Raman Spectroscopic Study on the Conformation of 1,2-Dimethoxyethane in the Liquid Phase and in Aqueous Solutions

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The conformation of 1,2-dimethoxyethane in the liquid phase and in aqueous solutions was studied by Raman spectroscopy. The conformation-sensitive Raman bands of 1,2-dimethoxyethane, located in the wavenumber region 300−600 cm^{-1}, were analyzed by means of the band decomposition based on normal coordinate analysis. The populations of the conformers of 1,2-dimethoxyethane, their relative energies, and their relative entropies in the liquid phase were estimated and compared with the relevant data for the gas phase of 1,2-dimethoxyethane. The condensed phase effects on the conformation of 1,2-dimethoxyethane were discussed on the basis of the experimental data. The populations of the conformers at 318 K in aqueous solutions with different concentrations were estimated. It was revealed that the populations of the TTT and TGG′ conformers of 1,2-dimethoxyethane decrease on increasing concentration of water, while the populations of the TGT and TGG conformers increase. The entropies of the less hydrophilic TTT and TGG′ conformers are higher than the entropies of the more hydrophilic TGT and TGG conformers. This experimental observation suggests that the inverse temperature solubility of poly(oxyethylene) in water originates from the conformational changes of the polymer chain.

Introduction

Vibrational spectroscopic studies on small model molecules can help us to understand the conformation of polymers. 1,2-Dimethoxyethane is a basic model compound of poly(oxyethylene). Despite its structural simplicity, the 1,2-dimethoxyethane molecule retains the most specific conformational features of the poly(oxyethylene) chain, which are the gauche preference around the C−C bond and the trans preference around the C−O bond. Therefore, the conformation of 1,2-dimethoxyethane has been extensively studied in all phases and in different solvents to elucidate the conformational behavior of the poly(oxyethylene) chain. Vibrational spectroscopy[1−16] and NMR spectroscopy[17−24] have been the main experimental methods in these studies.

By means of vibrational spectroscopy it has been established that 1,2-dimethoxyethane exists as a mixture of several principal conformers in the gas phase,[5,7,11,12] in the liquid phase,[1−3,5,6,8] and in various solvents.[6,8−10,14−16] These principal conformers are the TGT, TGG, TTT, TGG′, and TTG conformers, where T and G denote trans and gauche, respectively. The IR spectroscopic studies[11,13] have shown that the TTT conformer is the lowest-energy conformer in the gas phase followed by the TGT and TGG′ conformers. Substantial condensed phase effects on the conformation of 1,2-dimethoxyethane have been noticed on going from the gas phase to the liquid phase.[5] It has also been found that the TGT conformer is the lowest-energy conformer in the liquid phase[5] instead of the TTT conformer, and it solely constitutes the crystalline phase of 1,2-dimethoxyethane.[2,4,5] The TTG conformer has been shown to be the highest-energy conformer among those experimentally identified in the liquid phase.[5] However, a controversy still exists concerning the relative energies and stability of the TGG, TTT, and TGG′ conformers in the liquid state.

It is well-known that the gauche preference of the C−C bond is enhanced at low temperatures[5,17−24] and in hydrogen bonding or polar solvents,[6,8−10,14−22,24] while the C−O bond has an opposite conformational preference.[8,15,16,21,23,24] An interesting correlation between the conformations of the C−C bond and the C−O bond has been revealed throughout the experiments;[15,16,21,23,24] when the population of gauche C−C bonds increases the population of gauche C−O bonds decreases and vice versa. The same conformational trends have been observed for longer poly(oxyethylene) chains[6,9,10,14−19,21,24,25] and poly(oxyethylene)-containing compounds.[26] These experimental findings substantiate the choice of 1,2-dimethoxyethane as a model compound of poly(oxyethylene).

Great efforts have been directed at developing theoretical models that can explain the conformational preference of the 1,2-dimethoxyethane molecule as a function of its environment.[27−42] It has been demonstrated that the ab initio calculations are indispensable for modeling the gas-phase behavior of 1,2-dimethoxyethane, being capable of reproducing various experimental results.[31,32] The ab initio calculations cannot, however, be extended to the condensed phases because of practical computational limits. The alternative is to apply simplified models that treat the condensed phase environment as a continuum dielectric medium[27,28,34] or to perform Monte Carlo[28,30,38,39] and molecular dynamics simulations[35,36,41,42] by means of atomistic force fields. Smith and co-workers have undertaken systematic development of specific force fields for the interactions in the 1,2-dimethoxyethane molecule[33,40] and for the interactions between 1,2-dimethoxyethane and water[41]

