Thermodynamical Analysis of Rotation of Spin Probes in a Sodium Dodecyl Sulfate Micelle

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Abstract: ESR spectra of five spin probes in water, dodecane, and a sodium dodecyl sulfate (SDS) micelle were measured at various temperatures. Linearity was observed between the logarithm of rotational correlation time (τ_c) and $1/T$ in all systems. The τ_c value was analyzed by the theory of absolute reaction rate. The activation enthalpy ($\Delta H^{\ddagger}$) of hydrophobic probes in the micelle was between those in water and dodecane, suggesting that the core was liquid-like. On the contrary, $\Delta H^{\ddagger}$ of hydrophilic probes was greater than that in water. The activation free energy ($\Delta F^{\ddagger}$) of the probes in the micelle was about 1 kcal/mol greater than that in water. This increase of $\Delta F^{\ddagger}$ in the micelle was attributed to the small activation entropy ($\Delta S^{\ddagger}$) in the case of hydrophobic probes in contrast to that of hydrophilic probes, in which a large $\Delta H^{\ddagger}$ was responsible for the increase. The position of the probes in the micelle was discussed on the basis of solubility in water, $\Delta H^{\ddagger}$, and hyperfine coupling constants.

Introduction

The spin label or probe method, proposed by McConnell et al., has been used in micelle chemistry. This method gave much information about the position of a probe dissolved as a solubilizate in a micelle, determined from the hyperfine coupling constant, (a_N), about rigidity of the micelle, calculated from the rotational correlation time (τ_c), and about the cmc value, estimated from the concentration dependency of τ_c.

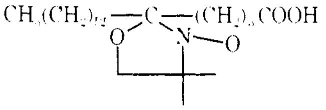
Though τ_c is generally correlated with the viscosity of a medium according to the Debye-Stokes-Einstein equation, a discrepancy remains between the theoretical and experimental values of the radius of the probe molecule when macroscopic viscosity is used. Therefore, it is not always suitable to discuss rigidity of the medium on the basis of τ_c. We proposed an analysis of τ_c by the theory of absolute reaction rate, and it was shown that the analysis enables one to discuss physical properties of the medium in detail.[1] In the present work, τ_c values of various spin probes were measured in water, dodecane, and a sodium dodecyl sulfate (SDS) micelle in order to study the structure of the micelle.

Experimental Section

Spin probes used throughout this experiment have the structure and molecular weight shown in Chart I.

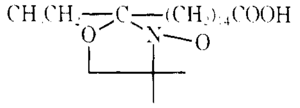
Chart I

2-(3-carboxypropyl)-4,4-dimethyl-2-tridecyl-3-oxazolidinyloxyl (I)



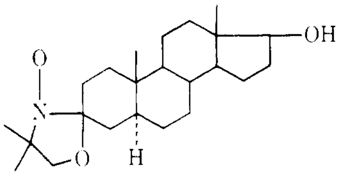
mol wt 384

2-(14-carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidinyloxyl (II)



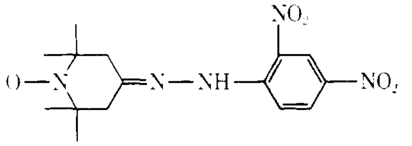
mol wt 384

17β-hydroxy-4',4'-dimethylspiro[5α-androstan-3,2'-oxazolidin]-3'-yloxyl (III)



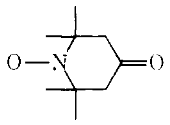
mol wt 376

2,4-dinitrophenylhydrazone of 2,2,6,6-tetramethyl-4-piperidone N-oxide (IV)



mol wt 350

2,2,6,6-tetramethyl-4-piperidone N-oxide (V)



mol wt 170

Probes I, II, and III were obtained from Syva Associates. The method for synthesis of IV and V was described in our previous papers.[2,3]

