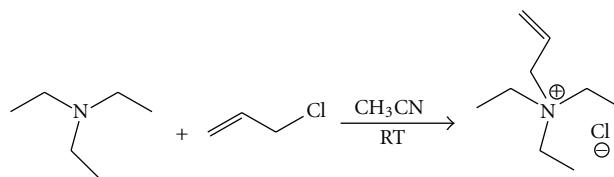
assembly, the 3/4 mm assembly can also be used to cover a wide range of dielectric constants. The data measured with 3/4 mm assembly also fits a polynomial equation well. The correlation factor (R^2) of 0.983 is even better compared to the data for the 4/5 mm assembly.

To test the methodology further, two unknown mixtures of water/dioxane were made up by a third party. These consisted of 82% water/18% dioxane (w/w%) and 58.3% water/41.7% dioxane. The EPR signal intensities for these samples were measured using the 3/4 mm coaxial assembly and their dielectric constants, determined from the calibration curve in Figure 5, were 61.8 and 38.6, respectively. Literature values for the dielectric constants were 63.2 and 41.0, respectively. Again the dielectric constants showed absolute errors of approximately 2 for both the unknowns. Correlating the measured dielectric constants with % water/% dioxane from the literature gave 79.8% water/20.2% dioxane and 54.3% water/45.7% dioxane. Again, there is an error of ca. 2% water content.

The 4/5 mm and the 3/4 mm assemblies both appear to be reasonable assemblies to measure the dielectric constants of unknown liquids. The only difference between the 3/4 mm and 4/5 mm coaxial assemblies was that the former uses even less sample for the measurements.

3.3. Application to Study Relative Kinetics for the Reaction of Triethylamine with Allyl Chloride. While the absolute errors in dielectric constants measured using this technique can be significant, especially at low values, the method is quite sensitive to measuring changes in dielectric constant for a single sample. In principle then, reactions in which the dielectric constant of the reaction mixture changes could be monitored using this technique. An example of such a reaction is pictured in Scheme 1 in which neutral triethylamine (TEA) and allyl chloride (AC) react to form a salt, which should increase the dielectric constant of the mixture.

The reaction in acetonitrile was monitored using the EPR technique for two different stoichiometric ratios: 1 mole TEA: 1.5 moles AC and 1 mole TEA: 1 mole AC. Both reactions were carried out under the same conditions. The



SCHEME 1: Reaction of triethylamine and allyl chloride to form a quaternary ammonium chloride.

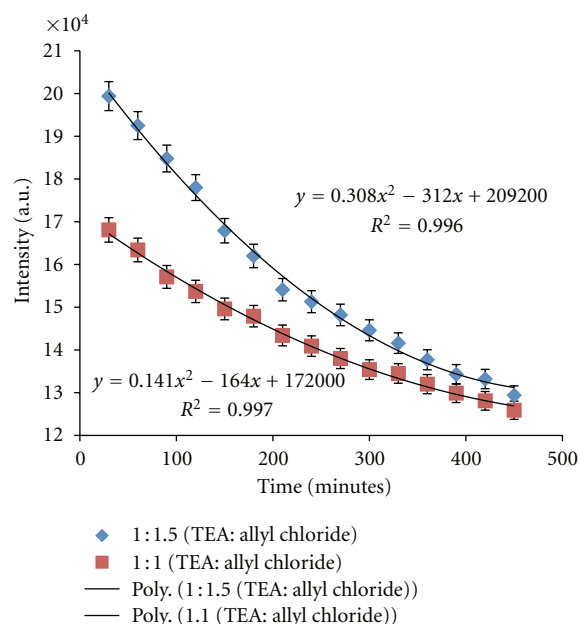


FIGURE 6: TEMPO reference EPR signal intensity (arbitrary units) as a function of time for the reaction of triethylamine and allyl chloride reaction in acetonitrile. The 3/4 mm coaxial tube assembly was used. Error bars of 1.7% are shown as discussed in the text.

reactants/solvent were mixed, a sample was placed in the 3/4 mm coaxial assembly, and this was positioned in the EPR cavity. Both the reactions were monitored every 30 minutes by measuring the EPR signal intensity. The results are shown in Figure 6.

