sential for efficient synthesis of AB. The formation of two maxima is conditioned by the fact that the thermal energies of the molecules ABC and AB + C are usually close. Therefore, the total energy of the system AB + C is higher than the energy of the initial substance by about the value of the energy D_{AB-C}. Thus, the average energy of the molecular ensemble AB formed at thermal dissociation turns out to be much higher than in the case of laser dissociation. Indeed, even though the molecules AB are formed directly at the dissociation instant cold, i.e., with energy close to $\epsilon^{D}_{AB-C} - D_{AB-C}$, under thermal reaction conditions they acquire quickly in collisions an additional energy D_{AB-C}, which they lack, to reach the equilibrium one.

This comes about in times shorter than the decay time, and so rigid after the dissociation of ABC the product AB is ready, too, for further dissociation. On the other hand, in the case of collisionless laser-induced dissociation the molecules AB remain cold. with MP excitation there is no decay of AB except when MP excitation pumps AB above ϵ^{D}_{A-B}.

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Registry No. $(CF_3)_3CBr$, 754-43-8; $(CF_3)_3CI$, 4459-18-1; CF_3Br, 75-63-8; SF_6, 2551-62-4; C_2F_6, 76-16-4; CF_3Cl, 75-72-9.

ARTICLES

Intramolecular Hydrophobic Association of Two Alkyl Chains of Oligoethylene Glycol Diethers and Diesters in Water

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The octanol–water partition coefficients *P* of $C_nH_{2n+1}O(CH_2CH_2O)_mC_nH_{2n+1}$ and $C_nH_{2n+1}COOCH_2CH_2OCOC_nH_{2n+1}$ are measured and analyzed on the basis of an empirical linearity between cavity surface area *S* and hydrophobicity. The slope *a* of log *P* vs. total alkyl chain length n_t plots of these double chain compounds is smaller than that, a_I, of oligoethylene glycol monoethers. The slope of log *P* vs. *m* plots at constant *n* is dependent on *n* and *m* for these diethers but is independent of *n* and *m* for the monoethers. These facts suggest that two alkyl chains of the diethers associate intramolecularly in water. As the distance *d* between two alkyl chains in the all-trans arrangement decreases, *S* of a solute molecule decreases. On the basis of the above results and the conformations of related compounds, several conformations of diethylene glycol diethers in water can be considered and the most probable conformation of $ROCH_2CH_2OCH_2CH_2OR$ is suggested as follows: tggttg′g′t. The conformations of ethylene glycol diethers and diesters are also suggested.

Introduction

Hydrophobic interactions play an important role in aqueous media for a wide variety of compounds and phenomena, such as high-order structures of biological membranes and proteins,[1] biological activities of drugs,[2,3] and partition equilibria.[1-3] This hydrophobic effect can cause intramolecular association of double alkyl chain compounds.[1,3] For instance, the critical micellization concentrations (cmc) of lecithins, major components of biomembranes, are explained by taking this effect into consideration,[1] and the antidepressant activity of dialkyl barbiturates is influenced by this effect.[3] The decreased hydrophobicity of double alkyl chain compounds relative to single chain isomers was suggested to result from the decreased surface area in contact with water,[1,3] but this interpretation has not yet been confirmed quantitatively.

Hermann developed a computer program for determining the molecular surface area *S* and showed that the solubilities C_w of alkanes in water are well correlated with *S* irrespective of branching and cyclization:[4]

$$\mu_l^\circ - \mu_w^\circ = kT \ln C_w = -\alpha S + \beta \qquad (1)$$

Here μ_l° and μ_w° denote the chemical potential of an alkane in the liquid state and the standard chemical potential of the alkane referred to infinite dilution, respectively. A similar conclusion was reached by counting the number of packed water molecules about the solute molecule constructed with CPK molecular models.[5] Surface area approaches were also applied for proteins.[6]

In this work, we report on the intramolecular association of oligoethylene glycol diethers and diesters in water from the viewpoint of cavity surface area. Oligoethylene glycol diethers and diesters are chosen, since most of these are commercially

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available and the partition coefficients P of these compounds between 1-octanol and water are easily determined. Octanol is chosen, since a number of P data for this oily phase are available in the literature.[7,8] The degree of intramolecular association should depend on the separation of two alkyl chains connected with a spacer group. Oligoethylene glycols are chosen as the spacers, since these are well characterized as part of polyethylene oxides,[9-11] nonionic surfactants,[12] and crown ethers.[13] Contrary to a naive expectation from the all-trans conformation, the degree of intramolecular association increases with an increase in oxyethylene units. This result will be discussed in terms of chain folding of the diethers and diesters in water.

