ARTICLES

Study of Multiple Relaxations in Crown Ethers by Dielectric Relaxation Spectroscopy

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An investigation was carried out on the dipole dynamics of low molecular weight crown ether series and related compounds by dielectric relaxation spectroscopy (DRS). An unexpected discovery regarding two main relaxations observed by DRS and calorimetric (DSC) measurements have been analyzed using neat and solvent-present formulations over a wide range of frequency and temperature. The presence of nonpolar, nonreactive, fully miscible solvent (*o*-terphenyl, OTP) produced a marked opposite effect on the apparent activation energy of these two relaxations. Interestingly, the location of the lower of these two transitions in the temperature domain was found to be practically unaffected by the presence of OTP, while a higher temperature relaxation changes its location systematically as a function of solvent concentration. To explore the molecular origin of these findings, a large number of cyclic compounds of similar structure have been analyzed by DRS, DSC, and molecular simulation. As a result of this effort, a conformational model that accounts for multiple relaxations observed in this family of materials is introduced.

Introduction

The use of broadband dielectric relaxation spectroscopy (DRS) to study dipole dynamics in glass-forming low molecular weight organic compounds and polymers has been extensively documented in the literature (e.g., refs 1−6 and references therein). Dipole relaxation has been used for years as a molecular probe tool for a wide range of nonreactive and reactive substances to account for physical and chemical changes that take place during various processes, such as chemical reactions, crystallization, phase separation, dissolution, or liquid crystal transformations (e.g., refs 6−13). The major incentive in most of these reports was to identify and describe the molecular origin of dipole motion in an applied electrical field and to correlate obtained information with a monitored physical process. This task has been accomplished by broadband DRS, used primarily to analyze the characteristic relaxation times of two major relaxation processes that are seen in the frequency domain, namely α and β, their temperature dependencies, activation energies, and the breadths and shapes of their distribution function.[6,14−16] Along these lines, in our recent studies of the reorientational dynamics of dipoles during the network formation in multifunctional epoxy−amine formulations,[17−19] dielectric data were analyzed in the time and frequency domain; it was found that the network dynamics could be classified into three regimes as a function of degree of cure. We proposed a methodology for the evaluation of the kinetics of network formation and advanced an interpretation of network dynamics in terms of intermolecular cooperativity based on the interplay between molecular and dielectric architecture. These studies had an additional dimension in that the results were generated by simultaneous DRS and fiber-optic Fourier transform infrared (FTIR) spectroscopy so that real-time chemical changes and specific molecular interactions were closely monitored and coupled with the observed dielectric signal.

Of interest here is to expand our knowledge on dielectric characterization in reactive polymer systems and apply it to a structurally very interesting group of low molecular weight crown ether materials. In the present work, we have used crown ethers containing hydrogen, carbon, and oxygen atoms, with each oxygen atom bound between two carbon atoms to form a ring, or crown, which usually acts as a “host” for certain metallic elements (i.e., Na, K). Metals reside in the center of the crown while being attached to the molecule by the exposed oxygen atoms via complex bonding. The high degree of selectivity enables the crown compound to link the “guest” atom of a suitable size in a solution and wrap around it in a lock-and-key fashion. Because of these characteristics, crown ethers could be potentially utilized in various applications: (1) to mimic an enzyme’s function, (2) to model the mechanism by which the body moves sodium and potassium into cells while simultaneously regulating their concentration in the blood, (3) to act as potential “scavengers” in removing certain elements from the environment, (4) to serve as a part of rotaxane systems (e.g., ref 20 and references therein) and to act as mechanical switches, etc. Crucial properties of these supramolecular systems are the strength, flexibility, and orientational ability of oxygen dipoles that are responsible for the overall bonding efficiency.

Different alkali complexes of crown ethers and their derivatives have been largely used to explore optimal conformation for a binding process between crown ring and the “guest” molecule. For instance, Ratcliffe and co-workers[21−23] studied solid molecular complexes of 18-crown-6 using ^{13}C CP/MAS, ^{1}H NMR, and ^{2}H NMR. Data suggested that the crown ring

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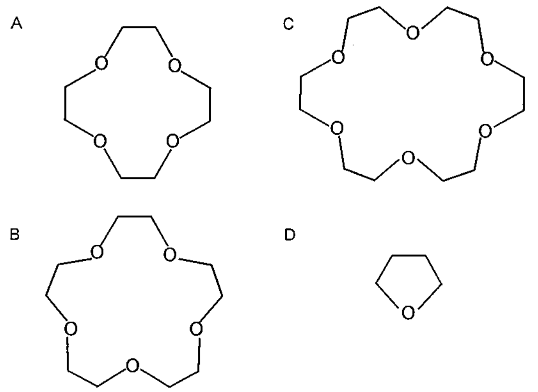

Figure 1. Schematic presentation of chemicals used in this study: (A) 12-crown-4; (B) 15-crown-5; (C) 18-crown-6; (D) tetrahydrofuran (THF).

undergoes a large-amplitude motion in the neighborhood of room temperature, resembling that of a "merry-go-round". This motion consist of a combined rotation and conformational adjustment of the ring, in which individual $-OCH_2CH_2-$ units jump to adjacent sites in the crystal phase. A similar pattern in solid complexes of 12-crown-4, 15-crown-5, and 21-crown-7 was also reported. The same group recently conducted a study on large-amplitude motions of 12-crown-4 ether in its LiNCS complex using solid state ^{2}H NMR line shape measurements.[24] Along with a "merry-go-round" mechanism, an independent motion was identified that occurs at a slightly different rate and involves two-site up−down flips of CH_2 groups. On the NMR time scale this is a rapid process that is initiated just below room temperature.

