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optically prepared  $S_2$  state takes place in competition with the internal conversion  $S_2^* \xrightarrow{h\nu} S_1^+$ . Furthermore, from the photoelectron kinetic energies, we have been able to obtain the energy levels of the  $S_2$  and  $S_1$  origins for trimethylamine.

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## Structure of Hydrogen-Bonded *sym*-Dialkylureas in Nonpolar Organic Media

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The trans-trans configuration of the  $-\text{NH}\cdot\text{CO}\cdot\text{NH}-$  groups in dialkylureas leads to their exceptionally strong association. However, we still lack a clear picture of the association mechanism and the structure of the species formed. Here we propose a model for *sym*-dialkylurea (DAU) aggregation in which molecules are linked by four hydrogen bonds, analogous to the associated water molecules. The model gives satisfactory predictions of the spectroscopic and static dielectric behavior of the ureas and allows one to explain the simple Debye nature of dielectric relaxation we observed at the megahertz frequency.

### Introduction

The interpretation of the results obtained for associated systems always presents some difficulties. To achieve reliable conclusions one usually has to combine various experimental techniques. This is a consequence of the complex nature of these systems and numerous molecular parameters affecting their aggregation.

Three active centers of the ureide group  $-\text{NH}\cdot\text{CO}\cdot\text{NH}-$ , capable of forming hydrogen bonds, determine the properties and activity of ureas in all media.<sup>1-4</sup> Ureas are known as the most self-associated compounds which easily dissolve in water and their solubility in organic solvents depends on the kind of substituents to the nitrogen atoms. We studied *sym*-dimethylurea (DMU) and *sym*-diethylurea (DEU), the solubility of which is generally poor in nonpolar organic solvents, yet sufficient for our measurements. The aim of this study was to determine, on the basis of dielectric and IR data, how the aggregation of DAU evolves as a function of concentration and to determine the basic thermodynamic parameters of this process as well as the geometric structure of the aggregates formed.

### Results and Discussion

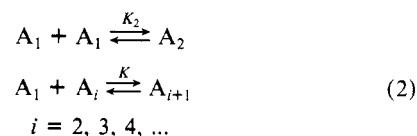
In static dielectric studies, the apparent dipole moment squared,  $\mu_{\text{app}}^2$ , is determined on the basis of measurements of electric permittivity, density, and refractive index.<sup>5</sup>  $\mu_{\text{app}}^2$  equals the dipole moment of a free molecule and it does not depend on the concentration of dipolar substance only for noninteracting systems. In real molecular systems, especially those which undergo strong molecular rearrangements caused by the formation of hydrogen bonds,  $\mu_{\text{app}}^2$  depends on concentration, and the shape of this de-

pendence is related to the structure of the molecular aggregates formed.<sup>6-8</sup>

The strong increase of  $\mu_{\text{app}}^2$  vs. concentration ( $c$ ) observed for DEU (Figure 1) indicates that molecules of this urea form chains with a considerable dipole moment. Of course, this is a progressive process, i.e. dimers, trimers, tetramers, etc. are formed successively. Thus, the experimental dependence of  $\mu_{\text{app}}^2$  on  $c$  is determined by real concentrations of successive multimers (these can be expressed by equilibrium constants) and their dipole moments:

$$\mu_{\text{app}}^2(c) = F(K_2, K_3, \dots, K_i, \dots, \mu_1^2, \mu_2^2, \dots, \mu_i^2 \dots) \quad (1)$$

To fit the theoretical dependence (eq 1) to the experimental data one has to assume a *thermodynamic model* of association for which the *concentrations* of multimers are calculated and to choose the *geometric model* of multimers allowing the determination of their *dipole moments*. Since, as will be seen later, the self-association of ureas develops very rapidly—for concentrations of about 0.05 M there is already a need to consider aggregates composed of as many as a few tens of molecules—one is forced to make some assumptions about the equilibrium constants. Only the first step of the association is considered separately, assuming that each addition of a successive molecule can be described by the same equilibrium constant:<sup>9</sup>



$$K_2 (= c_2/c_1^2) \neq K_3 = K_4 = \dots = K_i = K (= c_{i+1}/(c_1 c_i))$$

Using eq 2 and the values of both equilibrium constants one can calculate the molar concentrations ( $c_i$ ) of successive multimers