The reaction of TEA with AC goes through a nucleophilic substitution mechanism to give the product. Therefore, the rate of the reaction is given by either $\text{Rate} = k [\text{AC}]$ or $\text{Rate} = k [\text{TEA}][\text{AC}]$, where k is the rate constant for the reaction, $[\text{TEA}]$ is the concentration of triethylamine, and $[\text{AC}]$ is the concentration of allyl chloride [16]. It was chosen to vary $[\text{AC}]$, as the rate of the reaction depends on its concentration in any event. As expected, as reaction occurs and ammonium salt is formed, the dielectric constant of the mixtures increase, resulting in decreasing EPR signal intensities. It can be seen that rate of the reaction for 1:1.5 TEA:AC reaction was faster compared to that for the 1:1 TEA:AC mixture.

To determine the rate constants it would be necessary to know how the EPR signal intensity changed with varying concentrations of each reaction component which, in principal, could be done. Nevertheless, the initial rate of formation

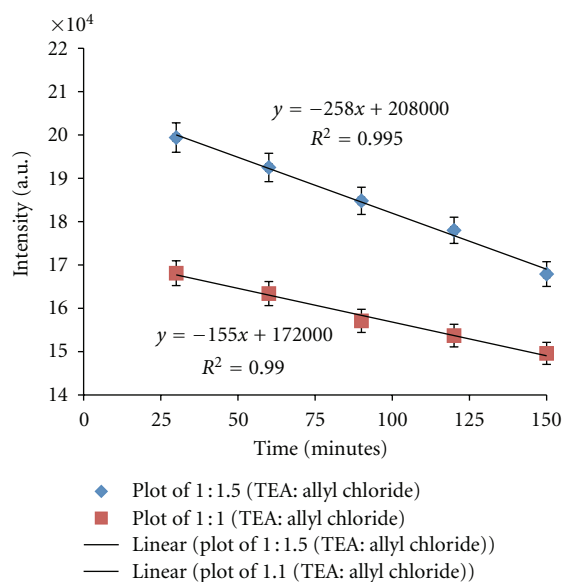


FIGURE 7: TEMPO reference EPR signal intensity (arbitrary units) as a function of time for the reaction of triethylamine and allyl chloride reaction in acetonitrile. The 3/4 mm coaxial tube assembly was used. Error bars of 1.7% are shown as discussed in the text.

of product in the 1 : 1.5 TEA:AC reaction should be 1.5 times faster than the 1 : 1 TEA:AC reaction. Taking the first five points of each curve of Figure 6 to reflect reasonably constant reactant concentrations (low conversion) and the initial rate of reaction to be approximately linear, comparison of the two slopes in Figure 7 shows that the 1 : 1.5 TEA:AC reaction proceeds ca. 1.66 times faster than the 1 : 1 TEA:AC reaction, agreeing reasonably well with the theoretical value of 1.5.

3.4. Use of Different Solvents as Standards to Investigate Dielectric Constants. While the use of water-dioxane mixtures allows calibration curves to be constructed over a wide range of dielectric constants, it was of interest to investigate the use of individual solvents as standards for the construction of calibration curves. These studies were also used to gauge the utility of different coaxial assemblies.