In addition to previous solid state investigations, we believe that a study of dipole dynamics of these materials in an electrical field will provide an additional insight into motions of characteristic crown ring moieties. It is anticipated that this analysis, which has not been previously reported in the literature, would aid understanding further a mechanism by which ether units approach the "guest" atom. Hence, the principal objective of present work is two-fold: (1) to explore dipole dynamics of crown ethers and related compounds using neat and nonpolar solvent formulations and (2) to introduce a model that would account for different types of relaxation that we have recently encountered in this family of materials.

Experimental Section

Materials. In Figure 1A−C we show a chemical structure of crown ethers used in this study: (A) 12-crown-4; (B) 15-crown-5; (C) 18-crown-6. Also, in Figure 1D, the structure of tetrahydrofuran (THF) is shown, which was used as a model of the dielectric behavior of crown ether analogues. In addition to THF, supplementary information was obtained from many other small organic compounds that will be mentioned throughout the text. Chemicals investigated in this study were purchased from Aldrich and used without further purification.

Techniques. *Dielectric Spectroscopy*. Our experimental facility for dielectric measurements consists of modified commercial and custom-made (in-house) instruments: (1) Solartron 1260 Impedance Gain/Phase Analyzer (10 μHz to 32 MHz) and (2) Hewlett-Packard 4284A Precision LCR Meter (20 Hz to 1 MHz). Both instruments were interfaced to a computer and a thermal chamber and were modified by the addition of a high impedance adapter. Further experimental details, including the cell configurations, have been described in detail elsewhere.[13,25]

Differential Scanning Calorimetry. Supporting evidence was obtained from DSC using a TA Instrument Co. DSC model 2920 at a heating rate of 10° C/min.

Results and Discussion

We start our analysis by presenting in parts A and B of Figure 2 a DSC thermogram of 15-crown-5, a glass former that can be easily supercooled below its glass transition temperature (T_g). Unexpectedly, we detected two well-separated endothermic steps at −119 and −92 °C, which suggest the presence of two transformations involving appreciable changes in configurational entropy of this material. Crystallization and melting are also observed, as expected, at higher temperatures. This experiment was repeated a number of times on different as-received samples, and the same result was always obtained. Two other crown ethers, 12-crown-4 and 18-crown-6, crystallize rapidly and could not be quenched to an amorphous glass. However, their DSC thermograms shown in parts A and B of Figure 3 indicate that the lower of the two temperature transitions (from hereafter, LTT, lower temperature transition) observed in Figure 2 for 15-crown-5 is still present here and its location varies slightly with structure. The fact that this calorimetric relaxation is detectable in fully crystalline samples (note the absence of a crystallization exotherm in parts A and B of Figure 3) suggests its localized character. The higher of the two temperature transitions (from hereafter, HTT, higher temperature transition) observed in 15-crown-5 is suppressed in two other crown ethers owing to high crystallinity. We reasoned that a decrease in crystallinity would bring about the HTT in 12-crown-4 and 18-crown-6 and decided to test this hypothesis by mixing these compounds with *o*-terphenyl (OTP), a completely miscible high molecular weight nonpolar solvent ($T_g = -25$ °C). The analysis of dipole dynamics in solvent media are considered an important analytical tool since we can use a wide range of frequency and solute/solvent concentrations to learn how dielectric relaxation behavior is affected by foreign nonpolar molecules.[4,26,27] Related to this topic, we have recently conducted a study on reorientational dynamics of dipoles in a multifunctional epoxy−amine system during network formation in the presence of different OTP concentrations.[18] The presence of OTP caused a decrease in the reaction rate but did not affect the reaction mechanism or interfere with the formation of hydrogen bonded complexes that accompanied gelation in this system. A pronounced broadening of the normalized α relaxation peak leading to a more symmetric shape was observed during cure. Consequently, this prevented us from getting good fits to the KWW stretched exponential function. It was suggested that the solvent molecules influenced dipole dynamics principally by increasing the distance between dipoles and introducing local strains that impede the relaxation process. In Figure 3C, a DSC thermogram of 50 wt % 12-crown-4 ether in OTP is shown. Interestingly, the location of LTT is almost unaffected by the presence of OTP, while HTT now becomes detectable with a location that varies as a function of solvent concentration.

The presence of two inherent calorimetric endotherms was surprising, particularly when one considers the relatively simple chemical structure of these crown ethers. Since a literature search on these and numerous related compounds revealed no reports of similar findings, we decided to explore further the molecular origin of these transitions by DRS. We set out to study neat crown ethers and their mixtures with a solvent over a wide range of frequency and temperature. A numerical conformational analysis was also performed on these materials in order to learn more about the direction of their dipole moments in space.