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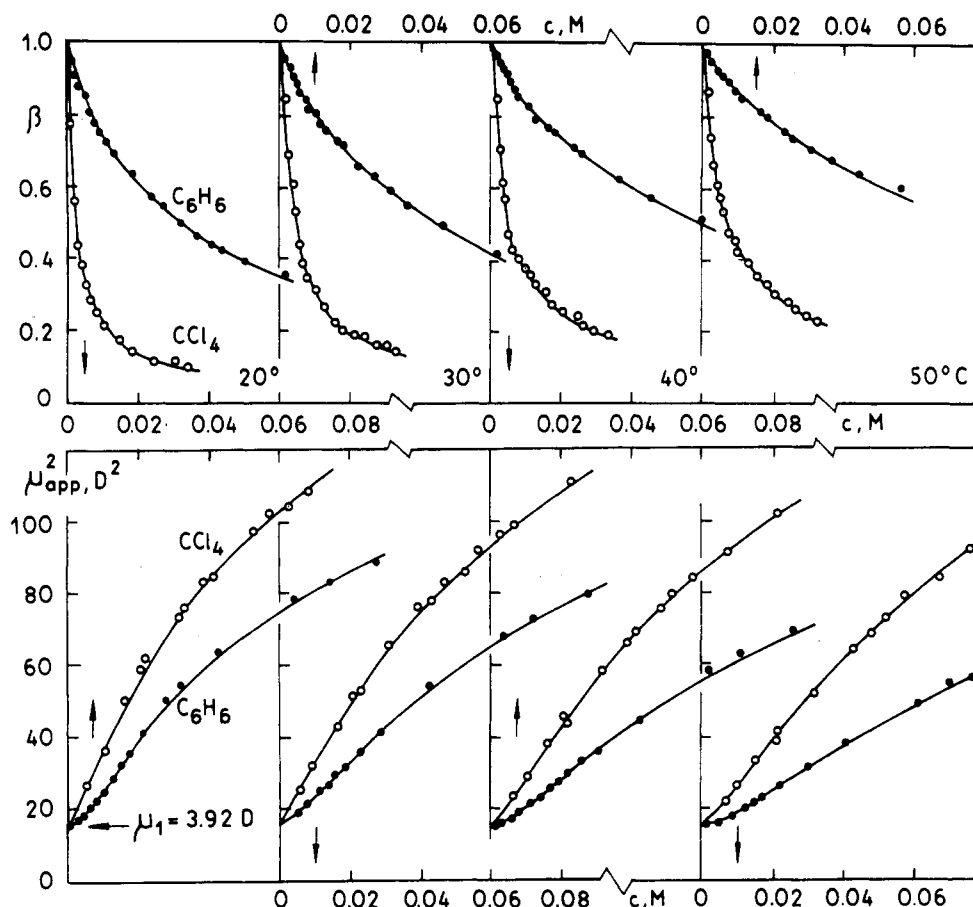


Figure 1. IR spectroscopic ( $\beta$ ) and static dielectric ( $\mu_{app}^2$ ) behavior of  $N,N'$ -diethylurea in nonpolar solvents. The solid lines correspond to our model (eq 5 and 7).