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on the basis of high-level ab initio molecular calculations.[32,41] They have aimed at establishing a relatively simple and computationally inexpensive model, which can predict the properties of poly(oxyethylene) in aqueous solution and, in particular, the inverse temperature solubility of this polymer. The force fields have been used for molecular dynamics simulations of neat 1,2-dimethoxyethane[36] and aqueous solutions of 1,2-dimethoxyethane.[41,42] An excellent agreement has been achieved between the simulated and the measured microscopic properties of aqueous solutions of 1,2-dimethoxyethane.[41,42] Smith and co-workers have also reported[36,41,42] a good qualitative agreement with the Raman and IR spectroscopic data on the conformation of 1,2-dimethoxyethane in the liquid phase and in aqueous solutions. They have not, however, been able to verify the calculated populations of conformers, as relevant experimental data have not been available. The distribution of conformers is sensitive to small variations of the parameters of the force fields, which are adjusted to reproduce ab initio conformer energies and geometries that are subjects of possible errors. Therefore, new experimental data on the conformer populations in the liquid phase and in aqueous solutions of 1,2-dimethoxyethane may help to improve the force fields for molecular dynamics simulations.[33,40,41] That is why we have decided to reinvestigate the Raman spectra of 1,2-dimethoxyethane in the liquid phase and in aqueous solutions on a quantitative basis and to estimate the populations of the conformers, their relative energies, and their relative entropies. We hope that our studies can support the theoretical efforts to develop a reliable model of the poly(oxyethylene)−water system.

Experimental Section

1,2-Dimethoxyethane of analytical grade (Katayama Chemical Industries Co., Osaka) was studied. Doubly distilled deionized water was used to prepare the aqueous solutions. The solutions were prepared by weight and were hermetically sealed in glass ampules for the Raman spectroscopic experiments. The Raman spectra were recorded on a JASCO NR-1800 Raman spectrometer equipped with a Princeton Instruments CCD detector. An NEC argon ion laser GLG 2162 operating at 514 nm was used for excitation. The spectral resolution was 1 cm^{-1} in all experiments. The Raman spectra of the neat 1,2-dimethoxyethane sample were measured at 15 temperatures in the range 180−320 K. The Raman spectra of the aqueous solutions were measured at 318 K, which is the temperature of the molecular dynamics simulations. The temperature of the samples was held constant within 0.1 K during each measurement by an Oxford Instruments Optistat cryostat. The experimental spectra were corrected for wavelength variations in spectrometer sensitivity. The fluorescence emission spectrum of coumarin 540a laser dye dissolved in methanol was used as a secondary intensity standard.[43]

Results

Spectral Analysis. The vibrations of a 1,2-dimethoxyethane molecule have been thoroughly studied by normal coordinate analysis at various theoretical levels, and the observed Raman bands have been assigned to normal vibrations of different conformers.[5−8,12] Some of the Raman bands have been subsequently utilized as experimental conformational probes.[5,6,8,10,14] From a practical point of view, the high-wavenumber Raman bands are preferable as the probes, as they have relatively high intensities, which greatly facilitate the experimental studies. The normal coordinate analysis[12] has shown that, in the wavenumber region above 800 cm^{-1}, the Raman bands of some of the conformers of 1,2-dimethoxyethane are heavily overlapped and are practically indistinguishable. Accordingly, the high-wavenumber conformational probes actually reflect the populations of the average conformations of the C−C and C−O bonds rather than the populations of the individual conformers. The normal coordinate analysis of 1,2-dimethoxyethane[12] has also suggested that information on the individual conformer populations can be obtained from the Raman spectra in the wavenumber region below 600 cm^{-1}, where the characteristic normal vibrations of the different conformers are relatively well separated. Therefore, our study was intentionally focused on this wavenumber region. Examples of the Raman spectra of neat 1,2-dimethoxyethane and aqueous solutions of 1,2-dimethoxyethane in the wavenumber region 300−600 cm^{-1} are shown in Figures 1 and 2.