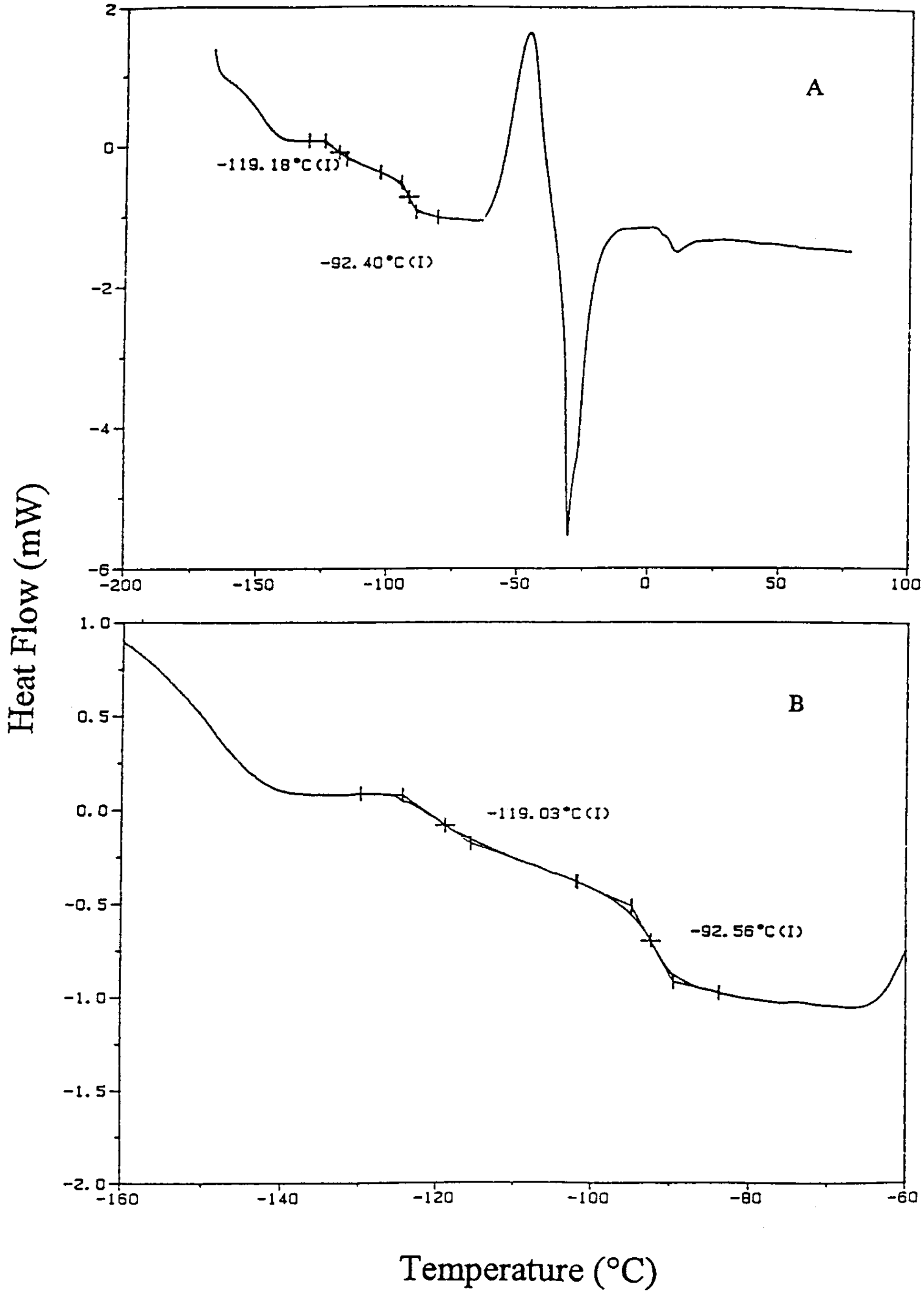

Figure 2. (A) DSC thermogram of 15-crown-5. Heating rate was 10 °C/min. (B) Enlarged view of the endothermic region.

DRS performed on neat 15-crown-5 ether also revealed two relaxations which were related to the two endothermic transitions observed by DSC. As an illustration, parts A and B of Figure 4 show dielectric loss of 15-crown-5 in the frequency domain with temperature as a parameter. The higher frequency peak, which corresponds to LTT, is seen in Figure 4A and is characterized by a significantly lower apparent activation energy than the HTT relaxation (ca. 10 vs 55 kcal/mol). It should be noted, however, that the determination of apparent activation energy for these processes in a neat sample was feasible only within a restricted frequency range (0.01−1 Hz) where Arrhenius temperature dependence was observed. In addition, the LTT peak appeared considerably broader owing to the distribution of different crown ether conformers of slightly higher energy. This will be further discussed later in the text. Two peaks merge rapidly with increasing temperature in the frequency range between 10 and 100 Hz, resulting in the increasing intensity of dielectric loss at temperatures above −95 °C. In Figure 4B, we see that the loss intensity increases further up to the point where crystallization begins. From that moment on, we start to observe a suppression of dielectric relaxation and a gradual decrease in the loss intensity. The influence of evolving crystalline structure on the reorientational ability of dipole units that originate in the amorphous phase is a separate issue and as such has been treated elsewhere.[28]

Dielectric data on different crown ether/*o*-terphenyl (OTP) formulations suggest that these two processes are affected by the OTP molecules, but in the *opposite* manner. To illustrate that, we consider Figure 5 which shows dielectric loss as a function of temperature with concentration as a parameter. The various solvent-containing formulations are defined throughout the text by the general form *X*/*Y*, where *X* represents the weight percentage of the solute (i.e., 15-crown-5) and *Y* represents the weight percentage of the solvent (OTP). For example, a 25/75