3.4.1. 3/5 mm Coaxial Assembly. Figure 8 shows a plot of dielectric constant versus average intensity plot for a 3/5 mm coaxial assembly. The intensity is an average of two different measurements taken on the same solvents at different times with the same assembly, keeping the instrumental parameters constant. With the 3/5 mm assembly it is difficult to obtain an EPR signal using jacket media with dielectric constants greater than 33. This is likely due to the relatively large volume of the jacket medium that absorbs the microwave radiation, making it difficult to tune the sample in the microwave cavity. Therefore, only a limited range of dielectric constants could be covered. Data analysis was done using two fits, linear ($R^2 = 0.910$) and polynomial ($R^2 = 0.953$, shown in Figure 8). As seen from the correlation coefficients, the polynomial fits better than the linear fit. To evaluate the data an iterative algorithm was used in which each point was removed from

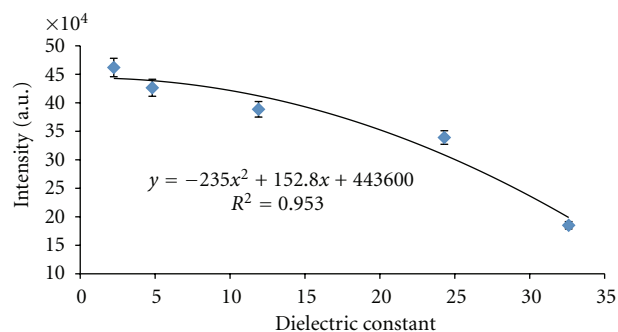


FIGURE 8: TEMPO reference EPR signal intensity (arbitrary units) as a function of dielectric constant for various solvents ($\epsilon = 2.24$ carbon tetrachloride, $\epsilon = 4.86$ chloroform, $\epsilon = 11.9$ t-BuOH, $\epsilon = 24.3$ ethanol, and $\epsilon = 32.6$ methanol). The 3/5 mm coaxial tube assembly was used. Error bars of 3.5% are shown as discussed in the text.

the curve, a fit was calculated from the remaining points, and treating the removed point as an unknown, its dielectric constant was calculated. This was done for each point and an average absolute error was calculated using known literature values. The average dielectric constant absolute error for the polynomial fit is 5.84 and is lower than the average error for linear fit (6.47). A cubic fit was also tried for the above data. Although the cubic fit was better, the average absolute error is much higher than that for the polynomial fit.

Since the 3/5 mm coaxial assembly could only cover a smaller range of dielectric constants, two different coaxial assemblies with smaller differences in coaxial diameter were used for further investigation, 3/4 mm and 4/5 mm.

3.4.2. 3/4 mm Coaxial Assembly. Data for the EPR intensities using the 3/4 mm assembly are shown in Figure 9. For this coaxial assembly a greater range of solvent dielectrics could be covered. Data analysis was again done using two fits, linear ($R^2 = 0.973$) and polynomial ($R^2 = 0.990$, shown in Figure 9). As seen from the correlation coefficients, the polynomial fits better than the linear fit. An average absolute error was calculated for each fit as described earlier. The average absolute error for the polynomial fit is 5.66 dielectric constant units and is lower than the average error for linear fit (7.91 dielectric constant units).

3.4.3. 4/5 mm Coaxial Assembly. Data for the EPR intensities using the 4/5 mm assembly are shown in Figure 10. Data analysis was again done using two fits, linear ($R^2 = 0.991$) and polynomial ($R^2 = 0.992$, shown in Figure 1). As seen from the correlation coefficients, the polynomial fits better than the linear fit. The average absolute error for the polynomial fit is 3.85 dielectric constant units and is lower than the average error for linear fit (5.07 dielectric constant units).

As seen from all the data above, it can be concluded that the coaxial assemblies could be used to estimate the dielectric constant of an unknown solvent by measuring its EPR intensity and the intensity of solvents with known dielectric constants to give a calibration curve, and then interpolating to find the dielectric constant of the unknown solvent. The