Experimental Section

Materials. 1-Octanol, ethylene glycol (EG) dialkyl ethers (methyl, ethyl, and *n*-butyl) and diesters (acetate and butyrate), EG and diethylene glycol (diEG) monoalkyl ethers (ethyl, *n*-butyl, and *n*-hexyl), and diEG dialkyl ethers (methyl, ethyl, and *n*-butyl) were obtained from Tokyo Kasei Organic Chemicals or Nakarai Chemicals. Ethylene glycol dipropionate was synthesized from EG and propionic acid in the presence of 2-naphthalenesulfonic acid as catalyst and purified by distillation. These materials were gas-chromatographically (GC) 99% pure or more. The ion-exchanged water was twice distilled before use.

Determination of Partition Coefficients. A solute was dissolved in 1-octanol previously saturated with water. This octanol solution (0.5 to 2 mol/L) was added into water (0.5- to 50-fold volume) previously saturated with 1-octanol and the mixture was shaken for 1–2 h. This mixture was allowed to stand for 1–2 h before separation of the two layers. In most cases, the concentration of the solute in the octanol and/or aqueous phase was determined by GC (Shimadzu gas chromatograph GC-3BT). For EG diesters, the solute concentration in the octanol phase was determined by GC and high-performance liquid chromatography (HPLC, Shimadzu LC-3A) and, furthermore, the concentrations of the dipropionate and the dibutyrate in the aqueous phase were determined by the chromotropic acid method[14] after hydrolysis with sodium hydroxide. These methods gave very similar partition coefficients. The partition coefficient of a solute was determined at four or five concentrations and was independent of the concentration. Relative errors in the partition coefficient values are within 7%.

Determination of Molecular Surface Area. The cavity surface area was calculated by two methods, viz. computer and CPK methods. The computer surface area S_{COM} of a molecule in water is defined as the area of the surface traced out by the center of a water molecule (the radius r_w is assumed to be 1.5 Å) rolling over the van der Waals surface of the solute molecule. Standard interatomic bond lengths, bond angles, torsional angles, and Bondi atomic radii[15] for a molecule are the required input for the program by Hermann.[4] The following atomic radii were used: 1.70 Å for carbon, 1.20 Å for hydrogen, and 1.52 Å for oxygen. The computation was made with a FACOM M-382 computer at the Data Processing Center, Kyoto University. The CPK surface area S_{CPK} was determined by packing spheres representing water molecules (radius assumed to be 1.0 Å) around CPK molecular models.[5] The number N of packed spheres is converted to the absolute surface area by devising a proportionality constant based on the surface area of hypothetical atoms (radius R); a proportionality constant of 3.99 is evaluated from $4\pi(R + r_w)^2/N$ and is independent of R.

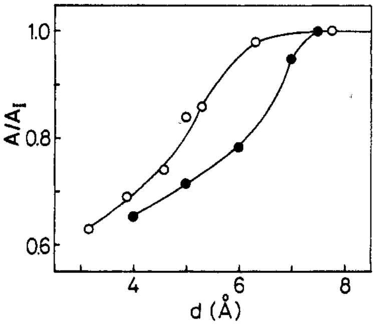

Figure 1. Computed quantity A/A_I of two alkyl chains as a function of the distance between these parallel chains. The open and filled circles are calculated by use of S_{CPK} and S_{COM}, respectively.

