Characterization of the Crystalline and Solution Phases in *N,N*′-Dimethylethylenediamine (DMEDA) with Sodium Triflate (NaCF₃SO₃)

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Linear poly(ethylenimine), [LPEI], is a synthetically versatile polymer host compared to poly(ethylene oxide), in that various groups can be attached to the backbone nitrogen atoms. The interactions of LPEI with sodium cations are modeled by solutions of *N,N*′-dimethylethylenediamine, DMEDA, containing dissolved sodium triflate [NaTf]. During these studies, the crystalline compound $(DMEDA)_2(NaTf)_5$ was discovered and characterized by X-ray diffraction, differential scanning calorimetry, Fourier transform infrared spectroscopy, and Raman spectroscopy. The compound crystallizes in polymeric chains in a triclinic unit cell of the P1 space group. In the crystal, the sodium ions are both five- and six-coordinate. A spectroscopic comparison of DMEDA, the $(DMEDA)_2(NaTf)_5$ crystal, and $(DMEDA)_xNaTf$ solutions over a composition range of 7.5:1 to 1.5:1 [DMEDA:NaTf, molar ratio] was conducted using infrared and Raman spectroscopy. In $(DMEDA)_2$-$(NaTf)_5$, the triflate ions vibrate as either $[Na_2Tf]^+$ or $[Na_3Tf]^{2+}$ species due to the coordination of the triflate ion by sodium ions. However, in solution, only the $[Na_2Tf]^+$ species is present at high NaTf compositions. At a 7.5:1 DMEDA/NaTf composition, contact ion pairs [NaTf] are the dominant species.

1. Introduction

The most widely studied polymer electrolyte is poly(ethylene oxide), PEO, complexed with various salts to form ionically conducting polymers.[1] Polymer-based electrolytes with lithium salts have attracted worldwide attention because of their applications in lithium rechargeable batteries.[2] The mechanism of ionic transport in these systems is not well understood, especially at the molecular level. Cation−anion interactions[3] and cation-polymer interactions[4] are believed to play a major role in the mechanism. The cation-polymer interactions[4] result in changes in the polymer backbone conformation,[5] whereas the cation−anion interactions[3] are associated with the formation of associated ionic species.[6] These local structures (ionically associated species and local backbone conformation) may be used to study the nature of those important interactions and provide essential insight needed to understand the mechanism of ionic transport.

Linear poly(ethylenimine), LPEI, is a highly crystalline polymer host that also has been studied as a polymer electrolyte since the mid 1980s.[7−11] However, LPEI-based polymer electrolytes exhibit poor conductivity due to the high crystallinity of LPEI. On the other hand, LPEI is a synthetically versatile polymer host compared to PEO, in that various groups can be attached to the backbone nitrogen atom. By adding various side chains (e.g., $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CN$) to LPEI, the crystallinity of the polymer host decreases, opening many possibilities for the preparation of new polymer electrolytes. However, a basic knowledge of LPEI is needed to better understand the behavior of the LPEI derivatives, therefore model compounds can be useful. Model compounds with vibrational modes similar to the analogous high molecular weight polymer have proved helpful in making vibrational assignments in the latter system, in part because the low molecular weight models

are amenable to computational studies.[12,13] Further, studies of ion-polymer coordinations in model compounds complexed with salts provide useful information about ion−polymer coordinations in the corresponding polymer−salt complex. This is especially true when a solved crystal structure of the model compound−salt complex is available. York et al. have previously reported work on *N,N*′-dimethylethylenediamine [(CH₃-NHCH₂)₂], DMEDA, with dissolved LiCF₃SO₃ (LiTf) as a model compound for LPEI complexed with LiTf.[12,14,15] DMEDA−NaTf systems have not been examined as a model for LPEI−NaTf systems. While studying solutions of DMEDA with NaTf, the formation of a crystalline compound was discovered. This paper describes the characterization of the crystalline and amorphous phases in DMEDA−NaTf systems using X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, and differential scanning calorimetry (DSC). Structural information obtained from the $(DMEDA)_2(NaTf)_5$ crystal provides a better understanding of the local environment of DMEDA and the triflate anion in $(DMEDA)_xNaTf$ solutions.