The purity of SDS (Wako Pure Chemicals Co., Tokyo) was 97%. Dodecane (Tokyo Kasei) was chromatographically pure. They were used without further purification. The concentration of the probe was always in the order of 10^{-4} M. Sample solutions were placed in a capillary tube of 1 mm o.d. in the presence of air for ESR measurement. ESR spectra were recorded on a Japan Electron Optics Laboratory Model JES-3BS.X spectrometer (X-band) with 100-kHz field modulation. The width of modulation was always smaller than the peak to peak width of the center line. Temperature was controlled using a high-precision variable temperature accessory within the accuracy of ±0.05 °C.[4]

Results and Discussion

1. Analysis of τ_c. τ_c was calculated by the following equation.[5]

$$\tau_c = A\Delta H_{(m=+1)}\,[(I_{(m=+1)}/I_{(m=-1)})^{1/2} - 1] \qquad (1)$$

$\Delta H_{(m=+1)}$ is the peak to peak width (in gauss) of the low-field absorption line and $I_{(m=+1)}$ and $I_{(m=-1)}$ are the peak to peak heights for the low- and high-field lines, respectively. The value of A was assumed as 6.6×10^{-10} s g^{-1} according to ref 5. τ_c is generally formulated by the Debye-Stokes-Einstein equation as follows:

$$\tau_c = 4\pi\eta a^3/3kT \qquad (2)$$

Here, a is the averaged radius of a molecule. In our preceding paper,[1] the following equation was derived from the theory of absolute reaction rate.

$$\begin{aligned} 1/\tau_c &= kT/h \exp(-\Delta F^{\ddagger}/RT) \\ &= kT/h \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \qquad (3) \end{aligned}$$

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Table I. Thermodynamic Quantities of Rotation of Probes in Various Systems[a]

solvent	probe	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal/mol
water				
	I	7.32	5.67	4.02
	II	7.44	6.50	3.66
	IV	6.40	4.93	3.53
	V	5.23	4.17	2.80
dodecane				
	I	4.85	1.26	4.12
	II	4.35	1.35	3.56
	IV	4.40	1.62	3.46
SDS micelle				
	I	5.76	0.94	5.21
	I + NaOH	5.58	0.20	5.46
	II	6.10	2.32	4.75
	II + NaOH	6.06	2.66	4.51
	III	7.25	3.19	5.39
	IV	7.29	4.41	4.72
	V	7.29	5.39	4.15

[a] $\Delta H^{\ddagger}$ was obtained from the slopes in Figures 1-4. $\Delta S^{\ddagger}$ and $\Delta F^{\ddagger}$ were calculated using $\Delta H^{\ddagger}$ and τ_c at 20 °C.

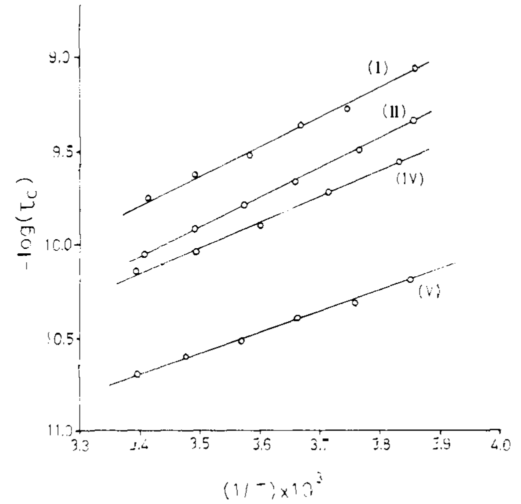


Figure 1. Relationship between $1/T$ and log (τ_c) of probes I, II, IV, and V in water.

Here T is the absolute temperature, and k, h, and R are Boltzmann's, Planck's, and gas constants, respectively. $\Delta F^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta H^{\ddagger}$ are the activation free energy, activation entropy, and activation enthalpy of the rotation of a probe, respectively.