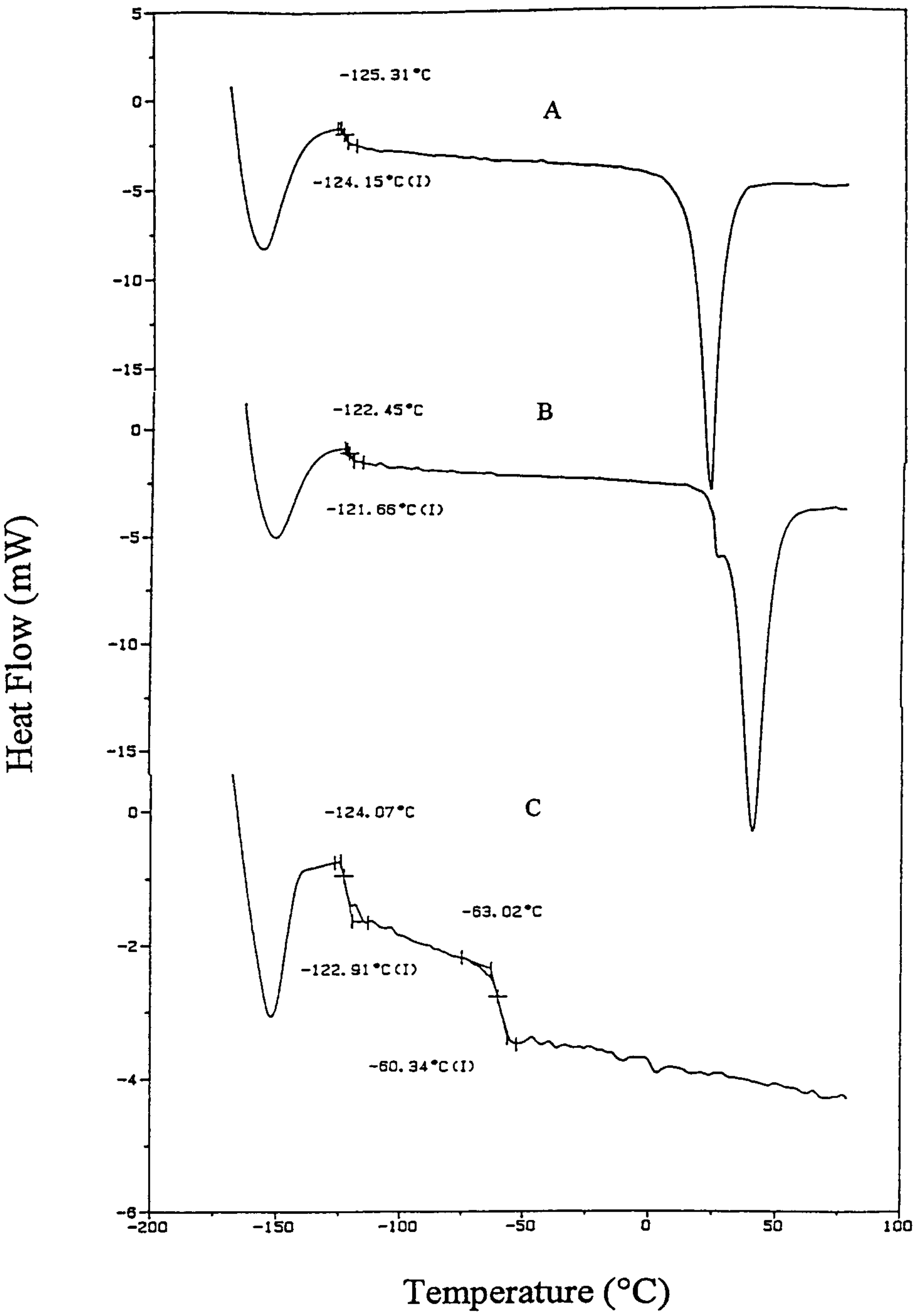

Figure 3. DSC thermogram of (A) 12-crown-4, (B) 18-crown-6, and (C) 12-crown-4 in the presence of *o*-terphenyl (50/50).

formulation is composed of 25 wt % of 15-crown-5 ether and 75 wt % of *o*-terphenyl. Numbers at the top of each peak in Figure 5 represent the apparent activation energy in kcal/mol for each formulation obtained from the frequency domain measurements. Plots of the most probable relaxation time versus reciprocal temperature were constructed and used to calculate the apparent activation energy for both processes, as exemplified in Figure 6 for the LTT peak. In all cases, a linear portion of the relaxation map was observed between ca. 100 Hz and 1 MHz, which is the nominal range for the instrument (HP 4284A) used in these measurements. Naturally, all α relaxations are inherently non-Arrhenius when viewed over 10 or more decades of frequency. Having that in mind, several important features were noted in Figure 5. For instance, the apparent activation energy of LTT relaxation decreases (from 17 to 9.6 kcal/mol) with increasing OTP concentration, but the temperature of the maximum peak remains practically unchanged. The HTT process, on the other hand, is characterized by the significant increase in the apparent activation energy (from ca. 35 to 63 kcal/mol) and, also, by the pronounced shift in the peak maximum toward higher temperature with larger solvent content. This is a direct consequence of the glass transition temperature of each formulation, which attains a value between those of the individual components ($T_g(100/0) = -92$ °C and $T_g(0/100) = -25$ °C). A similar trend was observed in the 12-crown-4 /OTP formulations, as shown in Figure 7. The apparent activation energy of each process was slightly lower than that in the formulations containing 15-crown-5 (see Figure 5), which is probably due to a smaller size of the 12-crown-4 molecule. The next question regards the observed opposite trend in the activation energy of LTT and HTT relaxations. We believe that an explanations for the underlying molecular mechanism lies in cooperativity. Williams and co-workers (e.g., ref 27 and references therein) studied the cooperative behavior of super-

