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Hydrogen Bonding in Chloroform Solutions of Ethylenedioxy Ethers. Spectroscopic Evidence of Bifurcated Hydrogen Bonds

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Chloroform solutions of 1,4-dioxane, 1,2-dimethoxyethane, and diethylene glycol dimethyl ether were studied by means of IR absorption spectroscopy. The intensity of the C−D stretching band of a small amount of deuterated chloroform added to the solutions was used as a probe of the strength of hydrogen bonding between the ethers and chloroform. A two-component model, which assumes that the chloroform molecules can be classified as hydrogen bonded and non-hydrogen bonded, was used to interpret the variations of the intensity of the C−D stretching band on changing the concentration of chloroform. In the frame of this model, the hydrogen bonding was considered as a chemical reaction between the lone electron pairs of the ether oxygens and the chloroform molecules. As a result, the equilibrium constant of hydrogen bonding was estimated and the stoichiometry of the hydrogen bonded complexes of ethers and chloroform was revealed. It was found that the lone electron pairs of the ether oxygens do not participate equally well in hydrogen bonding with chloroform, most probably because of steric hindrance. The analysis of the experimental results also suggested that chloroform can form strong bifurcated hydrogen bonds with the neighboring oxygens of the open-chain ethers. The bifurcated three-centered hydrogen bonds were confirmed by ab initio molecular orbital calculations.

Introduction

The C−H···Y hydrogen bond (Y = O, N, S, and Se) has long been considered as a secondary molecular interaction with a negligible influence on the properties of physicochemical systems. However, the number of known molecular phenomena controlled by C−H···Y hydrogen bonds has been steadily growing.[1−3] Nowadays it emerges that this type of weak interaction is probably ubiquitous in biological systems and is more influential than previously anticipated. The C−H···Y hydrogen bonds assist the structure of various molecular crystals.[1−4] They are strong enough to facilitate the design of new molecules with selective binding properties.[5] The C−H···Y hydrogen bond is an important factor in the conformational behavior of molecules that contain atoms with lone electron pairs as hydrogen bond acceptors and polarized C−H groups as hydrogen bond donors.[6−11] The C−H···Y hydrogen bond becomes stronger when the C−H bond is in the vicinity of electronegative atoms that are capable of withdrawing partially the electron charge from the hydrogen atom, making the C−H group more polar. A typical example of strong intermolecular C−H···Y hydrogen bonding is the hydrogen bonding between chloroform and Lewis bases. The first ever established C−H···Y hydrogen bond was, in fact, the hydrogen bond with the participation of the acidic C−H group of chloroform.[3]

IR spectroscopy is one of the powerful methods for identifying and characterizing the hydrogen bond. Nonetheless, IR absorption spectroscopy has only occasionally been applied to study the C−H···Y hydrogen bond.[3,12−20] The red wavenumber shift and intensity enhancement of the X−H (X = O, N, F, etc.) stretching vibration of the hydrogen bond donor are the most significant spectroscopic features of the X−H···Y hydrogen bond, manifested in the IR spectra. The red wavenumber shift is commonly used as a probe of the strength of hydrogen bonding.[21] However, when the hydrogen bonds are weak, as is the case with most of the hydrogen bonds with participation of C−H groups, the wavenumber shift of the X−H stretching vibration is rather small and its interpretation is insecure.[12,15] In some cases, even a blue shift of the C−H stretching vibration has been observed.[13,16,22,23] For weak hydrogen bonds, the intensity of the stretching vibration of the hydrogen bond donor is the more appropriate parameter for characterizing the strength of hydrogen bonding.[12] Moreover, the intensity enhancement of the stretching vibration of the hydrogen bond donor is exactly proportional to the strength of the hydrogen bond[15] and therefore can be used for quantitative analysis.

The aim of this work is to study the hydrogen bonding in chloroform solutions of several ethers that contain the ethylenedioxy group ($-OCH_2CH_2O-$) in the whole range of volume fractions by utilizing the intensity enhancement of the C−D stretching vibration of deuterated chloroform. The simple ethylenedioxy ethers considered here are 1,4-dioxane $[\overline{(OCH_2CH_2)_2}]$, 1,2-dimethoxyethane $[CH_3OCH_2CH_2OCH_3]$, and diethylene glycol dimethyl ether (or bis(2-methoxyethyl) ether) $[CH_3(OCH_2CH_2)_2OCH_3]$, which are among the model compounds of poly(oxyethylene). This polymer has various industrial applications associated with its excellent solubility in water.[24,25] It is well known, however, that when chloroform is added to aqueous solutions of poly(oxyethylene), the polymer chains are dehydrated and the solution phase separates. In fact, this property of chloroform is used for extracting poly-

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(oxyethylene)-containing compounds from the aqueous solutions. The observed phase separation evidences that the weak C−H···O hydrogen bonds may compete successfully with the stronger O−H···O hydrogen bonds in determining the macroscopic properties of some molecular systems. In addition, the C−H···O hydrogen bonding with chloroform might be responsible for the considerable swelling of poly(oxyethylene) gels in chloroform[26] as well as for the conformational changes of the poly(oxyethylene) chains on going from the liquid phase to chloroform solution.[27] Thus, a thorough spectroscopic study on the C−H···O hydrogen bonding between ethers and chloroform should enlighten several phenomena related to the peculiar properties of poly(oxyethylene).