Results

Cavity Surface Areas of Double Alkyl Chain Compounds. Computer and CPK methods were used for determining the cavity surface area, as described in the Experimental Section. There is no general agreement as to what cavity area is best correlated with hydrophobicity.[16] The cavity surface area of a molecule depends on the conformation of the solute molecule in water. For instance, 13 rotational conformers for *n*-heptane can coexist and have different cavity areas (S_{COM}), ranging from 322.1 to 350.6 Å^2/molecule.[4] With these in mind, we determined S_{COM} and S_{CPK} for 13 single-conformation alkanes including ethane and propane. Hermann did not include these gaseous alkanes[4] and Reynolds et al. included multiconformation alkanes for analysis.[5] For these 13 alkanes, log x_w is well correlated with S_{COM} and S_{CPK} (correlation coefficients are 0.9934 and 0.9959, respectively), yielding hydrophobic free energies per unit area α of 31 and 41, respectively.[17]

In general, the logarithms of the aqueous solubility C_w, cmc, and P of homologues are linear vs. the number of carbon atoms in an alkyl chain(s):

$$\log\,(C_w,\ \text{cmc, or}\ 1/P) = -an + b \tag{2}$$

As can be seen from comparison of eq 1 and 2, the value of a is proportional to the increment per methylene in free energy of transfer. In most cases, coefficient a does not depend on the kinds of compounds and quantities measured. However, the a value for double alkyl chain compounds is often smaller than that for single chain isomers.[3]

The most simple conformation of an alkyl chain conforming to the empirical equation, eq 2, is the all-trans arrangement of carbon atoms in the alkyl chain. Therefore we will assume this conformation for all alkyl chains hereafter. The fact that the a value for double alkyl chain compounds is generally independent of n and smaller than that for single chain isomers suggests that the two alkyl chains on a molecule are parallel. Therefore we calculated the S_{CPK} and S_{COM} of homologues in such an arrangement of two alkyl chains with an appropriate connecting group (spacer). In this case, the cavity surface areas increase linearly with an increase in n and for each homologue B is a constant:

$$S = An + B \tag{3}$$

Futhermore we determined A (increment per methylene in S) as a function of the distance d between the two parallel planes formed by the all-trans carbon atoms of the two alkyl chains. When d is large enough, A for double chain compounds conforms to that for single chain compounds, viz. A_I. Therefore we plotted A/A_I as a function of d in Figure 1. S_{CPK} is one of the smallest cavity areas whereas S_{COM} is one of the largest. Therefore, even if other cavity areas are used, A/A_I will fall between those for S_{CPK} and S_{COM}. When d is larger than 8 Å, two or more water molecules can penetrate between the two alkyl chains of a molecule. The minimum of A/A_I is about 0.65 for both methods.

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TABLE I: Partition Coefficients (in Molarity Units) of Oligoethylene Glycol Diethers and Diesters between 1-Octanol and Water at 25.0 °C

n	log P	n	log P
EG monoether		diEG monoether	
2	−0.35	2	−0.54
4	0.76	4	0.56
6	1.86	6	1.70
EG diether		diEG diether	
1	−0.21	1	−0.36
2	0.66	2	0.39
4	2.48	4	1.92
EG diester			
1	0.19		
2	1.19		
3	2.16		

TABLE II: Slopes of Eq 2 and the Distance between Two Parallel Chains Estimated from a/a_I and Figure 1

compd	a	a/a_I	d, Å	
			CPK	COM
EG monoether	0.553	1		
diEG monoether	0.560	1		
EG diether	0.448	0.81	5.1	6.2
diEG diether	0.380	0.68	4.0	4.6
EG diester	0.505	0.91	5.7	6.8
alcohol	0.570[a]	1		
ether	0.595[b]	1.04		

[a] Taken from ref 7. [b] Unpublished results.

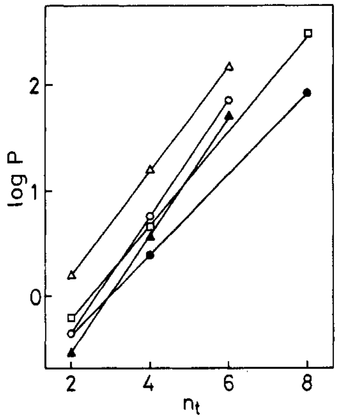

Figure 2. Logarithm of octanol–water partition coefficients of EG monoethers (○), diEG monoethers (▲), EG diethers (□), diEG diethers (■), and EG diesters (△) as a function of n_t at 25 °C.