provided that the concentration of monomers ( $c_1$ ) is known. The latter value can be calculated from the mass balance ( $\sum i c_i = c$ ). In our model this equation has the following form:<sup>10</sup>

$$c_1 + \frac{K_2 c_1^2 (2 - K c_1)}{(1 - K c_1)^2} = c \quad (3)$$

The determination of  $K_2$  and  $K$  was based on the IR spectral analysis of the concentration dependence of the molar extinction coefficients ( $\epsilon^{\max}$ ) at the maximum of the band corresponding to the *free* NH groups, i.e. monomers and terminal NH groups of multimers. The band appears at  $\sim 3400 \text{ cm}^{-1}$  and its position depends slightly on the nature of the substituents at the nitrogen atoms and on the solvent. In Figure 1 this extinction coefficient is expressed in a dimensionless form  $\beta = \epsilon^{\max} / \epsilon_{\infty}^{\max}$ , where  $\epsilon_{\infty}^{\max}$  denotes the value extrapolated to the infinite dilution of urea. This is a convenient way of presenting the spectroscopic data obtained at various temperatures. Moreover, if all kinds of multimers (including monomers) have the same number of terminal NH groups, as in case of *trans*-amides<sup>6-8</sup> and dialkylureas, then  $\beta$  directly expresses the reciprocal of the average degree of association  $\chi$ :

$$\beta(c) = \frac{\epsilon^{\max}(c)}{\epsilon_{\infty}^{\max}} = \frac{N_{\text{N-H, free}}}{N_{\text{N-H, total}}} = \frac{\text{no. of associated species}}{\text{no. of molecules}} = \frac{1}{\chi(c)} \quad (4)$$

Our proposed geometric structure for the *sym*-dialkylurea aggregates is shown in Figure 2. This is a chain of urea molecules linked by four N-H...O=C hydrogen bonds. This structure explains both the high stability of urea aggregates and the ease

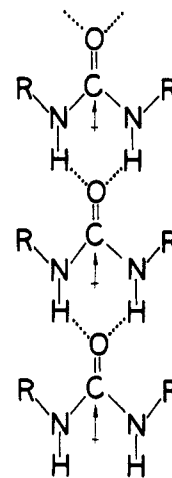


Figure 2. Aggregate of the four hydrogen-bonded  $N,N'$ -dialkylureas.

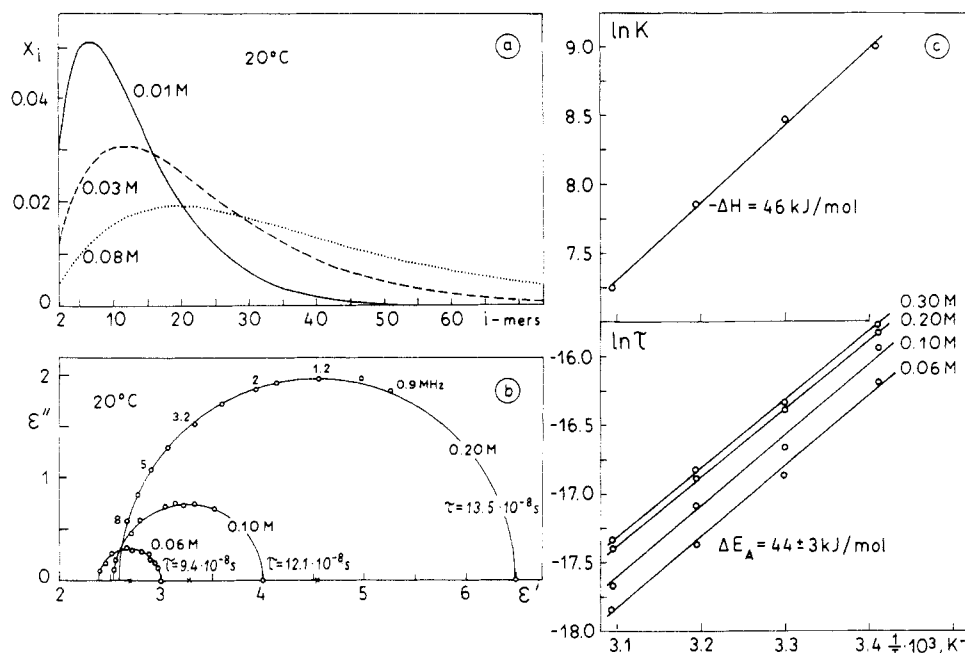
with which they can merge into the hydrogen-bonded structures of water. The above model coherently explains the spectroscopic and dielectric manifestations of the exceptionally strong self-association of ureas. If every real specimen appearing in the solution contains two free NH groups then, according to our thermodynamic model, eq 4 takes the following form:

$$\beta(c) = \frac{1 + K_2 c_1 / (1 - K c_1)}{1 + K_2 c_1 (2 - K c_1) / (1 - K c_1)^2} \quad (5)$$

where  $c_1$  is given by eq 3.