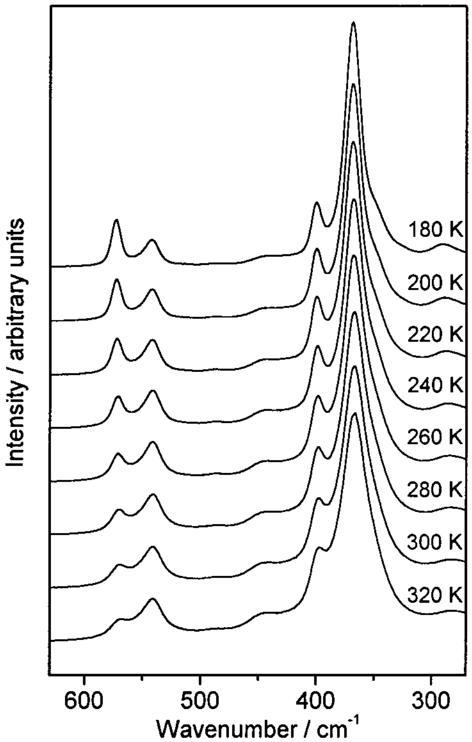

Figure 1. Examples of the Raman spectra of neat 1,2-dimethoxyethane. The temperature of the measurement is marked above each spectrum.

The characteristic normal vibrations of different conformers may have quite different Raman activities. Thus, the appearance of strong bands in the experimental spectra does not necessarily mean that the respective conformers are highly populated. Therefore, the knowledge of the Raman activities is crucial if we want to estimate the conformer populations. Fortunately, the calculation of Raman activities has recently become available to the experimentalists as a common part of the standard programs for molecular calculations. In this work, we use the Raman activities calculated by the GAUSSIAN 98 suite of programs[44] at the MPW1PW91/6-311+G** level of density functional theory. The calculations with GAUSSIAN 98 also provide the wavenumbers of the normal vibrations, which are in excellent agreement with the experimental ones, as can be seen in Table 1.

The Raman spectra of neat 1,2-dimethoxyethane and aqueous solutions of 1,2-dimethoxyethane were decomposed into Lorentzian bands by the GRAMS/32 program (Galactic Industries Corp., Salem, NH). An example of the band decomposition is given in Figure 3. The area, A, of the characteristic Raman band

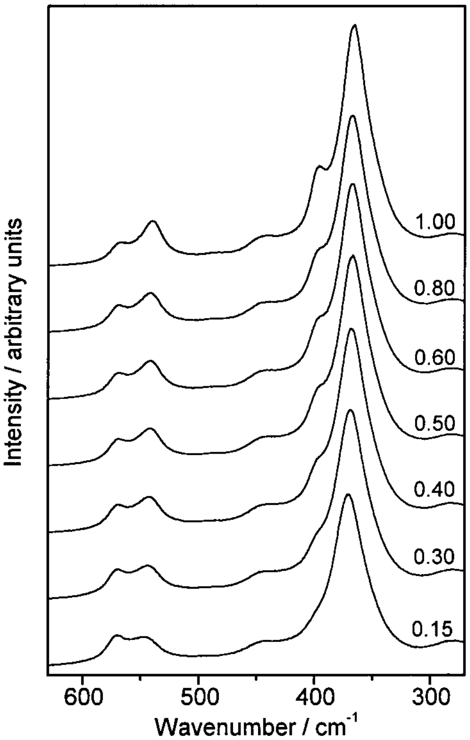

Figure 2. Examples of the Raman spectra of 1,2-dimethoxyethane in aqueous solutions. The mole fraction of 1,2-dimethoxyethane is marked above each spectrum.

of each conformer was transformed into the number of molecules, N, in this conformation by using a relation:[45]

$$N = \frac{A}{s} \cdot \frac{\nu\left(1 - \exp\left(-\frac{h\nu}{kT}\right)\right)}{(\nu_0 - \nu)^4} \tag{1}$$

where ν is the frequency of the molecular vibration, s is the Raman activity of the molecular vibration, ν_0 is the frequency of the exciting laser light, h is the Planck constant, k is the Boltzmann constant, and T is the absolute temperature. The calculated number of molecules, N, is proportional to the population of the conformer, n, defined as the number of 1,2-dimethoxyethane molecules in this conformation divided by the total number of 1,2-dimethoxyethane molecules:

$$N = \alpha n \tag{2}$$

where α is a coefficient that depends on the experimental conditions. The coefficient α in eq 2 has the same value for all Raman bands in a single measurement. Therefore, $n_{\mathrm{XXX}}/n_{\mathrm{YYY}} = N_{\mathrm{XXX}}/N_{\mathrm{YYY}}$ for any two conformers XXX and YYY (X and Y stand for T, G, or G′). To calculate the population of each conformer, we should know the total population of 1,2-dimethoxyethane molecules that take part in the Raman scattering process and contribute to the measured spectra. In general, all possible conformers of 1,2-dimethoxyethane might be present in the liquid phase, but only some of them have appreciable populations and can be experimentally detected.[5,12] These conformers are the TGT, TGG, TTT, TGG′, and TTG conformers. It is worth mentioning that they are the most populated conformers in the liquid phase according to the molecular dynamics simulations.[36] It is therefore reasonable to assume that the total number of 1,2-dimethoxyethane molecules is equal to the sum of the numbers of molecules in the TGT, TGG, TTT, TGG′, and TTG conformations. The population of 1,2-dimethoxyethane molecules in particular conformation can then be obtained by dividing the number of molecules in this conformation by the sum of the numbers of molecules in the five principal conformations.

Conformer Energies and Entropies. To interpret the conformational transformations of 1,2-dimethoxyethane molecules in the liquid phase on changing temperature, it is helpful to know the thermodynamical parameters that characterize the distribution of conformers. Let us assume that the equilibrium conformer populations follow a simple Boltzmann distribution:

$$\frac{n_{\mathrm{XXX}}}{n_{\mathrm{TTT}}} = \exp\left(\frac{S_{\mathrm{XXX}}}{R}\right) \exp\left(-\frac{E_{\mathrm{XXX}}}{RT}\right) \tag{3}$$

where n_{XXX} is the population of the XXX conformer (X stands for T, G, or G’), n_{TTT} is the population of the TTT conformer, S_{XXX} is the entropy of the XXX conformer, E_{XXX} is the energy of the XXX conformer, R is the gas constant, and T is the absolute temperature. The TTT conformer is chosen here as a reference conformer. Thus, $E_{\mathrm{TTT}} = 0$ and $S_{\mathrm{TTT}} = 0$. By taking a logarithm of both sides of eq 3, we get

$$\ln\frac{n_{\mathrm{XXX}}}{n_{\mathrm{TTT}}} = \frac{S_{\mathrm{XXX}}}{R} - \frac{E_{\mathrm{XXX}}}{RT} \tag{4}$$

The logarithms of the ratios of the conformer populations, $\ln(n_{\mathrm{XXX}}/n_{\mathrm{TTT}})$, are plotted as a function of the reciprocal temperature $10^3\ T^{-1}$ in Figure 4. The conformer energies and entropies were determined by fitting each set of the data points plotted in Figure 4 with a linear function. The obtained numerical values are given in Table 1. In agreement with the previous qualitative estimates,[5] the TGT conformer is the lowest-energy conformer and the TTG conformer is the highest-energy conformer in the liquid phase. The energy of the TGG conformer is next to the energy of the TGT conformer followed by the energies of the TTT and TGG′ conformers.

It is seen from Figure 4 that the TGT conformer is the most populated conformer at low temperatures. On increasing temperature, however, the populations of the other conformers gradually increase. Among them the TGG′ conformer is most rapidly populated. An extrapolation of the experimental data along the linear fits given in Figure 4 suggests that the TGG′ conformer becomes the dominant conformer in the liquid phase at high temperatures. To our knowledge, the high stability of the TGG′ conformer in the liquid phase has been neither experimentally discovered nor theoretically predicted so far. As we discuss later, the stability of this conformational form might be a key factor of the aqueous solution behavior of 1,2-dimethoxyethane and poly(oxyethylene).

Discussion

Factors of the Conformational Stability. It is anticipated that the polar conformational forms are stabilized in the condensed phases due to their electrostatic dipole interaction with the surrounding “continuum” dielectric medium.[46] The stabilization should be larger for conformers with larger dipole moments. This concept plays a central role in one of the theoretical models explaining the inverse temperature solubility of poly(oxyethylene) in water.[47] It is worthwhile therefore to examine how it works for neat 1,2-dimethoxyethane, which has a moderate dielectric constant ($\epsilon = 7.3$). According to the continuum dielectric theory of solvation, the energy of the