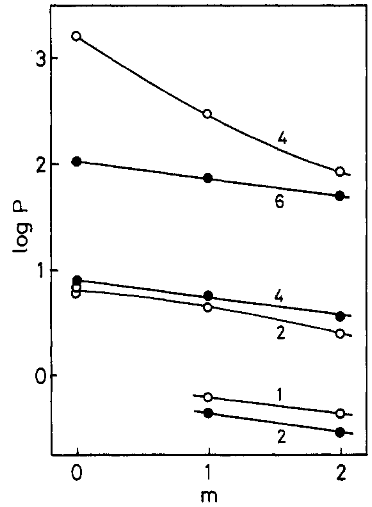

Figure 3. Logarithm of octanol–water partition coefficients of oligoEG monoethers (●) and diethers (○) as a function of the number of the EG unit, keeping the alkyl chain length n constant. The number attached to each line denotes n for $C_nH_{2n+1}O(CH_2CH_2O)_mH$ and $C_nH_{2n+1}O(CH_2CH_2O)_mC_nH_{2n+1}$.

TABLE III: Five Conformations of Diethylene Glycol Diethers with Different Torsional Angles

torsion angle	conformation				
	A	B	C	D	E
θ_1	180	180	180	194	180
θ_2	60	−120	−121	−110	180
θ_3	60	60	50	30	60
θ_4	180	180	163.5	180	180
θ_5	180	180	163.5	180	180
θ_6	−60	−60	50	30	−60
θ_7	−60	120	−121	−110	180
θ_8	180	180	180	194	180

Partition Coefficients of Oligoethylene Glycol Diethers and Diesters. The partition coefficients of EG monoalkyl ethers, diEG monoalkyl ethers, EG dialkyl ethers, and EG diacyl esters are shown in Table I. The transfer free energy of a molecule is usually regarded as the sum of a contribution $\Delta\mu_i°$ of each group i of the molecule. For $C_nH_{2n+1}O(CH_2CH_2O)_mC_nH_{2n+1}$, we may write the following equation:

$$\mu_1° - \mu_w° = 2\Delta\mu°_{CH_3} + 2(n-1)\Delta\mu°_{CH_2} + m\Delta\mu°_{CH_2CH_2O} + \text{constant} \quad (4)$$

For these ethers, we may rewrite eq 4 into the empirical form

$$\log P = 2an + bm + \text{constant} \quad (5)$$

As Figure 2 shows, log P of oligoEG diethers and diesters increases linearly with an increase in the total number n_t of carbon atoms in the alkyl chains for each homologue with constant m. In Table II, the slopes of log P vs. n_t plots in Figure 2 are shown for each homologue. A large body of data for such methylene increments have been compiled in reviews.[1,7,8] As expected from eq 4, the values of a for EG and diEG monoalkyl ethers and alcohols are very close to those for other single chain compounds and to those obtained from other parameters, such as aqueous solubility and cmc.[1,7,8] Therefore we can use the a value of single chain compounds (a_I) as a standard and regard a/a_I as a measure of the intramolecular hydrophobic association of double alkyl chains. Taking into consideration the slight dependence of a for single chain compounds on the functional group as standard single chain compound, we chose EG monoethers for EG diethers and diesters, diEG monoethers for diEG diethers, and alcohols for dialkyl ethers. Such a/a_I values are shown in Table II. From eq 1–3, we can obtain the following equation:

$$a/a_I = A/A_I \quad (6)$$

This equation connects partition coefficient data with cavity surface areas for double alkyl chain compounds.

In Figure 3, log P is plotted against the number of oxyethylene units, m, for $C_nH_{2n+1}O(CH_2CH_2O)_mH$ (n = 2, 4, and 6) and $C_nH_{2n+1}O(CH_2CH_2O)_mC_nH_{2n+1}$ (n = 1, 2, and 4). For the monoethers the slope of this plot is independent of n and m, but for the diethers it is dependent on n and m. Even if n is kept constant for the diethers, the state of the alkyl chains is much different; dialkyl ethers are in extended conformations[18] whereas diEG dialkyl ethers are in folded conformations. Therefore, this tendency is striking for dibutyl ethers.