Experimental Section

Chloroform, 1,4-dioxane, 1,2-dimethoxyethane, and diethylene glycol dimethyl ether were purchased from Katayama Chemical Industries, Osaka, Japan. They were dried over molecular sieves and used for spectroscopic measurements without further purification. Deuterated chloroform (deuteration degree not less than 99.8%) was purchased from Merck, Darmstadt, Germany. It was mixed with normal chloroform to obtain a partially deuterated solvent (mole ratio $CHCl_3$:$CDCl_3$ = 50:1). Solutions of the selected ethers in normal and partially deuterated chloroform were prepared by weight. The solutions were studied shortly after their preparation to avoid the possible degradation. The IR absorbance spectra of the solutions were recorded in transmission geometry on a Bruker IFS 66 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector, a potassium bromide beam-splitter, and a globar source by using a homemade cell with calcium fluoride windows. The nominal resolution of the spectra was 1 cm^{-1}. The thickness of the cell, 0.495 mm, was determined by the interference fringe method.

Spectral Processing

The C−H stretching band of chloroform, centered at about 3020 cm^{-1}, is partially overlapped with the C−H stretching bands of the ethers. Thus, the C−H stretching vibrations of neighboring chloroform and ether molecules might be intermolecularly coupled. The intermolecular coupling may alter the intensity of the C−H stretching vibration of chloroform, hampering its use as an accurate probe of the strength of hydrogen bonding. Therefore, it is more appropriate to study the hydrogen bonding in the solutions by using as a probe the C−D stretching band of a small amount of deuterated chloroform added to them. The C−D stretching band of the deuterated chloroform appears in a spectral region where no strong bands of fundamental vibrations of the ethers and normal chloroform exist. Due to the weak absorption, the deuteration could be partial and the IR spectra could be measured in transmission geometry, which simplified their analysis. Examples of the IR absorbance spectra of the ether solutions studied are shown in Figure 1. In all spectra, the C−D stretching band of the deuterated chloroform appears upon overtone and combination bands of the ethers and normal chloroform. The overtone and combination bands practically do not change under the partial deuteration of chloroform, which strongly suggests that the structure of the solutions and the conformation of the ethers are not altered by it. The background due to the overtone and combination bands was removed by subtracting the spectra of the solutions prepared in normal chloroform from the corresponding spectra of the solutions prepared in partially deuterated chloroform.

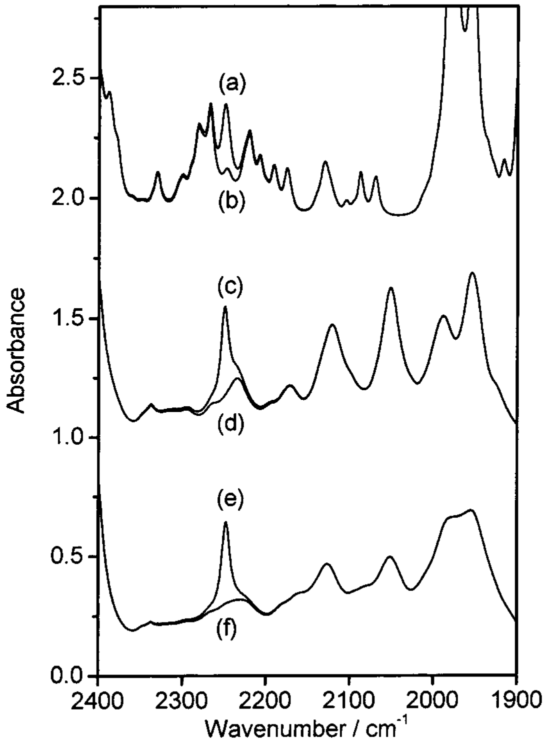

Figure 1. Examples of the IR absorbance spectra of the solutions of ethers in normal and partially deuterated chloroform (mole ratio of $CHCl_3$:$CDCl_3$ = 50:1): (a) 1,4-dioxane in partially deuterated chloroform, (b) 1,4-dioxane in normal chloroform, (c) 1,2-dimethoxyethane in partially deuterated chloroform, (d) 1,2-dimethoxyethane in normal chloroform, (e) diethylene glycol dimethyl ether in partially deuterated chloroform, and (f) diethylene glycol dimethyl ether in normal chloroform. The values on the ordinate scale apply only to the spectra (e) and (f).

Theoretical Model

Chloroform solutions of ethers have been studied previously by different methods.[12,13,28−31] It has been shown that some of their properties can be interpreted in terms of the formation of hydrogen bonded complexes. Hence, it is reasonable to classify the chloroform molecules into bound molecules that are hydrogen bonded to the lone electron pairs of the ether oxygens and free non-hydrogen bonded chloroform molecules. Let us assume, for convenience in the following notations, that all chloroform molecules are deuterated. Next, the hydrogen bonding can be regarded as a chemical reaction between the lone electron pairs (LP) of the ether oxygens and the chloroform molecules ($DCCl_3$):[13,32]

$$\mathrm{LP} + \mathrm{DCCl_3} \rightleftarrows \mathrm{LP{:}DCCl_3} \qquad (1)$$

with an equilibrium constant K given by

$$K = \frac{[\mathrm{LP{:}DCCl_3}]}{[\mathrm{LP}][\mathrm{DCCl_3}]} \qquad (2)$$

where [LP] is the molar concentration of the non-hydrogen bonded lone electron pairs, [$DCCl_3$] the molar concentration of the non-hydrogen bonded chloroform molecules, and [LP:$DCCl_3$] the molar concentration of the hydrogen bonded chloroform molecules. The molar concentration is defined as the number of moles of the component divided by the volume of the mixture. Two more equations with the meaning of the conservation law for the numbers of chloroform molecules and lone electron pairs can be added to eq 2 to form a system of equations, which can be solved with respect to the molar concentrations:

$$c_1 = [\mathrm{LP{:}DCCl_3}] + [\mathrm{DCCl_3}] \tag{3}$$

and

$$2nc_2 = [\mathrm{LP{:}DCCl_3}] + [\mathrm{LP}] \tag{4}$$

where c_1 is the molar concentration of chloroform in the solution, c_2 the molar concentration of the ether, and n the number of oxygen atoms in one ether molecule. Equation 4 assumes that all lone electron pairs (two per ether oxygen) are available simultaneously for hydrogen bonding with the chloroform molecules. As we show later, it may turn out, however, that some of the lone electron pairs cannot simultaneously form hydrogen bonds because of steric hindrance. Then, eq 4 should be rewritten in a more general form

$$anc_2 = [\mathrm{LP{:}DCCl_3}] + [\mathrm{LP}] \tag{5}$$

where a is the number of the lone electron pairs in one ether oxygen that can simultaneously participate in the hydrogen bonding reaction described by eq 1. By solving eqs 2, 3, and 5 together, one can obtain the molar concentrations of hydrogen bonded and free chloroform molecules as a function of the molar concentrations of chloroform and ether in the solution

$$[\mathrm{LP{:}DCCl_3}] = (1/2)\{c_1 + anc_2 + 1/K - [(c_1 + anc_2 + 1/K)^2 - 4anc_1c_2]^{1/2}\} \tag{6}$$

and

$$[\mathrm{DCCl_3}] = c_1 - [\mathrm{LP{:}DCCl_3}] \tag{7}$$

The empirical parameters K and a are not known in advance and therefore should be estimated on the basis of the experimental data. The dependence of the integral absorption coefficient of the C−D stretching band of chloroform on the molar concentration of chloroform can be used for that purpose as has been suggested in the early work of Lord et al.[13]

The integral absorption coefficient, α, of the C−D stretching band of the solutions can be expressed as a linear combination of the integral molar absorption coefficients, ϵ_B and ϵ_F, for the C−D stretching bands of the bound and free chloroform molecules, respectively:

$$\alpha = [\mathrm{LP{:}DCCl_3}]\epsilon_B + [\mathrm{DCCl_3}]\epsilon_F \tag{8}$$

The integral molar absorption coefficient, ϵ_F, of the free chloroform molecules can be easily determined, as it corresponds to the integral molar absorption coefficient of the C−D stretching band of deuterated chloroform dissolved in normal chloroform. The integral molar absorption coefficient, ϵ_B, of the C−D stretching band of the bound chloroform molecules could be determined similarly if we were able to study solutions with $[\mathrm{LP{:}DCCl_3}] \neq 0$ and $[\mathrm{DCCl_3}] = 0$. However, this is practically impossible at ambient temperatures because the hydrogen bonding between ethers and chloroform is relatively weak and part of the chloroform molecules remains non-hydrogen bonded even for very low concentrations of chloroform. The simple model described above can help us to overcome that difficulty. Substitution of eqs 6 and 7 in eq 8 gives

$$\alpha = (1/2)(\epsilon_B - \epsilon_F)\{c_1 + anc_2 + 1/K - [(c_1 + anc_2 + 1/K)^2 - 4anc_1c_2]^{1/2}\} + c_1\epsilon_F \tag{9}$$

which is written in terms of molar concentrations. In practice, however, it is more convenient to use the mole or volume fractions instead of the molar concentrations. Hence, the following relation is finally obtained after some trivial mathematical transformations:

$$\alpha = (1/2)c(\epsilon_B - \epsilon_F)\{v_1 + an(V_1/V_2)(1 - v_1) + V_1/K - [(v_1 + an(V_1/V_2)(1 - v_1) + V_1/K)^2 - 4v_1an(V_1/V_2)(1 - v_1)]^{1/2}\} + v_1c\epsilon_F \tag{10}$$

where v_1 is the volume fraction of chloroform, V_1 the molar volume of neat chloroform, V_2 the molar volume of neat ether, and c the molar concentration of chloroform molecules in neat chloroform ($c = 1/V_1$). The integral absorption coefficient, α, can be determined on the basis of the experimental absorbance spectra. Then, all parameters of our model (ϵ_B, ϵ_F, α, K, and a) can be estimated by means of nonlinear least-squares fitting of the dependence of the integral absorption coefficient, α, on the volume fraction of chloroform, v_1, by eq 10.

The model described here is in fact a modification of the model of Lord et al.[13] We should emphasize, however, that there is an important difference between the two formulations. We regard the hydrogen bonding as a chemical reaction between the lone electron pairs of the ether oxygen atoms and the chloroform molecules, whereas Lord et al. regard the hydrogen bonding as a chemical reaction between the ether molecules and the chloroform molecules. Consequently our formulation allows successive hydrogen bonding of several chloroform molecules, up to *an*, to one ether molecule, whereas the formulation of Lord et al. allows only the formation of 1:1 complexes of ether and chloroform. The suggested new modification is therefore essential for describing the hydrogen bonding between chloroform and oxygen-rich polyethers.