2. Water System. Figure 1 shows the relationship between the logarithm of τ_c measured in water and the reciprocal of the absolute temperature. Measurement of the ESR spectra of probe III was impossible because solubility of the probe was low. Similarly, solubility of probes I and II was low, so that NaOH (10^{-3} M) was added to the solution in order to increase their solubility. Most points were on a straight line in a narrow region of temperature, showing that analysis using eq 3 was possible within a sufficient accuracy. Resulting values of $\Delta F^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta H^{\ddagger}$ are listed in Table I.

η in eq 2 was always replaced by the macroscopic viscosity.[6] The activation energy of viscosity of water, calculated from viscosity data,[7] was 4.9 kcal/mol in this temperature range. $\Delta H^{\ddagger}$ of all probes must agree with the activation energy of viscosity of water, if eq 2 holds for all cases. It was reported that $\Delta H^{\ddagger}$ of a water molecule, obtained from the data of dielectric dispersion, agreed with the value.[8] However, all values of $\Delta H^{\ddagger}$ in water in Table I were larger than 4.9 kcal/mol and tended to increase with increasing radius of the probe molecule in contrast to expectation. This result suggests that activation for flowing of water is different from that for rotation of spin probes. The order of the amount of $\Delta S^{\ddagger}$ agreed with that of $\Delta H^{\ddagger}$.

3. Difference of $\Delta F^{\ddagger}$ between Probes I and II in Water. $\Delta F^{\ddagger}$ of probe I in water was different from that of probe II, in spite of their same molecular weight. This is apparently due to the difference of $\Delta S^{\ddagger}$.

The center of gravity of probe I is located between two carbons at 7 and 8 positions when the molecule adopts the fully extended conformation. In the case of probe II, the center is between two carbons at 10 and 11 positions. Assuming that the rotation of the N-O group is the sum of that around the center of gravity and that caused by internal rotation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of each rotation were designated as $\Delta H^{\ddagger}{}_{g}$, $\Delta H^{\ddagger}{}_{int}$, $\Delta S^{\ddagger}{}_{g}$, and $\Delta S^{\ddagger}{}_{int}$, respectively. τ_c was rewritten as follows:

$$1/\tau_c = kT/h\,\{\exp(\Delta S^{\ddagger}{}_{g}/R)\exp(-\Delta H^{\ddagger}{}_{g}/RT) + \exp(\Delta S^{\ddagger}{}_{int}/R)\exp(-\Delta H^{\ddagger}{}_{int}/RT)\} \quad (4)$$

As a linear relationship exists between log (τ_c) and $1/T$, the following approximation is possible.

$$\Delta H^{\ddagger}{}_{g} \simeq \Delta H^{\ddagger}{}_{int} = \Delta H^{\ddagger} \quad (5)$$

Accordingly,

$$1/\tau_c = kT/h\{\exp(\Delta S^{\ddagger}{}_{g}/R) + \exp(\Delta S^{\ddagger}{}_{int}/R)\} \times \exp(-\Delta H^{\ddagger}/RT) \quad (6)$$

The difference between $\Delta S^{\ddagger}{}_{g}$ of probes I and II must be small because they have the same molecular weight and a similar structure. On the contrary, the number of single bonds which are capable of free rotation between the N-O group and the center of gravity was 2 and 5 in I and II molecules. Therefore, $\Delta S^{\ddagger}{}_{int}$ of II is larger than that of I, resulting in the difference of $\Delta S^{\ddagger}$.

4. Dodecane System. Figure 2 shows the result in dodecane. As the width of each absorption line of every probe was far wider than that in water and the change of the ratio, $I_{(m=+1)}/I_{(m=-1)}$, was small, reliability of the values of τ_c, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ is low compared with that in water. $I_{(m=+1)}$ and $I_{(m=-1)}$ were nearly equal, especially in the spectra of probes III and V, which made calculation of τ_c impossible. The activation energy of viscosity of dodecane was 3.47 kcal/mol, and $\Delta H^{\ddagger}$ of three probes was larger than the value in water.