Discussion

Conformations of Oligoethylene Glycol Diethers and Diesters in Water. If a compound is present in water as an equilibrium mixture of two conformers with the ratio K of these conformers, we can expect the following equation:

$$-RT \ln K = \Delta G°_{\text{intrinsic}} + \Delta G°_{\text{hydration}} \quad (7)$$

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TABLE IV: Cavity Surface Areas S_{COM} of Diethylene Glycol Diethers for Conformations A and E

	S, Å^2/molecule		$S_{O(C_2H_4O)_2}$, Å^2/molecule		$S_{dialkyl}$, Å^2/molecule		
group	A	E	A	E	A	E	$\Delta G°_{hydrophobic}$, cal/mol[a]
methyl	353.8	383.2	254.9	244.0	98.9	139.2	−1250
ethyl	404.3	451.4	211.0	196.6	193.3	254.8	−1910
propyl	449.3	515.1	204.1	188.6	245.2	326.5	−2520
butyl	494.0	578.7	203.3	187.8	290.7	390.9	−3110

[a] These values are calculated from eq 9, viz. $31(S_A - S_E)$.

where $\Delta G°_{intrinsic}$ and $\Delta G°_{hydration}$ are the differences in free energy between the two conformers in the gaseous state and on hydration, respectively. For amphiphatic compounds such as diEG diethers, the hydration free energy may be separated into two terms:

$$-RT \ln K = \Delta G°_{intrinsic} + \Delta G°_{hydrophobic} + \Delta G°_{hydrophlic} \quad (8)$$

where $\Delta G°_{hydrophobic}$ and $\Delta G°_{hydrophilic}$ are the corresponding differences in interactions of the hydrophobic and hydrophilic groups with water, respectively. The value of $\Delta G°_{hydrophobic}$ may be written approximately as[4]

$$\Delta G°_{hydrophobic} = \alpha \Delta S_{alkyl} \quad (9)$$

where ΔS is the difference between the cavity surface areas of the two conformers and it is assumed that the difference in cavity surface area of the hydophilic group between the two conformers is small (see Table IV) and does not much contribute to the hydrophobicity (see Figure 3).

There is no study on the conformations of oligoEG diethers and diesters in water. Therefore we attempt to estimate the conformations of these compounds in water from those of polyethylene oxides,[10,11] crown ethers,[13] nonionic surfactants,[12] and model compounds.[18,19] In addition, from a/a_I values and Figure 1, we can estimate the distance between the two alkyl chains for EG diethers and diesters and diEG diethers, as shown in Table II. Conformations conforming to this distance must be considered.

Wieser et al. showed that the most stable conformation of diethyl ether is the extended (all-trans) form in the vapor phase, in the pure liquid, and in CCl_4 and CS_2 solutions.[18] Since the a/a_I value of dialkyl ethers is close to unity (see Table II), this conformation is suggested also in aqueous solution. Thus, since the dialkyl ethers do not fold around the ether linkage, the two alkyl chains cannot associate intramolecularly in water, despite of the shortness of the ether linkage and the tendency for association of the two chains.

The gauche (g) conformer of the OC–CO bond predominates over the trans (t) conformer, in the crystalline and liquid states and in solutions of benzene and dioxane.[9-11,13,19] By succession of this g conformation of the OC–CO bond, a polyethylene oxide molecule $(CH_2CH_2O)_m$ is in a 7_2 helix of $(ttg)_m$ in the crystalline state.[10] Thus, introduction of an ethylene oxide group into a dialkyl ether folds the formed EG molecule so that the two alkyl chains on the molecule can be approached more closely. Therfore, as the number of oxyethylene units increases, a/a_I decreases (Table II).