Results

The C−D stretching spectra of the deuterated chloroform in the solutions studied are shown in Figures 2−4. It is seen from these figures that the C−D stretching spectra change in a very similar way, independently of the type of the ether, on increasing the volume fraction of ether. Initially, the intensity of the C−D stretching band increases although the volume fraction of chloroform itself decreases. This initial intensity rise can be ascribed definitely to the formation of hydrogen-bonded complexes of chloroform and ether molecules and the concomitant enhancement of the intensity of the C−D stretching vibration through a polarization of the C−D bond. At high volume fractions of ether, most of the chloroform molecules are already hydrogen bonded. Therefore, any further increase in the volume fraction of ether mainly reduces the volume fraction of hydrogen bonded chloroform molecules and, as a result, the intensity of the C−D stretching band decreases. The observed intensity variations of the C−D stretching band suggest that the volume fraction of hydrogen bonded chloroform has a maximum for intermediate volume fractions of chloroform. More detailed information on the hydrogen bonding in the chloroform solutions of ethers can, indeed, be obtained by applying the two-component model developed in the preceding part of this paper.

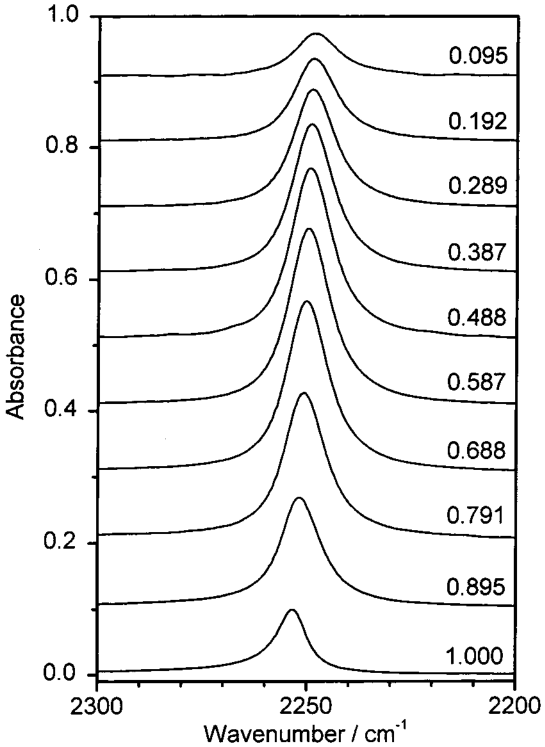

Figure 2. Examples of C−D stretching spectra of the deuterated chloroform in the chloroform solutions of 1,4-dioxane. The respective volume fractions of chloroform are marked above each spectrum. The values on the ordinate scale apply only to the spectrum for volume fraction 1.000.

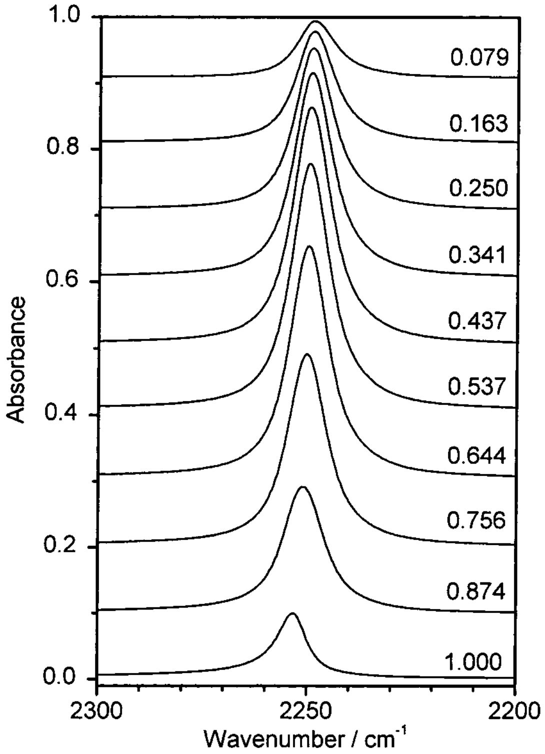

Figure 3. Examples of C−D stretching spectra of the deuterated chloroform in the chloroform solutions of 1,2-dimethoxyethane. The respective volume fractions of chloroform are marked above each spectrum. The values on the ordinate scale apply only to the spectrum for volume fraction 1.000.

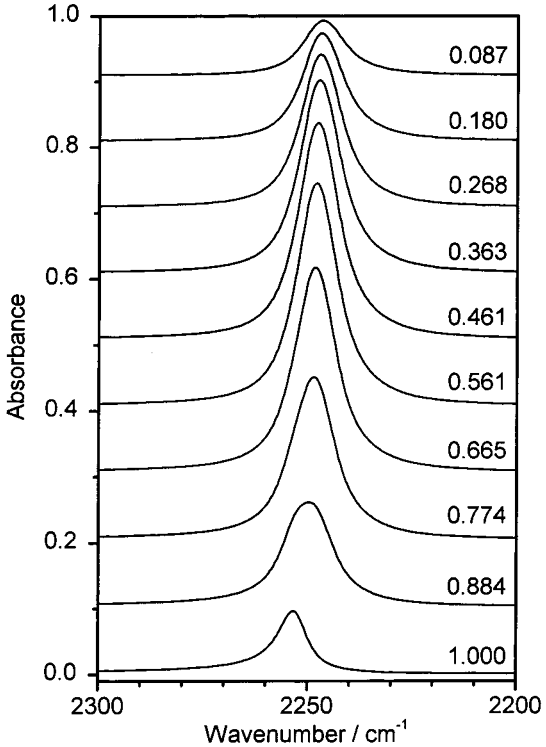

Figure 4. Examples of C−D stretching spectra of the deuterated chloroform in the chloroform solutions of diethylene glycol dimethyl ether. The respective volume fractions of chloroform are marked above each spectrum. The values on the ordinate scale apply only to the spectrum for volume fraction 1.000.