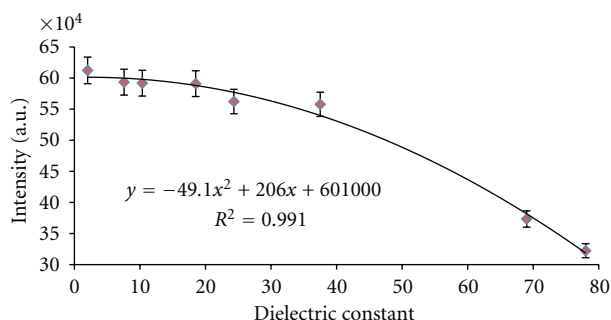


FIGURE 9: TEMPO reference EPR signal intensity (arbitrary units) as a function of dielectric constant for various solvents ($\epsilon = 2.02$ cyclohexane, $\epsilon = 7.58$ tetrahydrofuran, $\epsilon = 10.4$ dichloroethane, $\epsilon = 18.5$ methyl ethyl ketone, $\epsilon = 24.3$ ethanol, $\epsilon = 37.5$ acetonitrile, $\epsilon = 69.0$ propylene carbonate, and $\epsilon = 78.0$ water). The 3/4 mm coaxial tube assembly was used. Error bars of 3.5% are shown as discussed in the text.

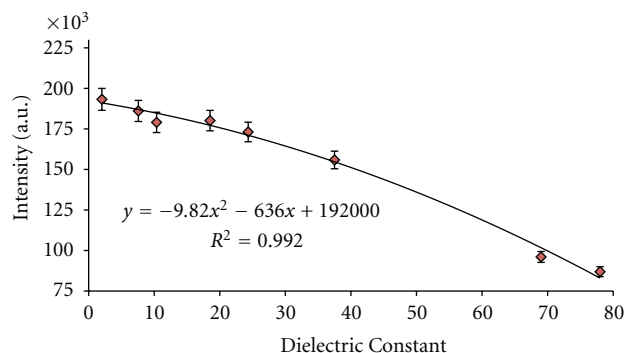


FIGURE 10: TEMPO reference EPR signal intensity (arbitrary units) as a function of dielectric constant for various solvents ($\epsilon = 2.02$ cyclohexane, $\epsilon = 7.58$ tetrahydrofuran, $\epsilon = 10.4$ dichloroethane, $\epsilon = 18.5$ methyl ethyl ketone, $\epsilon = 24.3$ ethanol, $\epsilon = 37.5$ acetonitrile, $\epsilon = 69.0$ propylene carbonate, and $\epsilon = 78.0$ water). The 4/5 mm coaxial tube assembly was used. Error bars of 3.5% are shown as discussed in the text.

errors involved in these measurements may come from the geometry of the coaxial assembly, impurities in the solvents used, and the positioning of the tube.

3.5. Systemic Error Studies. Different types of systemic errors were studied for the cell and the instrument. For all the error measurements, the 4/5 mm coaxial assembly was used.

3.5.1. Fluctuation in the Temperature of the Microwave Cavity. The temperature of the microwave cavity was measured to be $21.7 \pm 0.5^\circ\text{C}$ during a typical experiment. The data from Reference 13 for water-dioxane mixtures were used to estimate the potential magnitude of changes in dielectric constants due to this thermal fluctuation. For low dielectric solvents such as dioxane the dielectric constant is nearly temperature invariant. For a high dielectric solvent like water, the dielectric constant varies by only ca. 0.3°C between 20 and 30°C ,

so errors associated with thermal fluctuations should be fairly low, less than ± 0.2 .

3.5.2. Drift in Intensity Measurements over Time. For these measurements, two solvents with widely different dielectric constants were used as the jacket media, 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$ $\epsilon = 10.4$) and water (H_2O $\epsilon = 78$). EPR intensities were measured every 15 mins over a span of 2 hours. During the measurement the coaxial assembly was not moved at all in the cavity. Precautions were taken to prevent any loss of solvent by evaporation by sealing the coaxial assembly with Teflon tape. Statistical treatment of the data showed that the measured EPR intensities for 1,2-dichloroethane and water varied from the mean value by $\pm 1.36\%$ and $\pm 1.68\%$, respectively. Of course, these data would include any variations induced by thermal fluctuations during the duration of the measurements.