Iwamoto found that, in crystalline complexes of $RO(CH_2CH_2O)_mR$ with $HgCl_2$, an oligoEG oxide ($m \leq 4$) is in the following conformations:[19]

$$\begin{array}{cccccc} -CH_2- & CH_2- & O- & CH_2- & CH_2- & O \\ t & g & t & t & g' & t \end{array}$$

Futhermore, 18-crown-6-ether in its complex with a K^+ ion is in a similar conformation:[13]

$$\begin{array}{cccccc} (-CH_2- & CH_2- & O- & CH_2- & CH_2- & O)_3 \\ t & g & t & t & g' & t \end{array}$$

From these examples, diEG dipropyl ether in water is expected to be in the conformation tttgttg′ttt as a result of the hydrophobic interaction between the two propyl groups. In this conformation

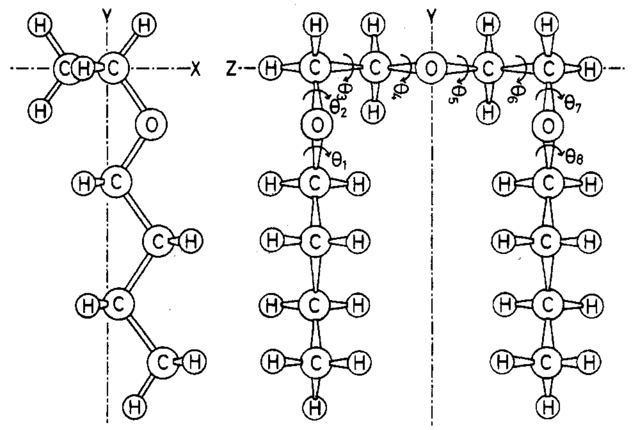

Figure 4. Definition of the torsional angles of diEG diethers and two views of conformation A of diEG dibutyl ether.

TABLE V: Distances between Two Parallel Chains and Increment per Methylene in S for Five Conformations of Diethylene Glycol Diethers

form	d, Å[a]	A, Å^2/molecule[a]	A/A_I
A	4.8	22.5	0.71
B	4.7	21.9	0.69
C	4.7	21.8	0.69
D	4.2	20.9	0.66
E	b	31.8	1

[a] Since the A value calculated from dimethyl and diethyl ethers is slightly larger than that from diethyl, dipropyl, and dibutyl ethers, this value is not included herein (such examples can be seen in Table IV). [b] In conformation E, the two alkyl chains are not parallel and therefore d cannot be determined.

(conformation E in Table III), the two propyl chains are not parallel, albeit close. The torsional angle of each bond of the diEG group can be expected to deviate slightly from 180° and ±60°, with a minor increase in energy, as is seen in the conformations of related compounds.[10,13,19] A number of conformations of diEG dialkyl ethers in water can be considered; four probable conformations (A, B, C, and D) are shown as a function of torsional angles in Table III. Definition of these torsional angles is shown in Figure 4.

The cavity surface area S_{COM} of dimethyl, diethyl, dipropyl, and dibutyl ethers were computed for conformations A, B, C, D, and E. The results for conformations A and E are shown in Table IV. For each conformation, the S values of these ethers except the methyl ether show a linearity to n and the slope of this line gives the A value, as shown in Table V. The relation between d and A/A_I computed independently conforms to the result shown in Figure 1.

In Table IV, the magnitude of $\Delta G°_{hydrophobic}$ for the conformational change of E to A is illustrated for four diEG diethers. As expected, $\Delta G°_{hydrophobic}$ increases with an increase in chain length.[20] Although $\Delta G°_{intrinsic}$ of the diEG diethers for conformations A and E has not been reported, these $\Delta G°_{hydrophobic}$ values

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(20) The increment per methylene in $\Delta G°_{hydrophobic}$ can be estimated from the equation, $2.303RT(a_I - a) = 2.303 \times 1.987 \times 298 \times (0.56 - 0.38) = 247$ cal/mol. This value is very close to that calculated from the $\Delta G°_{hydrophobic}$ values in Table IV.