All experimental spectra $A(\nu)$ were recorded as absorbance spectra with decadic absorbance ordinates. Therefore, the integral absorption coefficient, α, was calculated by using the following relation:

$$\alpha = \frac{2.303 \times 51}{d} \int A(\nu)\mathrm{d}\nu \qquad (11)$$

where d is the thickness of the cell. The integration in eq 11 was done over the wavenumber region 2300−2200 cm^{-1}. The numerical factor 51 appears in eq 11 because only a small part of the chloroform molecules were deuterated, whereas the integral absorption coefficient, α, in eq 8 was defined for solutions of ethers in fully deuterated chloroform. The C−D stretching spectra of solutions of ethers in fully deuterated chloroform can be obtained from the C−D stretching spectra of solutions of ethers in partially deuterated chloroform by a simple rescaling. In the present case, the C−D stretching spectra of the solutions of ethers in partially deuterated chloroform must be multiplied by 51, because the mole ratio $CHCl_3$:$CDCl_3$ is 50:1.

The relative molar volumes of the ethers were measured with respect to the molar volume of neat chloroform at the temperature of the experiment, 25 °C, by using a picnometer. The relative molar volumes thus obtained were used to calculate the volume fractions of chloroform in the solutions from the respective weight fractions assuming ideal mixing of the solution components. The deviations from the ideal mixing were found to be smaller than the accuracy of our volumetric measurements, and they could in general be neglected when compared with the possible errors in the integral absorption coefficients.

The dependencies of the integral absorption coefficients, α, of the C−D stretching band on the volume fraction of chloroform, v_1, are given in Figure 5, along with the best nonlinear least-squares fits of the experimental data points by eq 10. It is apparent from Figure 5 that our simple model can describe well the variations of the integral absorption coefficient

TABLE 1: Integral Molar Absorption Coefficients, ϵ_B and ϵ_F, of Bound and Free Chloroform, Respectively, Average Numbers of Lone Electron Pairs, *a*, of One Ether Oxygen that Can Simultaneously Form Hydrogen Bonds with Chloroform, Equilibrium Constants, *K*, of the Hydrogen Bonding between the Ethers and Chloroform, and Hydrogen Bond Enthalpies, ΔH

	solvent		
parameter	1,4-dioxane	1,2-dimethoxyethane	diethylene glycol dimethyl ether
$10^{-4}\ \epsilon_F$/cm mmol^{-1}	0.0307 ± 0.002	0.0305 ± 0.002	0.0306 ± 0.002
$10^{-4}\ \epsilon_B$/cm mmol^{-1}	0.29 ± 0.01	0.47 ± 0.02	0.43 ± 0.01
a	1.00 ± 0.04	0.72 ± 0.01	0.68 ± 0.01
K/mol L^{-1}	0.20 ± 0.03	0.21 ± 0.02	0.22 ± 0.02
ΔH^a/kJ mol^{-1}	6.0	8.5	8.0
ΔH^b/kJ mol^{-1}	7.1	9.5	9.1

[a] Calculated with respect to the hydrogen bonding in neat chloroform by substituting $\epsilon_F = 0.031$ in eq 12, where the integral molar absorption coefficient is expressed in units of 10^4 cm mmol^{-1}. [b] Calculated with respect to non-hydrogen bonded gas-phase chloroform by substituting $\epsilon_F = 0.013$ in eq 12.[14]

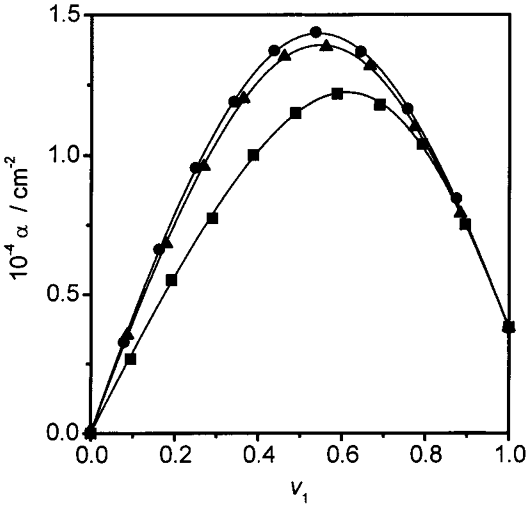

Figure 5. Dependencies of the integral absorption coefficient, α, of the C−D stretching band of the deuterated chloroform in the solutions studied on the volume fraction, v_1, of chloroform: ■ 1,4-dioxane, ● 1,2-dimethoxyethane, and ▲ diethylene glycol dimethyl ether. The solid lines are the best nonlinear least-squares fits of each set of the data points by eq 10.