2. Experimental Section

2.1. Sample Preparation. DMEDA and NaTf were obtained from Aldrich. DMEDA was used as received. NaTf was heated under vacuum at 120 °C for 48 h. The chemicals were stored and used in a dry nitrogen glovebox (VAC, ≤1 ppm H₂O) at room temperature. To prepare the solutions, NaTf was dissolved into DMEDA at various concentrations and stirred for at least 4 h. The compositions of the solutions are reported as a DMEDA to NaTf molar ratio (DMEDA/NaTf). The $(DMEDA)_{1.5}NaTf$ solution contained both a viscous liquid and a gellike phase. This composition is equivalent to a 3:1 N/Na⁺ molar ratio. After about 6 months, a thin plate of crystals had formed at the liquid−air interface, with a viscous liquid still present underneath the crystals. The crystals were isolated and allowed to dry in a nitrogen atmosphere.

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2.2. X-ray. A single crystal suitable for X-ray diffraction measurements was isolated from a 1.5:1 solution composition of DMEDA/NaTf. X-ray data were collected at 173 (2) K on a Bruker P4 diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects; an absorption correction was not applied, as it was judged to be insignificant. The structure was solved by the direct method using the SHELXTL system and refined by full-matrix least squares on F^2 using all reflections. All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were included with idealized parameters. The final R1 = 0.053 is based on 5863 "observed reflections" [$I > 2\sigma(I)$], and wR^2 = 0.156 is based on all reflections (6999 unique data).

2.3. Differential Scanning Calorimetry. A single crystal weighing approximately 2 mg was sealed in a 40-μL aluminum pan. The DSC data were collected using a Mettler DSC 820 calorimeter with Star software (v.6.10) under dry nitrogen purge. Data were collected during two heating and cooling cycles between 0 and 280 °C at a heating and cooling rate of 5 °C/min.

2.4. IR & Raman Spectroscopy. For IR measurements, the DMEDA and (DMEDA)$_x$NaTf solutions were placed between zinc selenide windows in a sealed sample holder. Finely ground (DMEDA)$_2$(NaTf)$_5$ crystals were prepared as a KBr pellet and a Nujol mull. IR data were recorded on a Bruker IFS66V with a KBr beam splitter over a range of 500−4000 cm^{-1} (1 cm^{-1} resolution; 64 scans). The spectra of the solutions were measured under a dry air purge; the crystal data were collected under vacuum (8 mbar). For the Raman measurements, the DMEDA and (DMEDA)$_x$NaTf solutions were placed in a solution well and covered with a glass cover plate, while the single crystal was sealed into a quartz cuvette in the glovebox. Raman data were recorded with a Jobin−Yvon T64000 system in the triple subtractive mode with a CCD detector using the 532 nm line of a diode-pumped Nd/YVO$_4$ laser for excitation. All Raman data were collected in a 180° scattering geometry at a laser power of 200 mW measured at the laser head.

3. Results and Discussion

3.1. Crystal Structure. The (DMEDA)$_2$(NaTf)$_5$ crystals form a triclinic unit cell in the P$\bar{1}$ space group, with a (DMEDA)$_2$/(NaTf)$_5$ asymmetric unit in the cell as illustrated in Figure 1. However, there are six Na cation positions because the Na(5) and Na(6) ions are situated at the inversion center and each component has a fifty percent occupancy. The packing forms a polymeric chainlike network in the *a* direction. In this network, two of the Na ions coordinate to the DMEDA molecules, and the remaining Na ions form a cluster that does not coordinate with the DMEDA molecules (Figure 2). In the crystal, the sodium ions occupy either five- or six-coordinate sites. Here, coordination is defined as a sodium−oxygen (Na−O) or a sodium−nitrogen (Na−N) bond length of 2.80 Å or less which is based on typical bond lengths of crystal structures of dimethyl ethers of ethylene oxides or glymes (i.e., CH$_3$(OCH$_2$CH$_2$)$_n$OCH$_3$ with $n = 1-4$, complexed with NaTf).[16]