TABLE 1: Wavenumbers and Raman Activities of Characteristic Vibrational Modes, Relative Entropies Calculated from the Multiplicity (S), Relative Entropies (S_{Liq}) and Energies (E_{Liq}) in the Liquid Phase, and Relative Energies (E_{Gas}) and Dipole Moments in the Gas Phase of the Conformers of 1,2-Dimethoxyethane

conformer (multiplicity)	exptl wavenumber cm^{-1}	calcd wavenumber[a] cm^{-1}	Raman activity $\mathrm{Å}^4\ \mathrm{amu}^{-1}$	S[b] $\mathrm{kJ\ mol}^{-1}$	S_{Liq}[c] $\mathrm{kJ\ mol}^{-1}$	E_{Liq}[c] $\mathrm{kJ\ mol}^{-1}$	E_{Gas} $\mathrm{kJ\ mol}^{-1}$	dipole moment[a] D
TGT (2)	572	573	0.46	5.8	−3.2 (0.8)	−4.1 (0.2)	0.7[d]	1.5
TGG (4)	553	554	1.18	11.5	−7 (2)	−1.3 (0.5)	8.0[a]	2.6
TTT (1)	399	401	3.46	0.0	0.0	0.0	0.0	0.0
TGG′ (4)	541	541	1.44	11.5	12.6 (0.8)	1.2 (0.2)	1.3[e]	1.7
TTG (4)	488	481	1.58	11.5	2 (3)	3.3 (0.5)	6.7[a]	1.8

[a] Calculated at the MPW1PW91/6-311+G** level of density functional theory. [b] $S = R \ln(m)$, where m is the conformer multiplicity. [c] Estimates of the upper limits of the errors in the calculated values of entropies and energies are given in parentheses. [d] Measured by matrix-isolation IR spectroscopy.[13] [e] Measured by IR spectroscopy in the gas phase.[11]

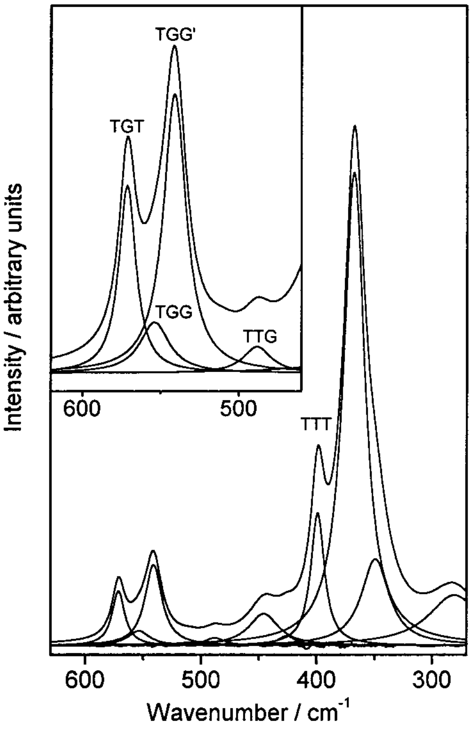

Figure 3. Example of band decomposition of the Raman spectrum of 1,2-dimethoxyethane in the wavenumber region 270−630 cm^{-1}.

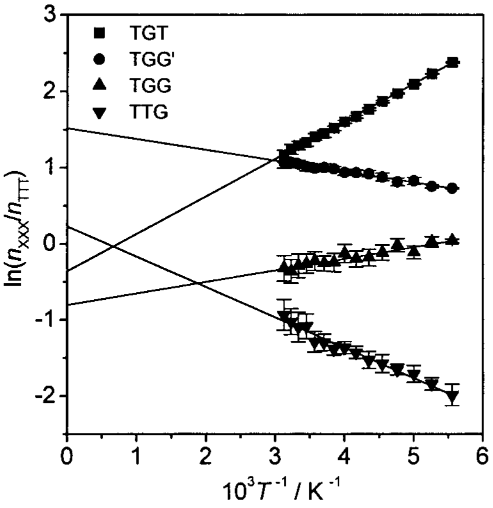

Figure 4. Dependencies of the logarithms of the ratios of the populations of the conformers of 1,2-dimethoxyethane, $\ln(n_{\mathrm{XXX}}/n_{\mathrm{TTT}})$, in the liquid phase on the reciprocal temperature 10^3T^{-1}. The solid lines are the least-squares fits of the experimental data points by linear functions.