5. Micelle System. Figures 3 and 4 show the results in a SDS micelle. As shown in Figure 4, marked deviation from the straight line was found in the region beyond $\tau_c > 1.6 \times 10^{-9}$ s. This deviation is taken as the result of eq 1 being used beyond the applicable limit ($\tau_c < 10^{-9}$ s).[9]

Interesting is the result when NaOH (10^{-2} M) was added to the SDS solution. τ_c of probe I increased by this addition, whereas τ_c of probe II decreased. The concentration dependency of this change was explained in detail in our previous paper.[10] However, $\Delta H^{\ddagger}$ hardly changed by the addition of NaOH, showing that the change was due to that of $\Delta S^{\ddagger}$. The terminal carboxyl groups of the probes have a possibility of distributing in the core and in the surface (Stern) layer of the micelle. Tokiwa et al.[11] reported that polar solubilizates penetrated more deeply into the core of a SDS micelle with increase in the volume of the hydrophobic moiety, on the basis of the NMR spectra of aromatic alcohols and phenols. A similar conclusion was obtained in the case of anionic surfactant micelles.[12] The hydrophobic alkyl part of probes I and II is taken as being large enough to incorporate the terminal carboxyl group in the core. Therefore, the probes are predominantly present in the core. This is the same assumption as proposed in our previous paper on the basis of the ratio of τ_c of them.[10] Carboxyl groups may be ionized by the addition

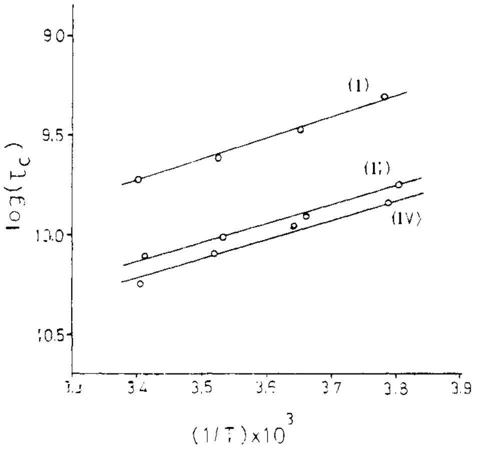


Figure 2. Relationship between $1/T$ and log (τ_c) of probes I, II, and IV in dodecane.

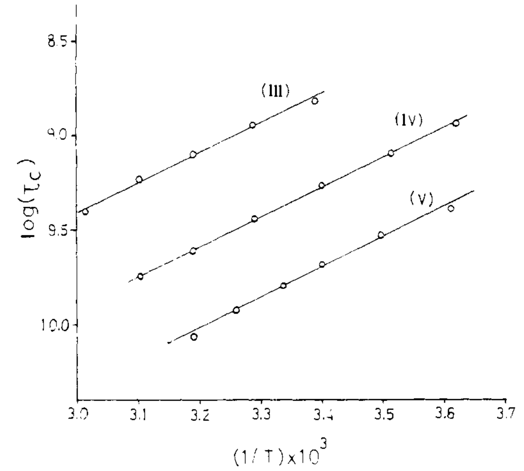


Figure 3. Relationship between $1/T$ and log (τ_c) of probes III, IV, and V in a SDS micelle (10% aqueous solution).

of NaOH and become energetically difficult to be incorporated in the core. As a result, the groups are fixed in the surface layer with sulfate groups and the mode of motion of the probes may change, resulting in hindered rotation around the center of gravity. Accordingly, $\Delta S^{\ddagger}{}_g$ is taken to be nearly zero in this case. However, $\Delta S^{\ddagger}{}_{\text{int}}$ becomes larger than that before the addition of NaOH because fixation of the end of the molecule on the surface affects the motion similarly, as the center of gravity was transferred to the end, and the number of single bonds which contribute to the internal rotation is increased. As a result, $\Delta S^{\ddagger}$ decreased in the case of probe I and increased in the case of probe II.