All sodium atoms coordinated to DMEDA molecules are six-coordinate. However, one of the these sodium atoms is coordinated to two nitrogen atoms and four triflate oxygen atoms; the other sodium atom is attached to four nitrogen atoms and only two triflate oxygen atoms. The remaining sodium atoms are coordinated only to the triflate oxygen atoms. Structural data of the (DMEDA)$_2$(NaTf)$_5$ crystal are summarized in Table 1; selected bond lengths and angles are listed in Tables 2 and 3.
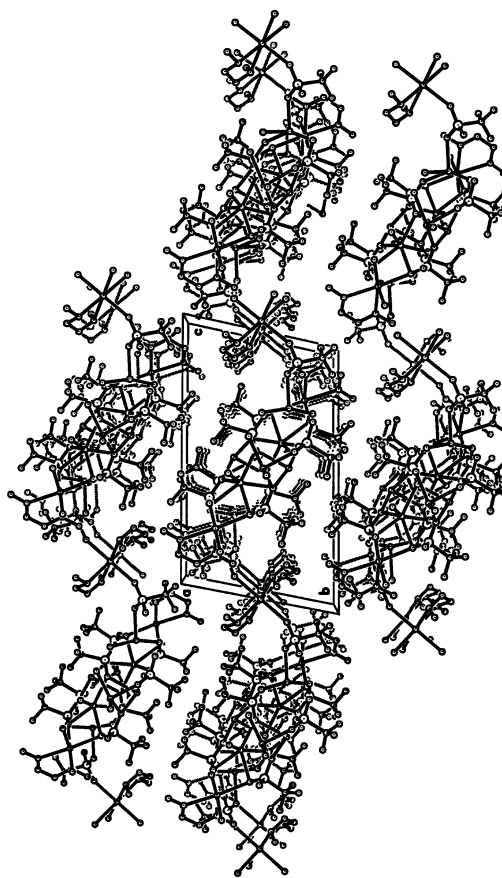

Figure 1. Packing diagram of the (DMEDA)$_2$(NaTf)$_5$ crystal. The crystals form polymeric chainlike structures that are stacked on top of each other.

The conformation of the DMEDA oligomers can be characterized in terms of the C−N−C−C and N−C−C−N dihedral angles (gauche, g, 60 ± 30°; gauche minus, $\bar{g}$, −60 ± 30°; skew, s, 120 ± 30° trans, t, ± 180 ± 30°). The N−C−C−N dihedral angle is of particular interest because it is most directly affected by the coordination of the cation to the nitrogen atoms. In the (DMEDA)$_2$(NaTf)$_5$ crystal (Table 2), the N−C−C−N dihedral angle of the DMEDA molecules is gauche (56.9°) and gauche minus (−34.5°), which results in $t\bar{g}t$ and sgt conformations.

3.2. Thermal Analysis. Differential scanning calorimetry (DSC) was used to characterize melting and recrystallization processes in the (DMEDA)$_2$(NaTf)$_5$ crystal. In the DSC thermogram (figure not shown), there are several small broad endothermic peaks before 200 °C and one sharp endothermic peak at 250 °C. The small broad peaks may be due to the loss of residual solvent and unresolved phase transitions. The sharp peak at 250 °C represents the melting of the crystalline compound. In the cooling cycle, the onset of recrystallization occurs at 249 °C. In a second thermal analysis cycle, the melting and recrystallization temperatures are consistent at 249 and 250 °C, respectively, indicating no thermal hysteresis.