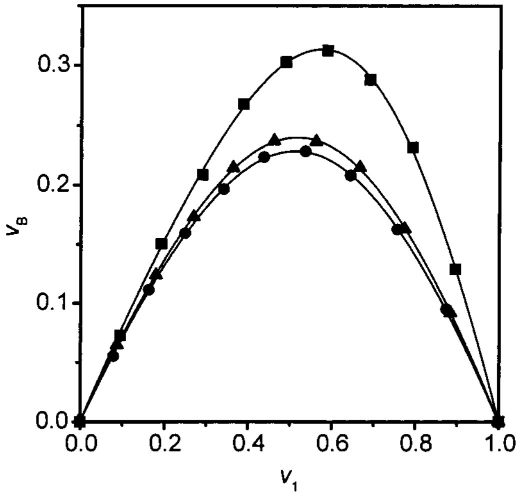

Figure 6. Dependencies of the volume fraction, v_B, of bound chloroform on the volume fraction, v_1, of chloroform. The symbols represent the volume fractions calculated from the integral absorption coefficient, α, and the integral molar absorption coefficients, ϵ_B and ϵ_F, of the bound and free chloroform, respectively, via eqs 7 and 8: ■ 1,4-dioxane, ● 1,2-dimethoxyethane, and ▲ diethylene glycol dimethyl ether. The solid lines represent the volume fractions of bound chloroform calculated via eqs 6 and 7.

on changing the concentrations of the solutions. Thus, the empirical parameters that characterize the equilibrium of hydrogen bonded and non-hydrogen bonded chloroform molecules were confidently determined. The numerical values of all empirical parameters are given in Table 1.

The molar concentrations of bound and free chloroform molecules and the respective volume fractions can be calculated by using eqs 6 and 7. Alternatively, they can be calculated, via eqs 7 and 8, from the integral absorption coefficient, α, and the integral molar absorption coefficients, ϵ_B and ϵ_F, of the bound and free chloroform. The dependencies of the calculated volume fractions of the bound chloroform, v_B, on the volume fraction, v_1, of chloroform are shown in Figure 6.

Discussion

Stoichiometry of the Hydrogen Bonded Complexes. The average numbers, *a*, of the lone electron pairs per ether oxygen that can participate simultaneously in hydrogen bonding with chloroform are 1.0, 0.7, and 0.7 for 1,4-dioxane, 1,2-dimethoxyethane, and diethylene glycol dimethyl ether, respectively (Table 1). In all cases, *a* is substantially lower than 2 and is actually very close to 1. Therefore, the lone electron pairs of the ether oxygens are not equally accessible for hydrogen bonding with the chloroform molecules. This interesting finding suggests that the hydrogen bonding with some of the lone electron pairs of the ethers is sterically hindered in the chloroform solutions. The steric hindrance may have intermolecular or intramolecular origin.

The intramolecular hindrance is not possible for the molecule of 1,4-dioxane. Because of the closed ring structure of this molecule, the lone electron pairs of the oxygen atoms in the molecule are always exposed for hydrogen bonding with the solvent chloroform molecules. However, even for 1,4-dioxane, *a* equals 1 rather than 2. Thus, we have to assume that there is substantial intermolecular hindrance of the hydrogen bonding with part of the lone electron pairs of the ether oxygens. In our opinion, when a hydrogen bond is formed between chloroform and ether, the bulky chloroform molecule occupies the space near the ether oxygen atom and therefore prevents the formation of a second hydrogen bond between the same oxygen atom and another chloroform molecule.

The intramolecular hindrance is possible for the open-chain ethers that have a rather flexible conformation. Moreover, one of the most stable conformational forms of 1,2-dimethoxyethane in the liquid phase is the trans−gauche−gauche′ (TGG′) conformer,[33] which is stabilized primarily by the intramolecular C−H···O hydrogen bond.[6] The intramolecular C−H···O hydrogen bond occupies one of the lone electron pairs of the participating oxygen and effectively screens this lone electron pair from the chloroform molecules. Our studies on water solutions of 1,2-dimethoxyethane[33] have shown that the hydrogen bonding with water is strong enough to rupture some of the intramolecular C−H···O hydrogen bonds and to transform the TGG′ conformers into other conformers. The hydrogen bonding of ethers with chloroform is, however, weaker than the hydrogen bonding with water, and the intramolecular C−H···O hydrogen bonds might be preserved to a much larger extent in the chloroform solutions than in the aqueous solutions. Actually, the intramolecular C−H···O interaction is very similar in its nature to the hydrogen bonding between ethers and chloroform. The strength of these similar interactions should also be comparable. Therefore, there will be little energy gain when the weak intramolecular C−H···O hydrogen bond is replaced by another weak intermolecular C−H···O hydrogen bond with a chloroform molecule. At the same time, there will be some entropy loss because the high-entropy TGG′ conformer will be transformed into low-entropy ones.[33] The intramolecular C−H···O hydrogen bonds should, indeed, be present also for the longer molecule of diethylene glycol dimethyl ether. The fact that the parameters a and ϵ_B are practically the same for the two open-chain ethers implies similar hydrogen bonding of these ethers with chloroform.