$\Delta H^{\ddagger}$ of probe IV in water was about 1 kcal/mol smaller than those of probes I and II, despite their comparable molecular weight. This may be explained by the concept that the length of probe IV along the molecular axis is shorter than those of probes I and II. However, $\Delta H^{\ddagger}$ of probe IV in the micelle was, on the contrary, larger than those of probes I and II. $\Delta H^{\ddagger}$ in the micelle is the largest in three systems, though the values of probes I and II are between those in water and dodecane. The 2,4-dinitrophenylhydrazyl group of probe IV is hydrophilic owing to the electronegative substituents, nitro groups. Oakes[13] claimed that this group was oriented in the surface layer of the micelle. From the intensity of the ESR spectra of saturated aqueous solutions, it was proved that the solubility of probe IV in water was larger than that of probes I and II, indicating that probe IV is more hydrophilic. Generally speaking, a hydrophilic molecule prefers a polar circumstance. Therefore, the position of probe IV in the micelle must be not in the core but near or in the surface layer. These facts leads us to one important conclusion, that $\Delta H^{\ddagger}$ becomes larger when a probe is present near or in the surface layer.

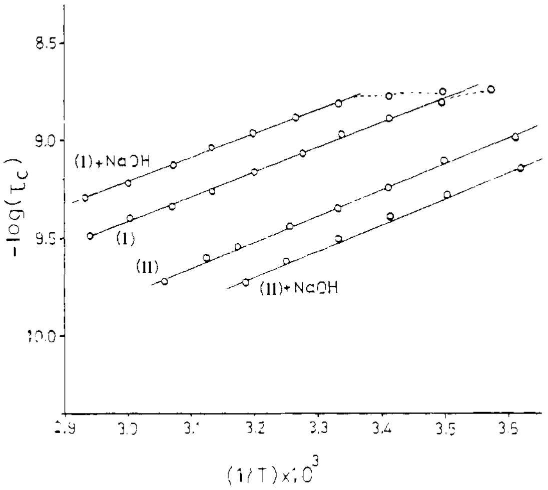


Figure 4. Relationship between $1/T$ and log (τ_c) of probes I, I + NaOH (10^{-2} M), II, and II + NaOH (10^{-2} M) in a SDS micelle (10% aqueous solution).

Table II. Difference between $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ in the SDS Micelle and Those in Water (kcal/mol)

probe	$\Delta(\Delta F^{\ddagger})_{\text{m-w}}$	$\Delta(\Delta H^{\ddagger})_{\text{m-w}}$	$\Delta(T\Delta S^{\ddagger})_{\text{m-w}}$
I	1.19	−1.56	−2.75
I + NaOH	1.44	−1.74	−3.18
II	1.09	−1.34	−2.43
II + NaOH	0.85	−1.38	−2.23
IV	1.19	0.89	−0.30
V	1.35	2.06	0.71

The molecular weight of probe V is smaller than one-half of those of probes I, II, and IV, and its $\Delta H^{\ddagger}$ in water is the smallest of them. However, $\Delta H^{\ddagger}$ of V in the micelle is the same as that of probe IV. From comparison of solubility in water, this molecule was proved to be most hydrophilic among the probes used in this study. Therefore, probe V may occupy the nearest position to the surface.

The solubility of probe III in water was too small to measure its spectrum, and τ_c was not calculated. Therefore, this molecule must be highly hydrophobic. However, $\Delta H^{\ddagger}$ of III in the micelle is considerably large. This is because the molecule is composed of a bulky condensed ring.

6. Difference of $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $T\Delta S^{\ddagger}$ between Micelle and Water. Differences between $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $T\Delta S^{\ddagger}$ in the micelle and those in water were calculated and are tabulated in Table II. In the case of $\Delta S^{\ddagger}$, T was multiplied in order to compare the extent of its contribution to $\Delta F^{\ddagger}$ with $\Delta H^{\ddagger}$. $\Delta(\Delta F^{\ddagger})_{\text{m-w}}$ is correlated with the ratio of τ_c in the micelle and in water. By assuming that eq 2 holds rigorously, $\Delta(\Delta F^{\ddagger})_{\text{m-w}}$ is equal to the logarithm of the ratio of viscosity in the micelle and that in water, and is independent of the properties of the probes. However, the values measured were different, suggesting that applicability of eq 2 is questionable and that viscosity in the micelle cannot be defined in a simple manner.