3.3. Vibrational Spectroscopy. *3.3.1. Ionic Association in the Crystalline Phase.* The δ_s(CF$_3$) region contains distinct bands due to different ionically associated species. In poly(ethylene oxide)−NaTf systems, the ionically associated species and their Raman-active bands are "free" ions at 753 cm^{-1}, contact ion pairs [MTf] (M = cation) at 756 cm^{-1}, the aggregate (I) species at 761 cm^{-1}, and the aggregate (II) species at 769 cm^{-1}.[17] In linear poly(ethylenimine)−NaTf systems, the "free" ions, contact ion pairs, and the aggregate species occur at 754, 756−757,
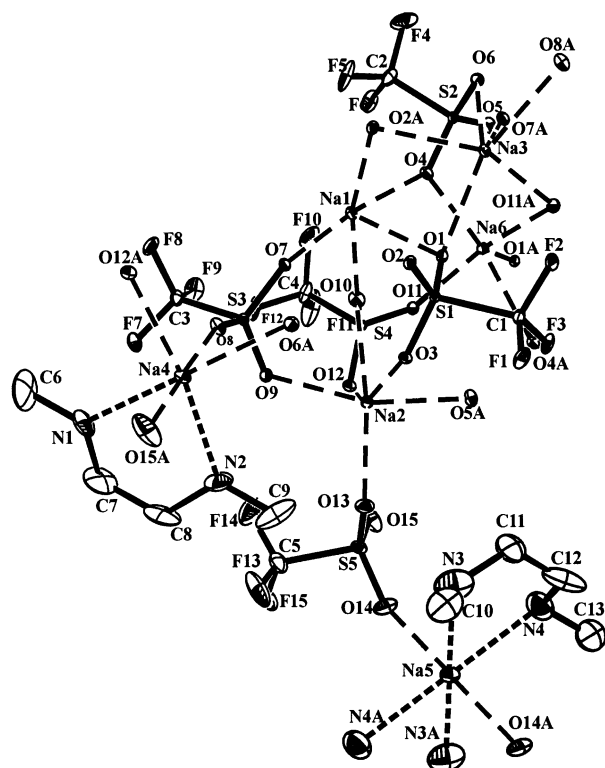
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Figure 2. A complex structure of the (DMEDA)$_2$(NaTf)$_5$ crystal. The structure does not include the hydrogen atoms. The Na−O bonds are represented as long dashes (− − −) and the Na−N bonds are represented as short dashes (- - -).

TABLE 1: Structural Data of the (DMEDA)$_2$(NaTf)$_5$ Crystal Obtained from X-ray Diffraction Study

crystal system	triclinic
space group	P$\bar{1}$
temp	173 (2) K
a (Å)	9.762 (2)
b (Å)	11.4111 (15)
c (Å)	18.989 (2)
α	99.664 (9)°
β	97.195 (12)°
γ	103.435 (13)°
volume (Å^3)	1998.2 (5)
Z	2
density (Mg/m^3)	1.723
R1	0.0530
crystal size (mm^3)	0.48 × 0.46 × 0.32

and 762 cm^{-1}, respectively.[18] For (DMEDA)$_x$LiTf solutions, York et al. have reported Raman frequencies of the ionic species occurring at 755 cm^{-1} ("free" ions), 758−760 cm^{-1} (contact ion pairs), and 763 cm^{-1} (aggregate species at).[19] Therefore, a spectral study of this region can provide information about the coordination of the triflate ion by the sodium ion(s). In the (DMEDA)$_2$(NaTf)$_5$ crystal, the δ_s(CF$_3$) bands occur at 761, 770, and 772 cm^{-1} in the IR spectra (Figure 3a) and at 762 and 772 cm^{-1} in the Raman spectra (Figure 3b). These bands will be discussed in detail later in this section.

The crystal structure reveals a complicated pattern for the coordination of the triflate oxygen atoms by the sodium ions, which is summarized in Table 3. Triflate ion number one, Tf-(1), is coordinated by two sodium ions and vibrates as an [Na$_2$-Tf]$^+$ species. Tf(2), Tf(3), and Tf(4) each appear to be coordinated by three sodium ions, although the relatively long O(1)−Na(1) bond distance (2.7499 Å) in Tf(2) might indicate that this triflate ion essentially vibrates as an [Na$_2$Tf]$^+$ species. However, Tf(3) and Tf(4) clearly vibrate as an [Na$_3$Tf]$^{2+}$

TABLE 2: Selected Bond Lengths (Å) and Angles (°) for (DMEDA)$_2$(NaTf)$_5$ Crystal