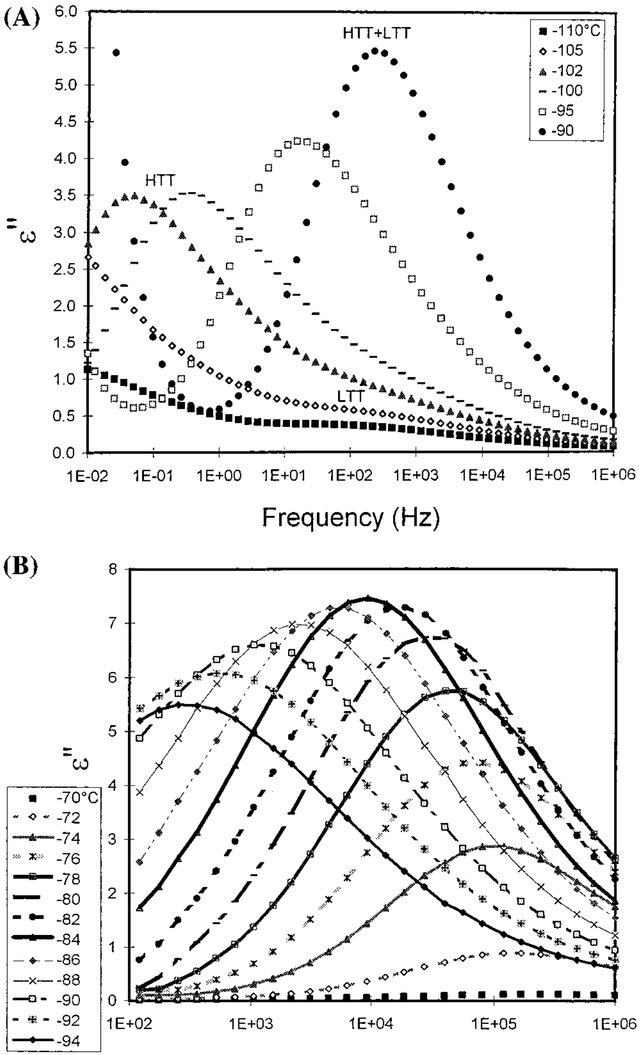

Figure 4. (A) Dielectric loss in the frequency domain as a function of temperature for 15-crown-5 at the low-frequency end where two relaxations merge. (B) Dielectric loss in the frequency domain as a function of temperature for 15-crown-5. Onset of crystallinity is observed at the frequency around 10 kHz.

cooled solutions of nonreactive solutes in *o*-terphenyl by DRS. They found that the activation energy of the α process was independent of the OTP concentration for some polar solutes, while in others it increased significantly. In addition, our earlier study[18] on network dynamics in the presence of OTP showed a substantial increase in activation energy of α relaxation in the later cure stage. This was explained by enhanced cooperativity between solvent molecules and the growing network. Here, the observed increase in apparent activation energy of the HTT process could be rationalized by the same phenomenon. Cooperativity of the LTT process, on the other hand, decreases gradually with increasing OTP content, suggesting that this dielectric relaxation is more localized and *not coupled* with the solvent. The principal role of the solvent is to separate dipole units that are at the origin of the LTT process, thus reducing the cooperative character of this particular molecular motion. It is worth noting that we also examined a series of benzene-substituted crown ether homologous including benzo-12-crown-4, benzo-15-crown-5, and benzo-18-crown-6 and observed the same two types of relaxations with identical trends in the apparent activation energy.

As a next step, a numerical conformational analysis was performed on crown ethers using molecular simulation Cerius2 software. We searched for information on the energetically favorable orientations of ether units in these compounds, since this is likely to be an important aspect of their dielectric properties. Figure 8 shows the lowest energy conformations obtained by numerical analysis for (A) 12-crown-4, (B) 15-crown-5, and (C) 18-crown-6. Filled circles represent an oxygen atom, while each knee is the location of the carbon atom of a CH_2 group. Interestingly, all ether dipole units (except one in the 12-crown-4 and 18-crown-6 ethers and two in the 15-crown-5) point to the same direction, out of the molecular plane toward the center of ring hole. The exceptions are marked by an asterisk (*) in Figure 8, with oxygen units oriented toward the *opposite* plane. It should be clearly emphasized that detailed conformational analyzes of lower crown ether analogues have been previously reported in the literature. Paulsen et al.[29,30] conducted an extensive study on conformational states of both uncomplexed and complexed 15-crown-5 using MM3 force field with

