

ABNORMALITY OF THE ACTIVATION ENTROPY OF THE ROTATION OF A SPIN PROBE IN A  
SDS MICELLE

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The ESR spectra of a spin probe, 2-(14-carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidinyloxy (16NS), dissolved in a SDS micelle were measured at various temperatures. The rotational correlation time was analysed by the theory of absolute reaction rate. The activation entropy of the rotation of the probe in the micelle was abnormally small compared with that in water, though the activation enthalpies were nearly equal in two cases.

Spin probe method has been used extensively in micelle chemistry<sup>1)</sup>. The motion of the probe is generally described in terms of the rotational or reorientational correlation time ( $\tau_c$ ). The  $\tau_c$  values increased in all cases when the probes were transferred from water into a micelle. When the  $\tau_c$  values were plotted against the concentration of the surfactants, the curve became flat in the region beyond the CMC<sup>2)</sup>. The  $\tau_c$  value is related to the viscosity ( $\eta$ ) of the medium according to the Debye-Stokes-Einstein's equation as follows.

$$\tau_c = (4\pi\eta a^3) / (3kT) \quad (1)$$

Here,  $a$  is the average radius of the molecule. Accordingly, the increase of the  $\tau_c$  value is attributed to that of the viscosity. On the other hand, the  $\tau_c$  value is taken as the time necessary for the molecule to rotate one radian. Therefore, rotational frequency ( $\nu$ ) is equal to  $1/(2\pi\tau_c)$ . The frequency is expressed by the theory of absolute reaction rate, as follows<sup>3)</sup>.

$$\nu = 1/(2\pi\tau_c) = (kT/h) \cdot \exp(\Delta S^\ddagger/R) \cdot \exp(-\Delta H^\ddagger/RT) \quad (2)$$

Here,  $k$  and  $h$  are Boltzmann's and Planck's constants and  $T$  is absolute temperature. The  $\Delta S^\ddagger$  and the  $\Delta H^\ddagger$  are activation entropy and enthalpy of the rotation of the probe, respectively. Similar formulation was proposed for the rotation of electric dipole moment<sup>4)</sup>.

In this report, the motion of the 16NS dissolved in a SDS micelle and in water were analysed using the equation (2). The probe ( $2 \times 10^{-4} M$ ) were dissolved in the 10% aqueous solution of SDS and in water, NaOH ( $10^{-3} M$ ) was added for the dissolution of the probe in the case of water because the solubility was very small. The ESR spectra were measured at various temperatures. The measurements were carried out even below  $0^\circ C$  in the case of water as it was possible to be supercooled, in order to obtain reliable data from wide temperature region. The  $\tau_c$  values were calculated according to ref.5.

Fig.1 shows the relationship between  $\log(\tau_c)$  and  $1/T$ . The  $\tau_c$  values in the micelle was about 7 times larger than that in water in measured temperature region. In the narrow region of temperature, it is linear and the  $\Delta H^\ddagger$  values were calculated from the slopes of the lines giving 7.4 and 6.5 Kcal/mole in water and in the micelle, respectively. Using these values, the  $\Delta S^\ddagger$  values were

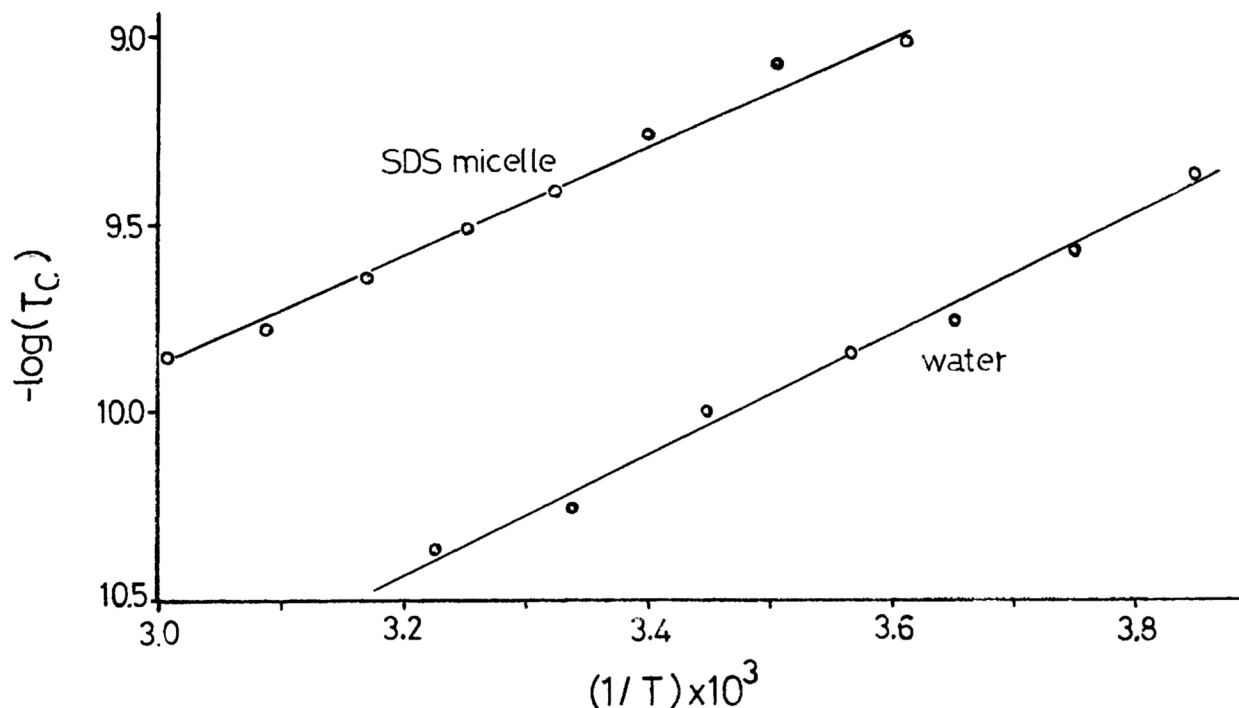


Fig. 1 Relationship between  $\log(\tau_c)$  and  $1/T$ .

obtained at 300K. They are 4.7 and 1.2e.u. From these results, it was found that the  $\Delta H^\ddagger$  values were not so different in two cases, but the  $\Delta S^\ddagger$  value in the micelle was about 1/4 times that in water. That is to say, the difference between the  $\tau_c$  values is attributed to this abnormal decrease of the  $\Delta S^\ddagger$  value in the micelle.

According to Eyring's theory<sup>3)</sup>, formation of holes or free volume in the medium resisting to intermolecular forces is necessary for liquid to flow. Most part of the activation energy of the viscosity were occupied by the energy for the formation of the holes. Activation entropy is the entropy difference between the activated flowing state and the ground state. Therefore, this value is related to the probability of the formation of the holes.

It is possible to apply a similar model for the rotation of the spin probe. The medium surrounding the probe must be in the activated flowing state for the rotation of the probe. So, it is necessary to form the holes around the probe. If the hole in the medium locates distantly from the probe, it does not contribute to the rotation of the probe. That is to say, the holes formed in a space having a certain size can only contribute to the rotation. If the probe is occluded in the space narrower than the size, the number of the holes may be decreased. This causes the decrease in the  $\Delta S^\ddagger$  value. It is a possible explanation that a SDS micelle acts as such a narrower space. Detailed analysis is now in progress.

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