Enthalpies of Hydrogen Bonding. The quantitative form of the correlation between the enthalpy, ΔH, of the hydrogen bond X−H···Y and the intensification, $\Delta\epsilon^{1/2} = \epsilon_B^{1/2} - \epsilon_F^{1/2}$, of the X−H stretching vibration of the hydrogen bond donor has been established by Iogansen.[15] For integral molar absorption coefficients expressed in practical units of 10^4 cm mmol^{-1} and enthalpies of hydrogen bonds in kJ mol^{-1}, Iogansen's correlation can be described by

$$\Delta H = 17.3\ \Delta\epsilon^{1/2} \qquad (12)$$

Note that the numerical coefficient 17.3 in eq 12 differs by a factor of $2^{1/2}$ from the numerical coefficient 12.2 in eq 5 of ref 15 due to the deuteration. The predictive power of eq 12 is remarkable. This equation can be utilized for estimating the enthalpies of various hydrogen bonds with different strength on a purely spectroscopic basis with accuracy comparable to the accuracy of calorimetric measurements. Unfortunately, eq 12 cannot predict the enthalpies of bent intramolecular hydrogen bonds. However, any failures of eq 12 are yet beneficial as they evidence the nonstandard configurations of hydrogen bonding that are difficult to be proved in different ways.

By using eq 12 we have calculated the enthalpies of the hydrogen bonds formed between the ethers and chloroform, and the results are given in Table 1. These results suggest that the hydrogen bonding of chloroform with the open-chain ethers is somewhat stronger than the hydrogen bonding with 1,4-dioxane.

Now we have at hand spectroscopic estimates of the enthalpies of the hydrogen bonds between the ethers and chloroform and also spectroscopic estimates of the volume fractions of the hydrogen bonded chloroform molecules. Let us further assume that each chloroform molecule forms a single hydrogen bond with a single ether oxygen atom. Then, the total enthalpies of hydrogen bonding per unit volume of solution can be estimated by multiplying the corresponding number of the hydrogen bonded chloroform molecules, which is equal to the number of the hydrogen bonds, with the enthalpy of one hydrogen bond. The total enthalpies of hydrogen bonding calculated in this way are shown in Figure 7. The hydrogen bonding is the strongest intermolecular interaction in the solutions studied, and therefore the total enthalpies of hydrogen bonding should resemble the heats of mixing of the solutions. The available experimental data[29,30] on the heats of mixing of chloroform with 1,4-dioxane and 1,2-dimethoxyethane are included in Figure 7 for comparison. It is seen from this figure that our spectroscopic estimates of the total enthalpies of hydrogen bonding parallel the heats of mixing measured for the chloroform solutions of 1,4-dioxane. There is only a small systematic deviation, which should be ascribed to the weak attractive interaction between the chlorine atoms and the ether oxygens.[34] We may therefore conclude that the spectroscopic method adopted in this work for evaluating the strength of hydrogen bonding gives excellent results for chloroform solutions of 1,4-dioxane. On the other hand, there is apparently no agreement between our spectroscopic estimates of the total enthalpies of hydrogen bonding and the calorimetric heats of mixing for the chloroform solutions of 1,2-dimethoxyethane. The spectroscopic estimates are nearly twice lower than the calorimetric heats of mixing. The observed difference is so large that it cannot be solely attributed to the weak attractive interaction between the chloroform chlorines and the ether oxygens, although this interaction is probably stronger in this case.[34]

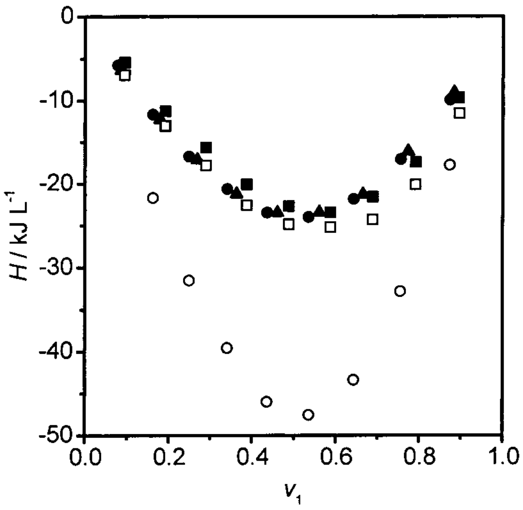

Figure 7. Dependencies of the total enthalpy of hydrogen bonding, H, per liter solution on the volume fraction, v_1, of chloroform. The notations are the same as in Figure 6. The open symbols represent the calorimetric heats of mixing of chloroform with 1,4-dioxane (□)[29] and 1,2-dimethoxyethane (○).[30]

Evidence of Bifurcated Hydrogen Bonds. To find out the source of the observed unacceptable inconsistency of spectroscopic and calorimetric data, it was necessary to review our procedure for spectroscopic estimation of the total enthalpies of hydrogen bonding. It should be noted at first that as a set of mathematical equations our model works rather well, being capable of describing the variations of the experimental integral absorption coefficient of the C−D stretching band for the whole region of chloroform volume fractions. Therefore, it is worthwhile to consider only the physical background of the calculation of the total enthalpy of hydrogen bonding rather than the model itself or its mathematical side. The estimation of the total enthalpies of hydrogen bonding is actually based on two important physical assumptions. The first is that the enthalpies of the hydrogen bonds can be deduced from the intensification of the C−D stretching vibration via eq 12. The second, used in estimating the number of the hydrogen bonds, is that each chloroform molecule forms a single hydrogen bond and therefore the number of the hydrogen bonded chloroform molecules in the solutions is equal to the number of the hydrogen bonds.