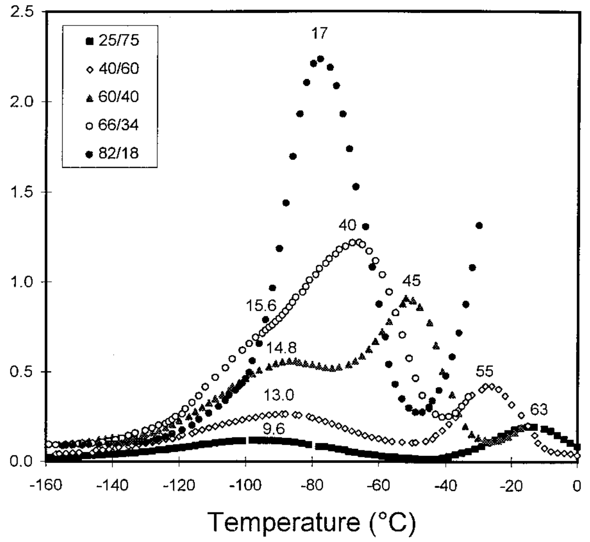

Figure 5. Composite plot of dielectric loss as a function of temperature at 25 kHz for the 15-crown-5/OTP mixture with weight ratio as a parameter: (■) 25/75 (25% of 15-crown-5 and 75% of OTP); (◇) 40/60; (▲) 60/40; (○) 66/34; (●) 82/18. The number on the top of each peak represents the apparent activation energy in kcal/mol obtained from dielectric measurements in the frequency domain.

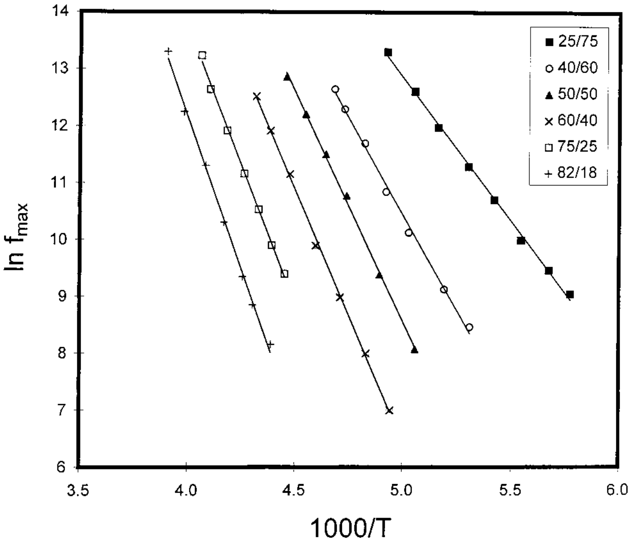

Figure 6. Natural log of frequency at dielectric loss maximum (f_{max}) versus $1/T$ for the LTT relaxation of 15-crown-5 for (+) 82/18 (15-crown-5/OTP), (□) 75/25, (×) 60/40, (▲) 50/50, (○) 40/60, and (■) 25/75 formulation. Data are shifted along horizontal axis for clarity.

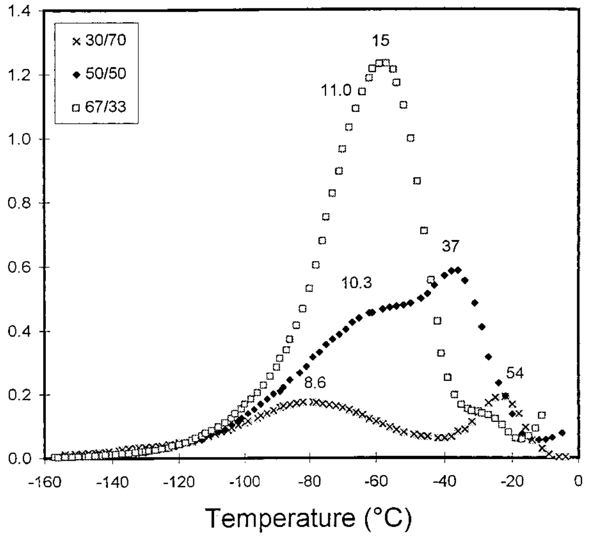

Figure 7. Composite plot of dielectric loss as a function of temperature at 25 kHz for the 12-crown-4/OTP mixture with weight ratio as a parameter: (×) 30/70; (◆) 50/50; (□) 67/33. The number on the top of each peak represents the apparent activation energy in kcal/mol obtained from dielectric measurements in the frequency domain.

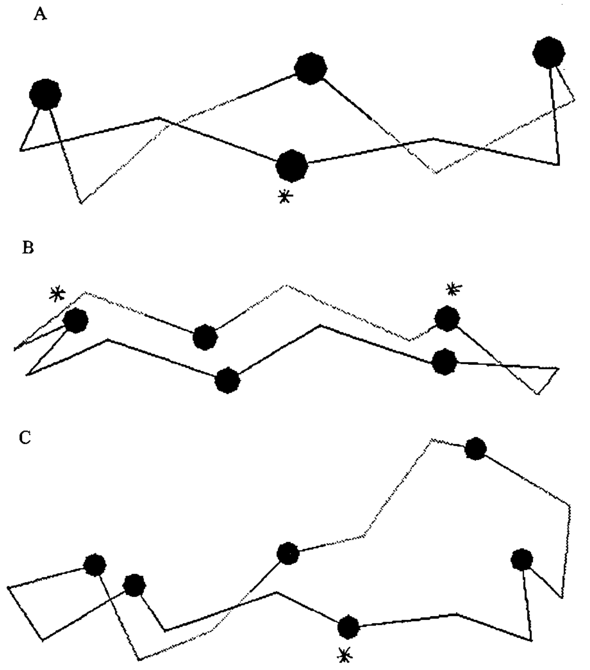

Figure 8. Conformation generated by molecular simulation of (A) 12-crown-4, (B) 15-crown-5, and (C) 18-crown-6. Asterisks indicate a dipole having the opposite direction from other dipoles in the molecule.