nonpolar TTT conformer should not change on going from the gas phase to the liquid phase. Hence it is convenient to discuss the energies of the conformers with respect to the energy of the TTT conformer and in what follows "conformer energy" always has this meaning unless something else is explicitly stated. The relative energies of the TGT, TTT, and TGG′ conformers in the gas phase have been experimentally determined.[11,13] The energies of the TGG and TTG conformers in the gas phase with respect to the energy of the other conformers have not been measured, but our ab initio calculations have shown that they are 8.0 and 6.7 kJ mol^{-1} higher than the energy of the TTT conformer (Table 1). These values are in agreement with the results of the previous calculations.[31,32] It is possible therefore to compare our experimental results for the relative conformer energies in the liquid phase with the relevant data for the gas phase of 1,2-dimethoxyethane. Such comparison confirms that the conformers with larger dipole moments are generally more stable in the liquid phase. The effect is most prominent for the TGG conformer with a dipole moment 2.6 D, whose energy with respect to the energy of the TTT conformer decreases by 9.3 kJ mol^{-1} on going from the gas phase to the liquid phase. The energy of the less polar TGT conformer with a dipole moment 1.5 D decreases by 4.8 kJ mol^{-1} and the energy of the TTG conformer with a dipole moment 1.8 D decreases by 3.4 kJ mol^{-1} in the liquid phase. However, the difference between the energies of the TGG′ conformer and the TTT conformer in the liquid phase, 1.2 kJ mol^{-1}, is nearly the same as in the gas phase. This is an apparent anomaly, as the dipole moment of the TGG′ conformer (1.7 D) is larger than the dipole moment of the TGT conformer (1.5 D) and is close to the dipole moment of the TTG conformer (1.8 D). This anomaly indicates that probably the higher multipole moments of 1,2-dimethoxyethane, which are seldom taken into account,[27] may also influence the stability of the conformers.

The thermodynamical stability of the conformers depends not only on their relative energies but also on their relative entropies. The TTT, TGT, and TGG′ conformers have very similar energies in the gas phase. Nevertheless, the TGG′ conformer is the most stable in the gas phase at ambient temperatures, as its multiplicity (4) is twice larger than the multiplicity of the TGT conformer (2) and four times larger than the multiplicity of the TTT conformer (1). The higher multiplicity implies higher entropy, lower Gibbs free energy, and higher thermodynamical stability of the respective conformer. It has been pointed out[24] that the conformational entropies in the liquid phase probably differ from the entropies, S, that can be calculated on the basis of the conformer multiplicities, m, as $S = R \ln(m)$. Our results, given in Table 1, support this suspicion. It is difficult to find any correlation between the multiplicities and the observed entropies of the conformers of 1,2-dimethoxyethane. This conclusion should be taken into account when developing a rotational isomeric state (RIS) model of 1,2-dimethoxyethane or poly(oxyethylene).[48] The preexponential factors in the RIS model should not be ignored for the sake of simplicity, as it may otherwise lead to less accurate estimates on the relative free energies and the populations of the conformers.

The molecular dynamics simulations of the liquid phase of 1,2-dimethoxyethane have been performed at one temperature 300 K.[36] They gave the following populations for the different conformers: 0.45 for TGT, 0.08 for TGG, 0.18 for TTT, 0.17 for TGG′, and 0.09 for TTG. Our experimental estimates on the conformer populations at 300 K are 0.42 for TGT, 0.09 for TGG, 0.12 for TTT, 0.33 for TGG′, and 0.04 for TTG. There is a good correspondence (less than 6% deviation) between the theoretical and the experimental results for the populations of four of the conformers of 1,2-dimethoxyethane. The population predicted for the TGG′ conformer is, however, significantly lower than our experimental result. It is underestimated nearly twice in the molecular dynamics simulation. Smith et al. have explained the low population of the TGG′ conformer in the liquid phase by relatively strong intermolecular CH···O interactions that replace the intramolecular CH···O interaction.[36] As we observe a rather high population of the TGG′ conformer in the liquid phase, this interpretation is somewhat questionable. Furthermore, there is experimental evidence that the conformation of the 1,2-dimethoxyethane molecule does not change much on going from the neat liquid to solutions of nonpolar solvents such as carbon tetrachloride or benzene,[16,24] which have no ability to accept hydrogen bonds. Thus, the intermolecular CH···O interaction should not be an important factor of the stability of the conformers of 1,2-dimethoxyethane in the liquid phase. The encountered inconsistency between the molecular dynamics simulations and the experiment indicates that there should be some differences between the mechanisms or the magnitudes of the intramolecular and the intermolecular CH···O interactions, which are not taken into account by the original force field of Smith et al.[33] Smith et al. have also proposed a modified form of the force field,[33] which describes more explicitly the intramolecular CH···O interaction. They have found, however, that the modified version of the force field does not improve the description of the conformational behavior of 1,2-dimethoxyethane in the gas phase. Accordingly, the modified force field was not applied to molecular dynamics simulations of the condensed phases, where, in our opinion, it might work better than the original one.