The best fit of this theoretical dependence to the experiment is shown in Figure 1 (solid lines), whereas the values of equilibrium constants resulting from this fit are collected in Table I. The table also contains the values of thermodynamic parameters obtained with the van't Hoff method.

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**Figure 3.** Main features of the *N,N'*-diethylurea association in  $\text{CCl}_4$ : (a) *i*-mer molar fraction distributions for various DEU concentrations, (b) dynamic dielectric characteristics of the system, (c) the same values of enthalpy  $\Delta H$  (IR spectroscopy) and activation energy  $\Delta E_A$  (dielectric relaxation) indicate that two hydrogen bonds are broken in the reorientation process of this molecule.

**TABLE I: Thermodynamic Parameters<sup>a</sup> of the *sym*-Dialkylurea Self-Association in Nonpolar Organic Media**

temp, °C	diethylurea in $\text{CCl}_4$		diethylurea in $\text{C}_6\text{H}_6$		dimethylurea in $\text{C}_6\text{H}_6$	
	$K_2$	$K$	$K_2$	$K$	$K_2$	$K$
20	1142	8136	214	791		
30	480	4812	157	493	396	906
40	504	2565	103	279	268	497
50	340	1422	77	162	170	251
$-\Delta H_2$ , kJ/mol	32.0		27.4		34.2	
$-\Delta S_2$ , J/(mol K)	50.5		48.7		62.9	
$-\Delta H$ , kJ/mol	46.1		42.1		52.1	
$-\Delta S$ , J/(mol K)	82.1		87.8		115.0	

<sup>a</sup> Equilibrium constants are expressed in molar fraction units. The values of enthalpy and entropy correspond to formation of two N-H...O=C hydrogen bonds (Figure 2).

Since in the proposed model the dipole moments of *i*-mers are a simple sum of moments of individual segments of a chain

$$\mu_i = i\mu_1 \quad (6)$$

one can reproduce the theoretical dependence  $\mu_{\text{app}}^2$  vs. *c*. As shown in Figure 3a, the chains of urea molecules may be quite long. That implies an anisotropy of their shapes which, as an important factor in the theory of dielectrics,<sup>11</sup> should therefore be considered here. We have approximated the shape of multimers with rotational ellipsoids. For mixtures of dipolar ellipsoids immersed in nonpolar solvents eq 1 takes the form:<sup>12</sup>

$$\mu_{\text{app}}^2(c) = \frac{1}{c} \sum c_i \mu_i^2 (1 - \delta \eta_i) \left[ \frac{1 + \eta_i}{1 - \lambda \eta_i} \right]^2 \quad (7)$$

where  $\delta$  and  $\lambda$  are the simple functions of electric permittivity and refractive index;  $\eta_i$  denotes the anisotropy of deformational polarizability of *i*-mer, which can be related to the shape anisotropy in the following way:<sup>12</sup>

$$A_i^a = \frac{1}{3} + \frac{n^2 + 2}{3(n^2 - 1)} \eta_i \quad (8)$$

The shape coefficients  $A_i^a$  (index *a* indicates that the dipole moment of multimer is directed along the long axis *a* of ellipsoid) are given by the following formula:

$$A_i^a = \frac{a_i b_i c_i}{2} \frac{ds}{(s + a_i)^{3/2} [(s + b_i^2)(s + c_i^2)]^{1/2}} \quad (9)$$

For the rotatory ellipsoid  $a \neq b = c$ , the evaluation of integral 9 is easy.<sup>7</sup> We assumed that for all multimers  $b_i = c_i = a_1$  (radius of monomer) and the long axis  $a_i = ia_1$ . Thus, it is a chain in which balls of radius  $a_1$  are set side by side along a straight line. The volume of the ellipsoid representing the *i*-mer is equal to the *i* multiplicity of the sphere representing the monomer.