After $\Delta(\Delta F^{\ddagger})_{\text{m-w}}$ was separated into two components, $\Delta(\Delta H^{\ddagger})_{\text{m-w}}$ and $\Delta(T\Delta S^{\ddagger})_{\text{m-w}}$, it was revealed that $\Delta(\Delta F^{\ddagger})_{\text{m-w}}$ was classified into two groups. In the case of probes I and II, the contribution of $\Delta(T\Delta S^{\ddagger})_{\text{m-w}}$ is larger than that of $\Delta(\Delta H^{\ddagger})_{\text{m-w}}$. These molecules are hydrophobic and were considered to be dissolved in the core as described above.

Table III. a_N in Water, Dodecane, and SDS Micelle (G)

probe	water	dodecane	SDS micelle	deviation from water,[a] %
I	15.93	14.10	15.29	35
I + NaOH			15.29	35
II	15.93	14.10	15.25	37
II + NaOH			15.43	27
III		14.20	15.43	
IV	16.25	14.33	15.79	24
V	16.16	14.38	15.75	23

[a] This is the value of $[a_N(\text{water}) - a_N(\text{micelle})]/[a_N(\text{water}) - a_N(\text{dodecane})] \times 100$.

Therefore, it is conceivable that $\Delta S^{\ddagger}$ decreased in the core of the micelle for a specific reason. On the contrary, the contribution of $\Delta(\Delta H^{\ddagger})_{\text{m-w}}$ is larger than that of $\Delta(T\Delta S^{\ddagger})_{\text{m-w}}$ in the case of probes IV and V. These molecules are hydrophilic and were considered to be dissolved near or in the surface layer.

According to Eyring's theory,[14] $\Delta H^{\ddagger}$ is the enthalpy difference between the ground state and the activated state in which probes are allowed to rotate.[1] Most of $\Delta H^{\ddagger}$ are occupied by the energy of forming holes or free volume in the medium resisting the intermolecular force, which is necessary for activation of the medium. Therefore, $\Delta H^{\ddagger}$ is a measure of intermolecular force. $\Delta H^{\ddagger}$ values of probes I and II in the micelle were between those in water and dodecane, suggesting that the core is "liquid-like".[15] On the other hand, $\Delta H^{\ddagger}$ of probes IV and V in the micelle considerably exceeded those in water. An electrostatic attractive force acts between sulfate ions and Na^+ ions on the surface. Furthermore, these ions are usually hydrated strongly, and the hydrogen bonds of the hydrated water molecules combine them in addition to the electrostatic force. Probes located near or in the surface layer must make a free volume resisting these attractive forces for rotation. It was reported that restriction on the motion of a surfactant molecule is most prominent in the surface layer; this was concluded from the spin-lattice relaxation time of the ^{13}C NMR spectroscopy.[16,17] That is to say, the intermolecular force in the surface layer is stronger than that in the core, which is consistent with the results described above.

$\Delta S^{\ddagger}$ is the entropy difference between the ground state and the activated state. $\Delta S^{\ddagger}$ values in associated liquids are generally large, as is $\Delta H^{\ddagger}$. On the rotation of the water molecule, for example, breaking of hydrogen bonds is responsible for large $\Delta H^{\ddagger}$ and increases freedom of motion of the activated medium, causing the increase of $\Delta S^{\ddagger}$. This is a possible explanation on the basis of a change in properties of the surrounding medium. Another factor may exist, which affects $\Delta S^{\ddagger}$. According to the "jump" model, the rate of rotation is determined by the product of the probability of jumping a potential barrier and the total number of orientations allowed.[18] This number correlates with $\Delta S^{\ddagger}$. Orientation of a long-chain molecule, probes I and II, perpendicular to the surfactant molecule may be suppressed considerably in the micelle and the number of orientations may be smaller than those in water or dodecane. This leads to the decrease of $\Delta S^{\ddagger}$, but its detailed analysis is a future problem.