	Bond	
Na(4)−N	2.424 (3)	2.436 (4)
Na(5)−N	2.480 (4)	2.490 (4)^a
	2.480 (5)*	2.490 (4)
	Bond sequence	
N1−Na(4)−N2	74.63 (10)	
N3−Na(5)−N4	73.02 (12)	
	Dihedral angle	**Conformation**
C−N1−C−C	−171.7 (6)	t
N1−C−C−N2	−34.5 (8)	$\bar{g}$
C−C−N2−C	172.1 (6)	t
C−N3−C−C	105.8 (6)	s
N3−C−C−N4	56.9 (7)	g
C−C−N4−C	175.8 (6)	t

^{a} Symmetry transformation ($-x - 2, -y + 1, -z$) used to generate equivalent atoms.
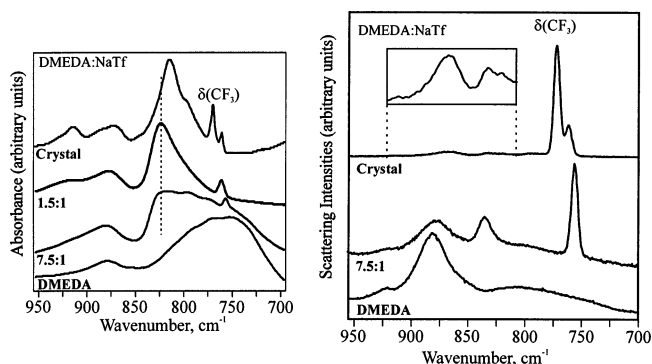

Figure 3. (a) IR spectra of DMEDA, (DMEDA)$_x$NaTf solutions ($x = 1.5$ & 7.5), and (DMEDA)$_2$(NaTf)$_5$ in the δ(CF$_3$) and conformation regions. The dashed line indicates the crystalline coordinative environment that is also found in solution. (b) Raman spectra of DMEDA, 7.5:1 DMEDA/NaTf solution, and (DMEDA)$_2$(NaTf)$_5$ in the δ(CF$_3$) and conformation regions.

TABLE 3: The Sodium−Oxygen Bond Lengths (Å) of the Five Symmetrically Inequivalent Triflate Anions (Tf) in the Asymmetric Unit

	bond	bond length
Tf(1)	O(13)−Na(2)	2.329 (3)
	O(14)−Na(5)	2.427 (3)
Tf(2)	O(3)−Na(2)	2.3297 (18)
	O(1)−Na(3)	2.4050 (18)
	O(1)−Na(1)	2.7499 (19)
Tf(3)	O(7)−Na(1)	2.2587 (19)
	O(9)−Na(2)	2.379 (2)
	O(8)−Na(4)	2.394 (2)
Tf(4)	O(4)−Na(6)	2.316 (3)
	O(4)−Na(1)	2.344 (18)
	O(6)−Na(3)	2.445 (2)
Tf(5)	O(10)−Na(1)	2.307 (2)
	O(11)−Na(6)	2.350 (3)
	O(10)−Na(1)	2.682 (3)
	O(12)−Na(2)	2.785 (2)

species. Tf(5) is coordinated by two sodium ions with a relatively short Na−O distance and two sodium ions with a relatively long Na−O bond distance; it essentially vibrates as an [Na$_2$Tf]$^+$ species. The bands at 770 cm^{-1} (IR) and 772 cm^{-1} (Raman) are assigned to the [Na$_3$Tf]$^{2+}$ species, while the bands at 761 (IR) and 762 (Raman) cm^{-1} are attributed to the [Na$_2$-Tf]$^+$ species. These ionic species along with these correlated frequencies will be discussed later using factor group analysis.