Deviations from eq 12 have been detected previously for only nonlinear intramolecular hydrogen bonds.[15] For bent intra-

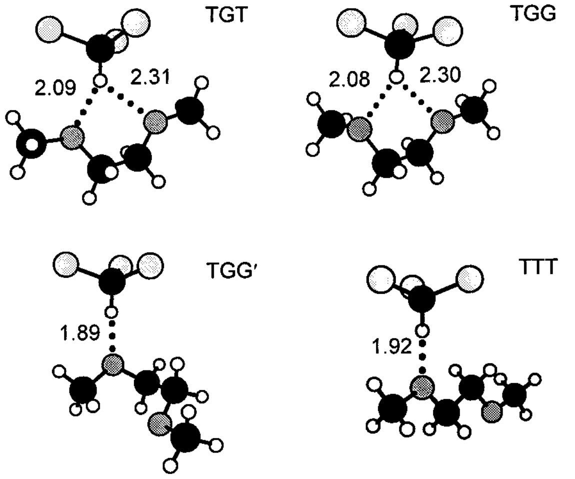

Figure 8. Plausible geometries of hydrogen bonded complexes of 1,2-dimethoxyethane and chloroform derived by ab initio molecular orbital calculations with the Hartree−Fock method using the 3-21G* basis set. The lengths of the hydrogen bonds in Å and the conformation of 1,2-dimethoxyethane are shown for each complex.

molecular X−H···Y hydrogen bonds, the intensification of the X−H stretching vibration is smaller than for the analogous linear X−H···Y hydrogen bonds. In that case, the intensification of the X−H stretching vibration does not properly reflect the strength of hydrogen bonding, and the estimated spectroscopic enthalpies are lower than the actual ones. As can be seen from Table 1, the enthalpy, ΔH, is already larger for the hydrogen bonding with the open-chain ethers than for the hydrogen bonding with 1,4-dioxane. Taking into account that the hydrogen bond acceptors (the ether oxygen atoms) are chemically very similar for all ethers studied, it seems unlikely that the stronger hydrogen bonds between chloroform and the open-chain ethers are weakened due to eventual bending of unknown origin. Then, to explain the observed difference between our spectroscopic estimates of the total enthalpies of hydrogen bonding and the calorimetric heats of mixing, we shall assume that in the solutions of 1,2-dimethoxyethane a lot of the chloroform molecules form bifurcated hydrogen bonds with two ether oxygen atoms simultaneously. Only in this case, the actual number of the hydrogen bonds will be larger than the number of the hydrogen bonded chloroform molecules, and consequently the calculated enthalpy of hydrogen bonding will increase to be closer to the measured heat of mixing.

Plausible Configurations for Bifurcated Hydrogen Bonds. Having the experimental evidence of bifurcated hydrogen bonds, we can consider without much difficulty the plausible configurations for them. It is most likely that the bifurcated hydrogen bond can be formed between chloroform and the TGT and TGG conformers of 1,2-dimethoxyethane in which the lone electron pairs of the neighboring oxygens are very close to each other. Unfortunately, our spectroscopic considerations cannot alone establish the geometry of the hydrogen bonded complexes with bifurcated hydrogen bonds. This kind of information can be obtained by ab initio molecular orbital calculations. Hence, we have carried out geometry optimizations on some of the possible intermolecular complexes of 1,2-dimethoxyethane and chloroform by the Hartree−Fock method with the 3-21G* basis set utilizing the Gaussian 98 suite of programs.[35] The input data for Gaussian 98 were prepared by using the graphical molecular modeling program Molda.[36] The optimized structures of the complexes are shown in Figure 8. It is nice to see in this figure that, according to the molecular orbital calculations, the TGT and TGG conformers of 1,2-dimethoxyethane do form three-centered bifurcated hydrogen bonds with chloroform in agreement with our spectroscopic conclusions.

Three-centered hydrogen bonds have been detected by X-ray scattering in molecular crystals and now can be considered as a well-established phenomenon.[2] Among them there are examples of three-centered hydrogen bonds with participation of C−H groups as hydrogen bond donors. Several representative examples of three-centered hydrogen bonds have been studied thoroughly by quantum mechanical molecular orbital calculations.[37] It is very difficult, however, to prove the existence of multicentered hydrogen bonds in liquids. The X-ray scattering cannot supply convincing evidence of bifurcated hydrogen bonds in liquids because of the substantial thermal disorder, and other methods such as IR and NMR spectroscopy should be used. Consequently, there are few known examples of multicentered hydrogen bonds detected in liquids.[38] The present work shows that bifurcated hydrogen bonds in solutions can be established by a careful analysis of the intensification of the X−H stretching vibration and the corresponding enthalpies of hydrogen bonding. It should be noted that this type of bifurcated hydrogen bonding, although with the O−H group as the hydrogen bond donor, has been very recently postulated for complexes of short chain poly(oxyethylene)s and water on the basis of quantum chemical molecular orbital calculations.[39] Some molecular dynamics simulations performed with empirical force fields have also shown that bridges of water molecules coordinated with three-centered hydrogen bonds to the poly(oxyethylene) chain are probably responsible for its helical structure and elastic properties.[40] Multiple C−H···O hydrogen bonds were essential for explaining the experimentally observed selective binding of macrocyclic polyether 1,5-dioxynaphtho-38-crown-10 and bipyridinium ion and the stability of the formed supramolecular complexes.[5] In all these cases, however, there was no direct experimental evidence of the assumed bifurcated hydrogen bonds relevant to solutions of poly(oxyethylene). As the three-centered hydrogen bond discussed here is twice stronger than the conventional hydrogen bond, it should not be a surprise if in the future it turns out that this type of hydrogen bond is a ubiquitous phenomenon that has been overlooked for solutions of poly(oxyethylenes)s in different hydrogen bonding solvents.

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