Conformational Preference of 1,2-Dimethoxyethane in Aqueous Solutions. The molecular dynamics simulations of aqueous solutions of 1,2-dimethoxyethane[42] have shown that the TTT, TTG, and TGG′ conformers interact unfavorably with the nearby water molecules, while the TGT and TGG conformers are favorably hydrated. These theoretical results have been partially confirmed in our laboratory by analyzing all conformation-sensitive Raman bands of aqueous solutions of 1,2-dimethoxyethane in a broad range of concentrations. The quantitative method of analysis of the low-wavenumber Raman spectra of 1,2-dimethoxyethane, adopted in the present work, can supply, on the other hand, clearer experimental evidence to support the theoretical conclusions.[42] Following the procedure described in the Results section of this paper, the populations of the conformers of 1,2-dimethoxyethane in aqueous solutions were determined. They are plotted in Figure 5 as a function of the concentration of 1,2-dimethoxyethane. The plots show that, on increasing water concentration, the populations of the TTT and TGG′ conformers decrease and they are replaced by the populations of the TGT and TGG conformers. The general tendency of the dependencies of the populations of these four conformers on the concentration of 1,2-dimethoxyethane is in agreement with the molecular dynamics simulations.[42] As the characteristic band of the TTG conformer has a very small area, it is difficult to form definitive conclusions on the behavior of this conformer in aqueous solutions on the basis of our experimental results.

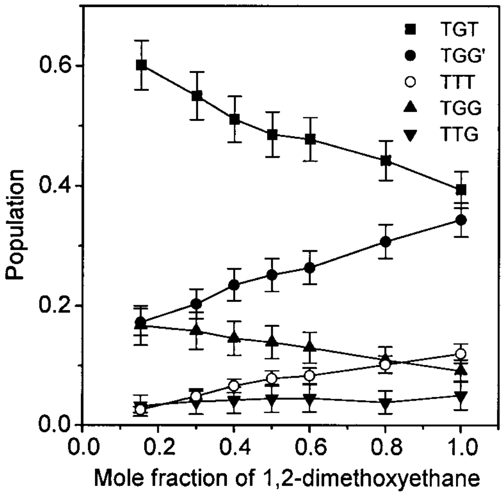

Figure 5. Dependencies of the populations of the conformers of 1,2-dimethoxyethane in aqueous solutions on the concentration of the solution.

We emphasize that the TGG′ conformer, which is more polar than the TGT conformer, does not become more stable in dilute aqueous solutions, though the dielectric constant of water ($\epsilon = 80.1$) is higher than the dielectric constant of 1,2-dimethoxyethane ($\epsilon = 7.3$). This experimental observation evidences that the stability of the conformers cannot be completely explained by dipole electrostatic interactions with the surrounding "continuum" dielectric medium. As pointed out in a preceding section, the higher multipole moments probably should also be taken into account when discussing the conformer stability. The strong hydrogen bonding between the 1,2-dimethoxyethane and water molecules can also be an important factor of the conformer stability in aqueous solutions. This can be assessed, to some extent, by comparative studies on the conformation of 1,2-dimethoxyethane in various solvents with different dielectric constants and different hydrogen bonding abilities. We have recently found that chloroform, which is a nonpolar but hydrogen bonding solvent, affects the conformation of 1,2-dimethoxyethane in a way similar to water. According to the continuum dielectric theory of solvation, we should observe contrasting changes of the conformation of 1,2-dimethoxyethane on going from the liquid phase to chloroform and aqueous solutions, as the dielectric constant of chloroform ($\epsilon = 4.8$) is lower than that of 1,2-dimethoxyethane ($\epsilon = 7.3$) while the dielectric constant of water ($\epsilon = 80.1$) is higher than that. The experimentally observed conformational preference of 1,2-dimethoxyethane can be reasonably explained, if we assume that the hydrogen bonding with the solvent molecules is a basic factor of the relative stability of the conformers in solution. More detailed studies on the influence of the hydrogen bonding on the conformational behavior of 1,2-dimethoxyethane in different solvents are in progress and will be reported elsewhere.