The frequency of the SO$_3$ symmetric stretch, ν_s(SO$_3$), is also affected by the coordination of the triflate ion with the cation. The Raman-active bands at 1032, 1037, and 1050−1058 cm^{-1}
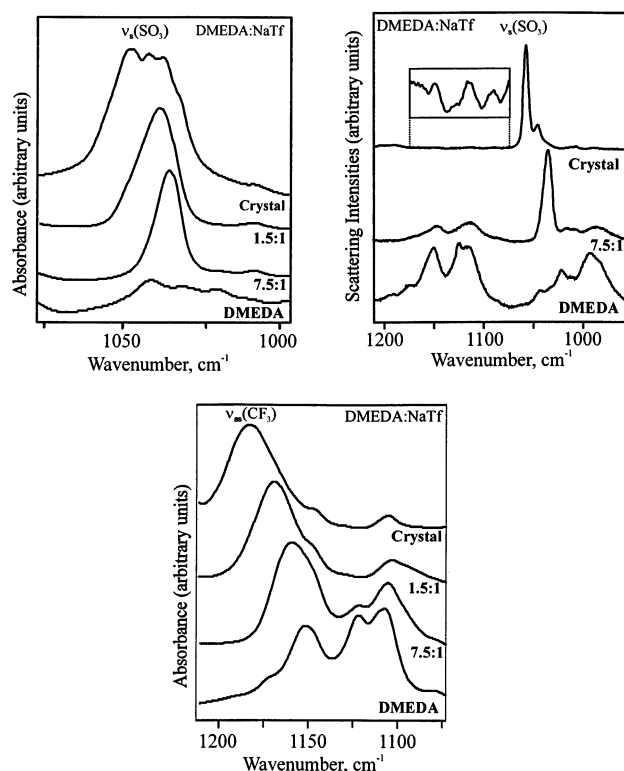
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Figure 4. (a) IR spectra of DMEDA, (DMEDA)$_x$NaTf solutions (x = 1.5 and 7.5), and (DMEDA)$_2$(NaTf)$_5$ in the 1000−1075 cm^{-1} region. This region includes the ν_s(SO$_3$) mode. (b) Raman spectra of DMEDA, 7.5:1 DMEDA/NaTf solution, and (DMEDA)$_2$(NaTf)$_5$ in the 1000−1200 cm^{-1} region. This region includes only the ν_s(SO$_3$) mode. (c) IR spectra of DMEDA, (DMEDA)$_x$NaTf solutions (x = 1.5 and 7.5), and (DMEDA)$_2$(NaTf)$_5$ in the 1075−1200 cm^{-1} region. This region includes the ν_{as}(CF$_3$) mode.

correspond to "free" ions, contact ion pairs, and aggregate species in poly(ethylene oxide)-NaTf systems.[17,20] Similar assignments are made for the IR-active bands. For the (DMEDA)$_x$-LiTf solutions, York et al. have reported the triflate species to be composed of "free" ions at 1032−1033 cm^{-1}, contact ion pairs at 1038−1044 cm^{-1}, and aggregate species at 1050−1054 cm^{-1} based on Raman measurements.[19] In the (DMEDA)$_2$-(NaTf)$_5$ crystal, the ν_s(SO$_3$) region in IR contains bands at 1047, 1042, 1037, and ∼1033 cm^{-1}, as illustrated in Figure 4a. In the Raman spectrum of the ν_s(SO$_3$) region (Figure 4b), there is a strong band at 1057 cm^{-1} and a weak band at 1045 cm^{-1} associated with the ν_s(SO$_3$) mode.

The intramolecular vibrations of the triflate ion in a unit cell are correlated through intermolecular forces, yielding a vibrational multiplet structure that can be described by a symmetry-based analysis.[21] The resulting normal modes belong to the various irreducible representations of the unit cell group (factor group). For modes originating in the A$_1$ vibration of an isolated triflate ion, a factor group analysis predicts five Raman active A$_g$ modes and five IR active A$_u$ modes for both the symmetric SO$_3$ stretching modes and the symmetric CF$_3$ deformation modes

$$\Gamma(\nu_s(SO_3)) = \Gamma(\delta_s(CF_3)) = 5A_g + 5A_u$$

The observation of four IR active modes (1033, 1037, 1042, and 1047 cm^{-1}) and two Raman active modes (1045 and 1057 cm^{-1}) in the ν_s(SO$_3$) region, none of which are coincident in frequency, indicates that the vibrations of the triflate ions in the unit cell are indeed correlated through the center of inversion.

The case of the δ_s(CF$_3$) modes presents a very different situation. Here, there are three IR-active modes (761, 770,

and 772 cm^{-1}), two of which are coincident with the two Raman-active modes (762 and 772 cm^{-1}). This coincidence argues that the modes are not correlated through the inversion. The IR data show that the intensities of the δ_s(CF$_3$) modes are very weak compared with the strong, sharp ν_s(SO$_3$) absorptions.