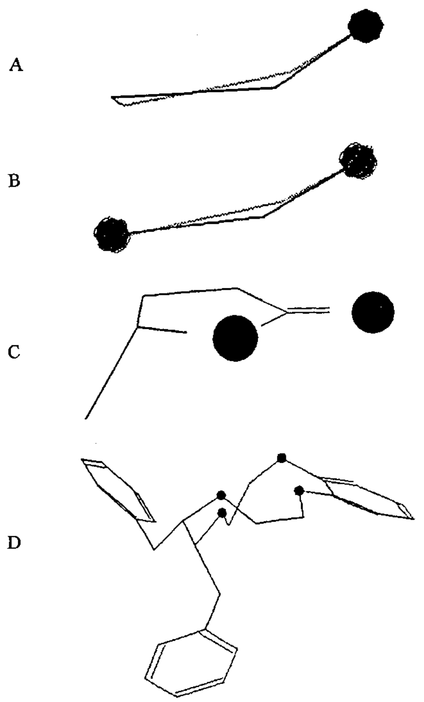

Figure 9. Conformation generated by molecular simulation of (A) THF, (B) 1,3-dioxolane, (C) α-methyl-γ-butyrolactone, and (D) a hypothetical compound based on 12-crown-4 having all ether units oriented in the same direction.

a Saunders stochastic search algorithm. They presented (Figure 1 in ref 29) stereoviews of eight uncomplexed conformers of the lowest steric energy, which closely match the conformational model shown in Figure 8B. The only difference between conformers illustrated in ref 29 arises from the various spatial arrangements of ether oxygens facing up or down the projected molecular plane. For our study, an important feature of their analysis is the fact that in all low-energy conformers *at least* one oxygen unit is directed toward the opposite plane from the rest of the ether population. A similar conclusion was drawn from other molecular dynamic simulations on the isolated but more complex 18-crown-6 sample.[31,32] Also, numerical calculations of this very flexible molecule in solution showed a large number of possible conformations having only slightly different energies.[33,34] To analyze further dielectrically important conformational features of these materials, we decided to examine a cyclic ether of even simpler structure. Our immediate choice was tetrahydrofuran, or THF, a compound that can be viewed as a model for crown ethers whose chemical structure is displayed in Figure 1D. The results of a conformational analysis of THF are shown in Figure 9A. There are four carbon atoms in the same plane, while the remaining oxygen (filled circle in Figure 9A) is located above the plane. Perhaps the easiest way of describing this spatial arrangement is by envisioning the location of the oxygen atom as at the tip of the flap of an open envelope. We will return to this model later to describe motions that are responsible for LTT and HTT relaxations.

Dipole dynamics of THF in the presence of solvent were examined next. Substantial data emerged as we detected two relaxations similar to those found in crown ethers. In this system, however, the locations of LTT and HTT processes are shifted to lower temperatures due to the simpler molecular structure of THF. Data in Figure 10 are analogous to those in Figures 5 and 7 for 15-crown-5 and 12-crown-4, respectively. Due to the lower number of possible conformers for the THF molecule, the observed peak distribution appeared narrower than those in the crown ether series. Unfortunately, LTT relaxation in THF/OTP has been observed at a very low temperature (−180 °C at 25 kHz), as seen in Figure 10, and therefore could not be detected by calorimetric measurements. Nevertheless, it is reasonable to assume that the same molecular motions are at the origin of LTT and HTT relaxations (seen by DRS) in crown ethers and THF.

To generalize further the above-described findings, we analyzed a number of cyclic compounds of similar structure by DRS, DSC, and molecular simulation. Presenting the details of all these tests would serve no purpose here; instead, we summarized our findings as follows.

(1) DRS results for tetrahydropyran (THP, $((CH_2)_5O)$), a six-member ring, were analogous to those for THF. The most probable arrangement of THP atoms is the well-known chair

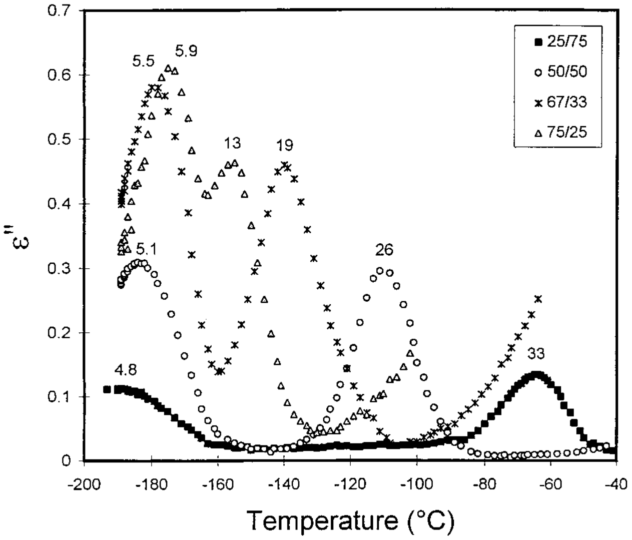

Figure 10. Composite plot of dielectric loss as a function of temperature at 25 kHz for the THF/OTP mixture with weight ratio as a parameter: (■) 25/75; (○) 50/50; (×) 67/33; (△) 75/25. The number on the top of each peak represents the apparent activation energy in kcal/mol obtained from dielectric measurements in the frequency domain.