This simplified model fairly well describes the experimental dependences of  $\mu_{\text{app}}^2$  on the concentration of urea in nonpolar media (solid lines in Figure 1). For benzene solutions, in which the self-association of urea is not as extensive as in carbon tetrachloride, eq 7 (together with eq 6 and the equilibrium constants given in Table I) reproduces the experimental data with excellent accuracy (better than 1%). Very long multimers are frequently not linear; if that is the case, the resultant dipole moment of a chain is reduced. We observed this for carbon tetrachloride solutions for which we slightly modified eq 6 in order to achieve a satisfactory reproduction of the experimental data ( $\mu_i = 0.9i\mu_1$ ).

The dynamic dielectric behavior of *sym*-dialkylureas in nonpolar solvents was not easy to predict. Unexpectedly, the dielectric relaxation of these systems appeared within a relatively low-frequency range (MHz). The main features of this relaxation for DEU in carbon tetrachloride are shown in Figure 3b. Despite the complexity of the system (Figure 3a) the observed relaxation reveals a Debye behavior over the whole studied range of concentration and temperature, whereas the relaxation time slightly depends on the concentration of urea, i.e. on the degree of self-association.

It is well-known that the dielectric relaxation of water, observed at gigahertz frequencies, also is of the Debye type.<sup>13</sup> The essential difference in relaxation behavior of these two systems (frequency range differs by three orders of magnitude) can be explained within the frame of our model. The identical values of enthalpy  $\Delta H$  and activation energy  $\Delta E_A$ , determined from Arrhenius plots of equilibrium constants and dielectric relaxation times (Figure 3c), show that the reorientation of the diethylurea molecules results in two broken hydrogen bonds. For water, the dependence  $\ln \tau \sim T^{-1}$  gives  $\Delta E_A$  of about 23 kJ/mol which corresponds to the

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energy of one hydrogen bond.<sup>13</sup>

The direct relation between the activation energy  $\Delta E_a$  (and therefore the dielectric relaxation time) and the hydrogen bonds energy  $\Delta H$  has been confirmed in the studies performed for solutions of DEU in benzene. The IR studies showed (Table I) that in benzene the value of  $\Delta H$  is lower by 4 kJ/mol, i.e. by 1.6 in

RT units, in comparison with that obtained in  $\text{CCl}_4$ . This leads to a shift of the relaxation region to a higher frequency. For the 1.7 M solution of DEU in benzene the dielectric relaxation time equals  $22.7 \times 10^{-9}$  s at 20 °C. The ratio  $\ln \tau_{\text{CCl}_4} / \ln \tau_{\text{C}_6\text{H}_6} \approx 1.8$  is close to the value (1.6) evaluated on the basis of the difference in the hydrogen bond energy in these two media.

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## Coherent Anti-Stokes Raman Scattering Spectrum of $\text{O}_2$ Adsorbed on a ZnO Optical Waveguide

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The vibrational spectrum of physically adsorbed molecular oxygen has never been observed on oxide surfaces. Using the planar optical waveguide geometry has made it possible to observe the CARS spectrum of this species on ZnO at an  $\text{O}_2$  pressure of 1 atm. The required CARS sensitivity was achieved by establishing an interference condition within a ZnO waveguide to eliminate the contribution from the nonresonant susceptibility of the ZnO and by taking advantage of the short penetration depth of the guided waves into the region above the surface. The observed vibrational frequency was  $1549 \text{ cm}^{-1}$ . The nature of the adsorption site is discussed in terms of interactions of  $\text{O}_2$  with the ZnO, surface hydroxyl groups, and adsorbed water.