Vibrationally induced dipoles are the major contribution to the intermolecular forces that couple the vibrations of the triflate ions in the unit cell. Therefore, it is not surprising that the vibrations of modes originating in ν_s(SO$_3$) are highly correlated, whereas the modes originating in δ_s(CF$_3$) show little or no correlation. The existence of three δ_s(CF$_3$) bands in the IR is due to the different potential energy environments of the triflate ions in an asymmetric unit (see Table 3). In other words, the δ_s(CF$_3$) vibrations of the two asymmetric units are the same, because the vibrations of the triflate ions in one unit are more or less independent of the vibrations of its symmetrically equivalent partner in the cell. An asymmetric unit has trivial C$_1$ symmetry; therefore, the symmetry species of the triflate ion δ_s(CF$_3$) vibrations may be written as

$$\Gamma(\delta_s(CF_3)) = 5A$$

The combined infrared and Raman data show three distinct bands, two of which occur in a frequency range usually attributed to a [Na$_3$Tf]$^{2+}$ species and the other band to a [Na$_2$Tf]$^{+}$ species.[16] An examination of Table 3 shows that the triflate ions Tf(1), Tf(2), and Tf(5) each have two Na−O distances in the range 2.30−2.43 Å, with the remaining Na−O distances greater than 2.74 Å. (Tf(5) is the exception to this generalization, with an additional Na−O distance = 2.682 Å). To a first approximation, if the perturbation of the triflate ion by sodium ion at a Na−O distance greater than 2.43 Å is negligible, those three triflate ions each vibrate independently as [Na$_2$Tf]$^{+}$ species with essentially the same frequency.

Tf(3) and Tf(4) each have three Na−O distances less than 2.45 Å. These two ions vibrate as [Na$_3$Tf]$^{2+}$ species, although the perturbation of the two triflate ions differs sufficiently so that two [Na$_3$Tf]$^{2+}$ bands can be distinguished with a separation of 2 cm^{-1}.

3.3.2. Ionic Association in the Solution Phase. In the spectra of the 7.5:1 DMEDA/NaTf solution (Figures 3a,b), the δ(CF$_3$) band occurs at 757 (IR) and 756 cm^{-1} (Raman), a frequency range that is assigned to contact ion pairs. In the 1.5:1 DMEDA/NaTf solution, there are contact ion pairs (∼757 cm^{-1}) and the [Na$_2$Tf]$^{+}$ aggregate species (761 cm^{-1}) present.

In the (DMEDA)$_x$NaTf solutions, the ν_s(SO$_3$) band (IR) is centered at 1035 cm^{-1} in the 7.5:1 solution and 1038 cm^{-1} in the 1.5:1 solution (Figure 4a), which correspond to contact ion pairs. However, this band in the 1.5:1 DMEDA/NaTf solution appears to have two weak shoulders at ∼1035 and ∼1042 cm^{-1}. This latter band probably corresponds to the [Na$_2$Tf]$^{+}$ species. Therefore, there are ionically associated species present in the solutions that appear to be similar to certain associated species found in the crystal.

3.3.3. Comparison of the Cation-DMEDA Interactions in Crystalline and Solution Phases. The frequencies and intensities of bands from 800 to 1000 cm^{-1} are sensitive to conformational changes that result from the coordination of the cation by the nitrogen atom in DMEDA.[19] Similar conformational studies have been reported in salt complexes of ethylene oxide-based systems.[5,17,22−26]

Because the bands in this spectral region of the crystal are relatively weak, they are shown in the inset of Figure 3b. Particularly noteworthy is the new band that appears at 831 cm^{-1} in the crystal, and the shift in the broad DMEDA band at 881−
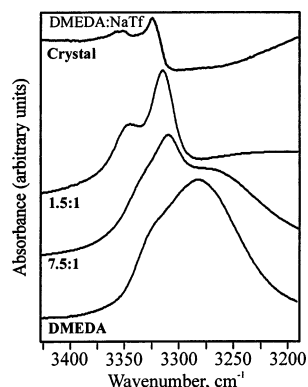
Figure 5. IR spectra of DMEDA, (DMEDA)$_x$NaTf solutions ($x = 1.5$ and 7.5), and (DMEDA)$_2$(NaTf)$_5$ in the NH stretching region.