seem to be comparable with $\Delta G^\circ_{\text{intrinsic}}$ for other compounds.[21] Thus, a conformational change of diEG diethers may be induced by the hydrophobic interactions between the two alkyl chains in water. Two views of conformation A for the diEG dibutyl ether are shown in Figure 4. This seems to be the most probable conformation, since this conformation may be stabilized by hydrogen bonding of two terminal oxygen atoms ($d_{O-O} = 4.80$ Å) with a water molecule while $\theta_2 = -120^\circ$ and $\theta_7 = 120^\circ$ for conformations B, C, and D are not stable torsional angles.[21]

For the conformations of EG diesters and diethers in water, too many possibilities can be considered and two or more conformers may coexist in equilibrium. In crystals of 1,2-dilauroylphosphatidylethanolamine, the two lauroyl chains are parallel and the distance between them is 4.8 Å.[22] Although this compound has a structure similar to EG diesters, this distance is too small to explain the present result (Table II).

Scope and Limitations of the Present Work. For the determination of S, two assumptions are made: one is the assumption that water is a spherical molecule. A nonspherical water molecule is more realistic[23] but then there emerges uncertainty about the orientation of the water molecule around a solute molecule. Second, only the first hydration layer is taken into account but actually the hydration at the surface of an alkane molecule forms multilayers, called an iceberg.

Recently, the gauche/trans ratio of n-butane in water was predicted by microscopic theories based on an integral equation[24] and Monte Carlo method[25] for liquids. However, this ratio for n-butane in water has not yet been determined experimentally. In this work, an alkyl chain is assumed to be in all-trans conformation. As the alkyl chain length decreases, the population of the all-trans conformer increases. Since we deal with short-chain ethers and esters, this assumption will be permitted as a first approximation. On the basis of the present results, four possible conformations of diEG diethers in Table I can be considered and conformation A seems to be the most stable conformation. Spectroscopic studies are underway to confirm this conformation.

By using the present results, we can predict the values of cmc,[1] C_w, and P[3] and the conformations of double alkyl chain compounds which are difficult to determine experimentally. For example, the cmc's of diacylphosphatidylcholines[1] and the P values of dialkyl barbiturates can be predicted more accurately by taking into consideration such interactions.[3]

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Registry No. 1-Octanol, 111-87-5; dimethyl ethylene glycol, 110-71-4; diethyl ethylene glycol, 629-14-1; dibutyl ethylene glycol, 112-48-1; diacetate ethylene glycol, 111-55-7; dibutyrate ethylene glycol, 105-72-6; ethyl diethylene glycol, 111-90-0; butyl diethylene glycol, 112-34-5; hexyl diethylene glycol, 112-59-4; dimethyl diethylene glycol, 111-96-6; diethyl diethylene glycol, 112-36-7; dibutyl diethylene glycol, 112-73-2; dipropionate ethylene glycol, 123-80-8.

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Photolysis of 3-Bromo-3-methyldiazirine

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The photolysis at 354 nm of 3-bromo-3-methyldiazirine in gas phase has been studied. After a careful search of the various possibilities we have found that all available evidence points toward the intermediary formation of hot vinyl bromide, presumably via isomerization of the corresponding carbene. Its unimolecular decomposition can take place by two different paths: one is the molecular detachment of HBr and the other the radical scission of the C–Br bond. This last way of radical formation is responsible for the apparently confusing experimental data. According to our results the activation energy for the radical decomposition is closer to that of the molecular detachment than previously thought.

Introduction

The work reported in this paper represents a continuation of our efforts to determine the nature of the processes occurring in the gas-phase photolysis of diazoalkanes and their cyclic isomers diazirines (see ref 1 and references therein). The subject has been recently reviewed by Liu.[2] The study of the partitioning of energy which takes place upon decomposition has shown some defined trends.[3] While the photodecomposition of diazo compounds seems to take place directly in one step from the electronic state reached by the transition, the photolysis of diazirines is more complicated and probably at least one step in the dissociative process is a function of statistical factors.[4]

One of the controversial points about the mechanism of diazirine gas-phase decomposition is the participation of diazo compounds as reaction intermediaries. This participation suggested by Amrich and Bell in the early 1960s[5] was soon disregarded by Moore and

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