conformation, shown in Figure 9A, which is the same as that in THF but with an additional CH_2 unit located bellow the main plane. Since this part of the molecule is dielectrically inactive, similar dipole dynamics in THF and THP were expected.

(2) A substitution of the oxygen atom in THF with S (sulfur), N−H, C═O, or P (phosphorus) does not alter the lowest energy conformation. Although multiple relaxations were not reported for crown ethers, they were observed in compounds such as pyrrolidine, cyclopentanone, tetrahydrothiophene, etc. in different solvents (ref 4 and references therein), but little has been said about the nature of these relaxations and their temperature dependence.

(3) A substitution of the carbon atom with one more oxygen unit in a five-membered structure has no effect on the conformation. This is exemplified in Figure 9B where we show the structure of 1,3-dioxolane. DRS data of this compound exhibit the same trend as those for THF.

(4) The addition of double bonds introduces planarity in these cyclic compounds. A good example is furan ($(CH)_4O$), the unsaturated analogue of THF. A consequence of the imposed planarity in this and other cyclic compounds investigated herein (including pyridine, pyrrole, thiophene, etc.) is the appearance of only one α relaxation in the dielectric spectrum. Planarity can also be achieved by inserting the ester unit into the ring. An example of this is α-methyl-γ-butyrolactone, whose structure is shown in Figure 9C. DRS data obtained for this compound confirmed a single relaxation process.

From careful examination of all these results, the following concept has emerged. First, we propose that the two relaxations (LTT and HTT) are caused by nonplanar conformation of dipole units. A conformation, schematically shown in Figure 11, is put forward to explain the observed multiple relaxations in these systems. Due to the fact that DRS mostly provides information about nonspecific types of motions when it comes to the exact dynamics, we stress that a certain degree of speculation might exist regarding the exact nature of the dielectric model. We envision the model as an *open envelope*, where the flap represents an ether unit sticking out of plane. There are two motions anticipated with this conformation that are triggered at different temperatures. The lower temperature relaxation, or LTT, is caused by the motions of the flap only (the AOB plane in Figure 11). In the case of crown ethers, this flap is formed by each oxygen-containing unit with a dipole moment pointing in the direction opposite from other dipoles. The remaining part of the molecule, e.g., the ABCD plane in Figure 11, starts to relax (both calorimetrically and dielectrically) at a higher temperature in unison with the LTT. In the presence of solvent, the larger scale motion (HTT) at these temperatures becomes influenced by the neighboring OTP units, and the resulting glass transition temperature of the solute/solvent formulation starts to change systematically with solvent concentration (see Figures 5, 7, and 10). The location of this relaxation is shifted, accordingly, to higher temperatures followed by an increase in cooperativity.

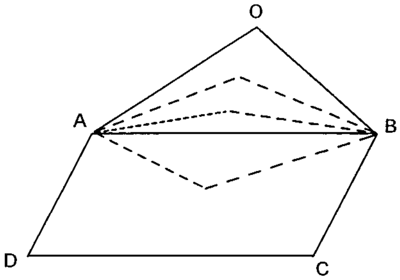

Figure 11. Schematic representation of the proposed “envelope” model that accounts for multiple relaxations in crown ethers and structurally similar saturated cyclic ethers.

Our final comment in this communication regards the potential dielectric (and/or calorimetric) analysis of crown ether where all dipole units point in the same direction. According to our concept, these compounds would have only one endothermic transition and hence one dielectric relaxation. An example of such hypothetical molecules showing its lowest energy conformation obtained by molecular simulation is given in Figure 9D. At this moment, however, we cannot comment on the plausibility of synthesizing this compound. Another interesting point would be to synthesize a polymer with crown ether units attached to a nonpolar backbone and investigate it by DRS.

Conclusion

We have analyzed a series of crown ethers and other related compound by DRS to explain the presence of two low-temperature transitions observed by calorimetric measurements. We found that these two processes correspond to two dielectric relaxations, both in neat and solvent-containing systems. More interestingly, however, dielectric data on different crown ether/OTP formulations suggest that these relaxations were affected by solvent molecules but in the opposite manner. The apparent activation energy of the higher temperature process (HTT) increases, while that of the other one (LTT) decreases with increasing solvent concentration. We rationalized this phenomenon by the opposite trend in cooperativity.

Supporting evidence obtained from the numerical conformational analysis and a careful examination of various related compounds that simulate molecular motions in crown ethers enabled us to propose a concept that would explained multiple relaxations in this generic group of materials. We envision the model as an *open envelope*, where the flap represents an ether unit sticking out of the molecular plane. Two motions, associated with this conformation are triggered at different temperatures and give rise to two separate relaxations seen by DSC and DRS.

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