### Introduction

Spectroscopic studies of surface oxygen have proven to be valuable in the elucidation of catalytic oxidation mechanisms. The types of chemisorbed oxygen which have been spectroscopically detected on metal oxide surfaces are  $\text{O}_2^+$ ,  $\text{O}_2^-$ , and  $\text{O}_2^{2-}$  which have vibrational frequencies of 1905, 1075–1195, and 790–932  $\text{cm}^{-1}$ , respectively.<sup>1</sup> These strongly chemisorbed species have been extensively investigated for many years. However, there is no reliable spectroscopic evidence for the existence of the neutral oxygen molecule adsorbed on the surface of any metal oxide, even though its existence has been confirmed by heat of adsorption and thermal desorption experiments.<sup>2</sup> In principle, molecular oxygen physisorbed on an oxide surface can be seen with IR spectroscopy by virtue of the breaking of the symmetry of  $\text{O}_2$  through interactions with the surface. In practice, if  $\text{O}_2$  is weakly bound through van der Waals interactions the induced absorption cross section will be small. To date, the only related data was reported by Forster and Schuldt,<sup>3</sup> who used IR spectroscopy to find a vibrational frequency of  $1557 \text{ cm}^{-1}$  for physisorbed oxygen inside the zeolitic matrices, Na-A and NaCa-A, at 135 K and 0.2 Torr. With spontaneous Raman spectroscopy on oxide powders, the  $\text{O}_2$  vibration would be detectable were it not for the low density of  $\text{O}_2$  on the surface at room temperature.

In the vibrational spectroscopy of adsorbates on oxide surfaces, three major problems have been encountered. First, both IR absorption and spontaneous Raman scattering are so insensitive that samples with large surface areas must be used. When powders are used, the surfaces are rough and can neither be characterized by Auger or photoelectron spectroscopies nor be cleaned by ion sputtering. Electron energy loss spectroscopy (EELS) is very sensitive but lacks both spectral resolution and the ability to be performed under non-UHV conditions. Second, IR and Raman suffer from interfering signals from the bulk oxide. Third, these

techniques are not sufficiently surface-specific to be generally useful over the full range of interesting chemical situations.

Waveguide surface coherent anti-Stokes Raman scattering (CARS) presents an attractive solution to these problems.<sup>4</sup> The concept is to perform three-wave mixing with the evanescent fields above an optical waveguide. Using the planar optical waveguide geometry has allowed the efficient generation of CARS signals in polystyrene waveguides.<sup>5</sup> The anticipated surface sensitivity, utilizing an interference effect in the waveguide film, was realized by the detection of a CARS spectrum from a thin film of  $\text{TiO}_2$  on a  $\text{Nb}_2\text{O}_5$  waveguide.<sup>6</sup> Identification of adsorption sites for pyridine and phenol on a hydroxylated ZnO surface demonstrated the value of waveguide CARS as a surface spectroscopy.<sup>7</sup> In this work, we utilize the unique attributes of surface CARS to obtain the vibrational frequency of very weakly bound  $^3\Sigma_g^- \text{O}_2$ .

### Theory

Figure 1 shows the experimental geometry in which laser beams are coupled into and out of a thin film optical waveguide. The waveguide structure consists of a silica substrate of refractive index  $n_3$ , a film (thickness  $\approx 1 \mu\text{m}$ ) of index  $n_2$  and a superstrate of index  $n_1$ . When  $n_2$  is greater than  $n_1$  and  $n_3$ , a field will be constrained by total internal reflection and will propagate through the film as a guided wave. The films can be made of transparent materials such as polymers and oxides. To obtain a CARS spectrum of the film or the surface, fields at  $\omega_1$  and  $\omega_2$  are coupled into the film through an optically contacted prism, and the field at  $\omega_3 = 2\omega_1 - \omega_2$ , which is generated as a guided wave, is coupled out of the film through another prism. The Raman shift is  $\Delta = \omega_1 - \omega_2$ .

Coherent Raman scattering benefits from the waveguide geometry to a much greater extent than spontaneous Raman

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