868 cm^{-1}. In the 7.5:1 solution spectrum, the new band is at 836 cm^{-1}, and the broad band is centered at ~878 cm^{-1}, which is intermediate between its values in pure DMEDA and in the crystal. This vibrational pattern is the spectroscopic signature of the $t\bar{g}t$ and sgt conformational sequences seen in the crystal and probably reflects the $\bar{g}$ and g N−C−C−N dihedral angles. The fact that this vibrational pattern appears in the 7.5:1 solution argues that the sodium ions interact with the DMEDA molecules to produce a conformation that bears a significant resemblance to the conformation found in the crystal.

In the 1000−1200 cm^{-1} region, there are several spectral differences in the (DMEDA)$_2$(NaTf)$_5$ crystal and (DMEDA)$_x$-NaTf solution data (Figure 4). Modes in this region consist of a mixture of C−C and C−N stretching, CH$_2$ rocking and twisting, CH$_3$ asymmetric deformation, and N−H parallel bending motions with a significant amount of C−N stretching.[14] The IR band at 1107 cm^{-1} in DMEDA (Figure 4c) decreases in intensity and shifts to a slightly lower frequency upon crystallization. In addition, the intensity of the DMEDA band at 1122 cm^{-1} diminishes with increasing NaTf composition. In the Raman spectra (Figure 4b), the bands at 1125 and 1150 cm^{-1} in DMEDA shift to 1114 and 1140 cm^{-1} when NaTf is added. This is due to the sodium ions coordinating the nitrogen atoms, which delocalizes the electron densities in the C−N bonds, thus lowering these band frequencies. We note in passing that the band associated with the CF$_3$ asymmetric stretching motion in the 7.5:1 sample (1160 cm^{-1}) shifts to a higher frequency (1182 cm^{-1}) upon crystallization.

The IR spectra of the NH stretching region shown in Figure 5 are especially interesting. There is a large broad feature in DMEDA centered at 3282 cm^{-1} with a shoulder at 3330 cm^{-1}. Upon addition of NaTf to bring the solution to a 7.5:1 composition, the shoulder shifts to ~3335 cm^{-1}, and a new band at 3310 cm^{-1} rises out of a very broad feature. In the 1.5:1 solution, this new band is more intense and shifts to 3315 cm^{-1}, while the shoulder shifts to 3344 cm^{-1} and becomes more prominent. Upon crystallization, these two bands shift to 3324 and 3352 cm^{-1}, respectively. These shifts in band frequencies in the NH region are due to the formation of intermolecular hydrogen bonding in the crystal and the loss of intramolecular hydrogen bonding based on computational analysis.[19]

4. Conclusions

Single crystals of (DMEDA)$_2$(NaTf)$_5$ have been isolated and characterized using X-ray diffraction, DSC, IR, and Raman techniques. The complex structure of the crystal, in particular

the formation of polymeric chains, reflects the hydrogen bonding interactions of the DMEDA NH group. By contrast, these interactions are nonexistent in the crystal structure of the related *N,N,N′,N′*-tetramethylethylenediamine/NaTf compound, (TMED-A)NaTf, whose unit cells contain discrete tetrameric units.

The coordination of the triflate ion by sodium ion consists primarily of contact ion pairs in the 7.5:1 composition. In the 1.5:1 solution, spectra of the triflate ion in the $\nu_s(SO_3)$ region suggest the presence of more highly coordinated [Na$_2$Tf]$^+$ species such as are found in the crystal. However, there is no evidence for the presence of an [Na$_3$Tf]$^{2+}$ species in solution.

The similarity of the vibrational mode frequencies and intensities in the spectral region sensitive to the conformation of the DMEDA molecule argues that the conformation of DMEDA in the more concentrated salt solutions is similar to that in the crystal. This conclusion is supported by the comparison of modes in the 1100−1200 cm^{-1} range.

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