Impact of Conformational Entropies on the Aqueous Solution Properties of Poly(oxyethylene). The most important finding of the present study, in our opinion, is that the less hydrophilic TTT and TGG′ conformers of 1,2-dimethoxyethane have higher inherent conformational entropies than the more hydrophilic TGT and TGG conformers. As a result, the less hydrophilic conformational forms replace the more hydrophilic ones at high temperatures. This entropy effect is most evident for the TGG′ conformer, which becomes the dominant conformer in neat 1,2-dimethoxyethane at high temperatures. The conformational preference of 1,2-dimethoxyethane resembles to some extent the conformational preference of the poly(oxyethylene) chain. We may therefore expect that, at high temperatures, the $CH_2O-CH_2-CH_2-OCH_2$ structural segments in the poly(oxyethylene) chain will also acquire the less hydrophilic TTT and TGG′ conformations instead of the more hydrophilic TGT and TGG conformations. For short poly(oxyethylene) chains, the appearance of less hydrophilic or partially hydrophobic segments within them will not affect the phase structure of their aqueous solutions, because the entropy of mixing is large in this case and always favors the homogeneous solution. For long poly(oxyethylene) chains, however, it may lead to lower solubility and phase separation. The conformational model of the inverse temperature solubility of poly(oxyethylene) suggested by Karlström[47] is essentially based on these ideas. The only difference is that the less hydrophilic conformational forms (the high-temperature forms) in his model are identified with the nonpolar conformational forms. In light of our experimental results and the molecular dynamics simulations of Smith et al.,[42] the $CH_2O-CH_2-CH_2-OCH_2$ segment in the TGG′ conformation should also be classified as partially hydrophobic one although it has a large dipole moment. Moreover, our experimental results have revealed that the TGG′ conformer is the most rapidly populated conformer on increasing temperature, as it is the conformer with the highest entropy. Therefore, the appearance of the $CH_2O-CH_2-CH_2-OCH_2$ segment in the TGG′ conformation within the poly(oxyethylene) chain can be a basic mechanism of the phase separation observed in aqueous solutions of poly(oxyethylene) and poly(oxyethylene)-containing compounds. There are indirect evidences supporting this hypothesis. It has been demonstrated that on increasing temperature the poly(oxyethylene) chain becomes less hydrated and collapses.[49−52] The same trend is observed on subjecting aqueous solutions of poly(oxyethylene) to a high pressure.[53] Both processes—the dehydration and the collapse of the polymer chain—will be greatly facilitated by the appearance of the TGG′ conformational segments within the chain, leading eventually to a phase separation.

It has been known for a long time that the entropy of mixing of water and poly(oxyethylene) is negative independently of the mole ratio of both compounds and the length of the polymer chain.[49] The negative entropy of mixing is usually explained by structuring of water around the poly(oxyethylene) chain. The results of our Raman spectroscopic study indicate that the negative entropy of mixing should partially originate from the conformational transformations in the poly(oxyethylene) chain itself. Indeed, the structuring of water around the poly(oxyethylene) chain cannot be ignored as a source of the negative entropy of mixing. It has been established that, in dilute aqueous solutions, the water molecules form structured cages around the poly(oxyethylene) chain, which are characterized by low molecular mobility[54] and enhanced hydrogen bonding.[55−57] In concentrated solutions, however, the water structuring mechanism should be of less importance as the hydrogen bond network between the water molecules is severely disrupted.[56−58] In this case, the changes of the conformational entropy of the polymer should be dominant in the negative entropy of mixing of water and poly(oxyethylene).

Conclusions

1,2-Dimethoxyethane exists as a mixture of several principal conformers in the liquid phase and in aqueous solutions. These conformers are the TGT, TGG, TTT, TGG′, and TTG conformers. The TGT conformer is the lowest-energy conformer in the liquid phase followed by the TGG, TTT, TGG′, and TTG conformers in order of their increasing energies. The polar conformers are generally more stable in the liquid phase than in the gas phase. The polar TGG′ conformer is, however, not stabilized with respect to the nonpolar TTT conformer on going from the gas phase to the liquid phase. This single exception points out that the energies of the conformers in the condensed phases depend also on their multipole moments.

The TTT and TGG′ conformers interact unfavorably with water, while the TGT and TGG conformers are favorably hydrated. The entropies of the conformers are important factors of their thermodynamical stability. For the liquid phase of 1,2-dimethoxyethane, the entropies of the conformers cannot be calculated on the basis of the conformer multiplicities and should be determined experimentally. The less hydrophilic TTT and TGG′ conformers have higher entropies than the more hydrophilic TGT and TGG conformers. This experimental observation supports the conformational model of the inverse temperature solubility of poly(oxyethylene) in water proposed by Karlström.

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