3.5.3. Intensity Variation due to Coaxial Assembly Placement in the Cavity. Because the microwave cavity is very sensitive to perturbation, a series of EPR intensity measurements were carried out as discussed above, but where the coaxial assembly was removed from the cavity and placed back in the cavity before taking another measurement. Statistical treatment of the data showed that the measured EPR intensities for dichloromethane (CH_2Cl_2 $\epsilon = 8.9$) and water varied by $\pm 0.79\%$ and 1.38% , respectively. Of course, these data would include any variations induced by thermal fluctuations or instrument drift during the duration of the measurements.

3.5.4. Reproducibility of Intensity Data for a Given Jacket Medium. To study overall reproducibility of the technique for given samples, measurements were carried out as discussed above, but where the coaxial assembly was removed from the cavity, the solvent was emptied from the cell and replaced with fresh solvent, and the assembly was placed back in the cavity before taking another measurement. Statistical treatment of the data showed that the measured EPR intensities for methylene chloride and water varied from the mean value by up to 0.87% and 3.48% , respectively. Of course, these data would include any variations induced by thermal fluctuations or instrument drift during the duration of the measurements. Since most of the measurements discussed earlier involved the changing of the jacket medium after every measurement, systemic error bars of 3.5% were applied to the EPR intensity results, except for the kinetic data, where the error bars (1.7%) reflect that the samples were not changed or repositioned.

From the discussion above it appears that while the precision of the measurements is reasonably good (max. 3.5% error observed), the absolute error using this technique for measuring dielectric constants is significant, especially for low dielectric constant samples. As this technique to determine dielectric constants relies on the construction of a calibration curve, it is likely that the more significant absolute errors in dielectric constants stem from the standards used. In all cases, reagent grade solvent samples were used and values of dielectric constants were taken for pure solvents

from the literature. In some cases, for example, cyclohexane, this assumption is likely reasonable, but for others, for example, tetrahydrofuran, the presence of significant amounts of impurities, for example, water or dissolved gases, could cause significant changes in the dielectric constant of the standard, thus causing deviations in the calibration curve. This explanation is consistent with the observation that the absolute errors in dielectric constant measurement were much lower when the dioxane/water mixtures were used for construction of the calibration curves. Even if the solvents were impure (most likely the dioxane), the internal consistency of using the same two solvents for construction of the calibration curve would lead to a general increase in its accuracy, especially for moderate dielectric constant samples. Experiments to verify this and to improve the standards using purified and/or solvents with dielectric constants verified by another method are ongoing.

4. Conclusions

Using a coaxial cell with an inner paramagnetic reference, EPR spectroscopy can be used to study the dielectric properties of liquids. If an EPR spectrometer is available, the technique is simple and inexpensive. The method is fairly sensitive to changes in dielectric constant and is perhaps best suited to study such changes qualitatively. The use of this technique to measure dielectric constants requires the construction of a calibration curve for each set of experiments. These initial experiments suggest that the standards used for construction of the calibration curve are likely responsible for significant absolute errors for this application. Several avenues of investigation are currently underway to improve the use of this technique for measuring dielectric constants: (1) improvement of the standards by using purified solvents or standardizing values for solvents used by alternative methods, (2) using iterative methods by first determining the approximate dielectric constant of a material, then using standards of attenuated range to increase the accuracy of the measurement, and (3) using alternative cell geometries to reduce “lensing” effects that may occur for the coaxial geometry, especially for high dielectric samples [10, 17]. Initial experiments using iterative methods have already shown that the absolute errors in such dielectric constant measurements may be easily improved to be ca. 1.

Since the technique is sensitive to changes in dielectric constant, preliminary experiments show the method to be applicable to studying phase transitions or processes where a change in dielectric constant occurs. Aside from the use of this technique to study the relative kinetics of an appropriate reaction discussed above, experiments to probe the use of this technique to study melting/crystallization, surfactant solutions, liquid crystals, and electrolyte solutions are ongoing.

Acknowledgments

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