7. a_N. In the above discussion, the position of probes in the micelle was estimated on the basis of solubility and $\Delta H^{\ddagger}$. This estimate was generally made from a_N. It is well known that a_N is small in nonpolar solvents and becomes large in polar solvents.[19,20] However, few papers reported the quantitative analysis. In the present work, a_N of probe V in various solvents was plotted against their dielectric constants (ϵ), as shown in Figure 5. At first glance, it was known that a_N is not determined simply by ϵ, that is, the points were not on one line. However, linearity was observed for a_N in the solvents possessing a hydroxyl group. a_N in these solvents was larger than those obtained by the assumption that a_N was determined only by polarity of a solvent and the limiting values of a_N are those in dodecane and water. This was explained as follows. The N-O group of probes is in equilibrium with the following two structures:

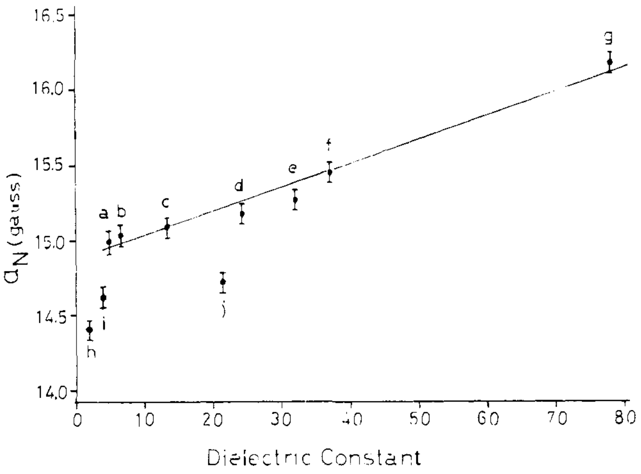
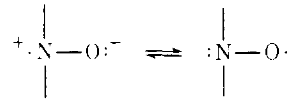
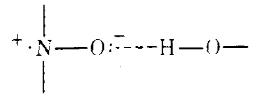


Figure 5. Relationship between a_N and dielectric constant: a, chloroform; b, dodecanol; c, hexanol; d, ethanol; e, methanol; f, ethylene glycol; g, water; h, dodecane; i, ethylene glycol dimethyl ether; j, acetone.



$$^{+}\cdot\overset{|}{\underset{|}{N}}-O:^{-} \rightleftharpoons :\overset{|}{\underset{|}{N}}-O\cdot$$

A hydroxyl group must stabilize a polarized structure through the hydrogen bond, and the density of the unpaired electron increases, resulting in the increase of a_N.



$$^{+}\cdot\overset{|}{\underset{|}{N}}-O:^{-}\cdots H-O-$$

From the energy point of view, a hydroxyl group approaches the N-O group more easily than the alkyl group, so that a_N becomes larger than that expected from ϵ. As acetone is a considerably polar solvent, a_N is relatively small because it has no hydroxyl group. On the contrary, a_N is large in chloroform, whose hydrogen is active and is able to form a hydrogen bond.

a_N of probes in three systems is listed in Table III. The values in the last column indicate how a_N in the micelle deviates from that in water. In other words, it is a measure of hydrophobicity around the probe. A characteristic feature is that all values of a_N are considerably large showing that probes are in polar circumstance, in spite of hydrophobic probes being included. Waggoner et al.[21] also found that a_N of hydrophobic probes possessing a large alkyl group was large in a SDS micelle. The fact that deviation of probes I and II from water was larger than those of probes IV and V is consistent with the above-described conclusion that probes I and II are more hydrophobic. On the assumption that probes are interacting with water in the micelle, ϵ around probe V is 55 using the line in Figure 5. Similarly, the circumstance around hydrophobic probes I and II is more polar than methanol. Two explanations are proposed for the large a_N of probes I, II, and III. One of them is that the N-O group is essentially hydrophilic and sometimes interacts with a polar surface. However, it is impossible to consider that the probes stay on the surface so long as a_N is large, from the comparison of their $\Delta H^{\ddagger}$ with those of probes IV and V. The other is that water molecules penetrate into the core, resulting in the increase of ϵ. Griffith et al.[19] proposed a model of penetration of water molecules into a lipid bilayer. Müller and Birkhahn[22,23] suggested penetration of water molecules in the core of a micelle from ^{19}F NMR chemical shifts. Therefore, it is reasonable to consider that penetration of water molecules is responsible for the large a_N.

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Deviations from Bond Additivity in Compton Profiles: The Relation to Strain Energy in Hydrocarbons

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Abstract: Strained cyclic hydrocarbons and unsaturated hydrocarbons show a characteristic deviation of their theoretical Compton profiles from bond additivity of computed carbon–hydrogen and carbon–carbon single bond Compton profiles. For both classes of molecules we tentatively attribute this deviation from bond additivity to strain.

Introduction

In a Compton scattering experiment on molecules, the probability distribution of frequency shifts of X-rays[1,2] or γ-rays[3,5] scattered through a fixed angle is measured. Under the impulse approximation[5] this distribution of photon frequency shifts is interpreted as the Compton profile, $J(q)$, the probability distribution of a molecular electron momentum in the direction of photon momentum change. A comprehensive review of research on electron momentum distributions and their relation to chemical bonding has been provided by Epstein.[6]

It was pointed out by Coulson[7] and by Epstein[8] that the molecular electronic kinetic energy can be computed from an experimental Compton profile. Because of the relation through the virial theorem of the kinetic energy to the total energy, it is possible to compute total energy from Compton profiles. Thus changes of Compton profiles attributable to strain energy can, in principle, be employed to compute the strain energy.

Since 1920 there have been published a number of empirical methods to express the heat of atomization ΔH_a of a hydrocarbon as a sum of bond contributions.[9,10] For example:

$$\Delta H_a = n_{CH}E_{C-H} + n_{CC}E_{C-C} \qquad (1)$$

where n_{CH} is the number of C–H bonds and n_{CC} is the number of C–C bonds in the hydrocarbon. Both E_{C-H} and E_{C-C} are empirical bond energy terms. To improve such empirical methods, terms for bond interactions[11,12] were subsequently added. Other quite accurate empirical schemes to predict heats of formation of hydrocarbons employ group increments, where the groups are CH_3, CH_2, CH, and C.[13,14] If the parameters of these empirical methods of predicting reaction heats are fixed on acyclic, "unstrained", saturated hydrocarbons, then when they are applied to predict heats of formation of strained, saturated, cyclic hydrocarbons, the stability of the strained molecules is predicted to be greater than is observed. The discrepancy in the heat of formation is referred to as strain energy. Generally saturated, cyclic molecules are found to be strained when the angles between vectors to atoms bonded to a carbon deviate greatly from the tetrahedral angle of 109.47°.

Ethylene is occasionally looked upon as a highly strained two-member ring, cycloethane,[15] in which two tetrahedrally hybridized carbon atoms are joined by highly bent bonds as originally described by Pauling.[16]

It was first suggested by Hicks[17] that the various types of chemical bonds in hydrocarbons may have characteristic Compton profiles from which the molecular profiles can be constructed additively.

Guided by the success of empirical methods by chemists, Eisenberger and Marra[18] used experimental Compton profiles to develop $J_{C-H}(q)$ and $J_{C-C}(q)$ for an electron in a C–H bond and C–C single bond, respectively. They also generated an empirical Compton profile $J_{C=C}(q)$ for an electron in a carbon–carbon double bond (C═C). The three empirical Compton profiles were taken to fit experiments on methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4). It was found that by adding these bond Compton profiles the measured Compton profiles of the unstrained hydrocarbons propylene, benzene,

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