

## Physical Organic Studies on Bimolecular Reactions in Reversed Micelles: Addition of Cyanide Ion to the *N*-Methyl-3-carbamoylpyridinium Ion in Hexadecyltrimethylammonium Bromide Reversed Micelles

Ayako Goto\*

Department of Chemistry, University of Shizuoka, Yada, Shizuoka 422, Japan

Hiroshi Kishimoto

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuhoku, Nagoya 467, Japan

The bimolecular reaction of cyanide ( $\text{CN}^-$ ) ion with *N*-methyl-3-carbamoylpyridinium ( $\text{S}^+$ ) ion, in the water pool of the reversed-micellar system water/hexadecyltrimethylammonium bromide (HTAB)/chloroform–iso-octane (3:2, v/v) has been studied at various temperatures (15–40 °C) by measuring spectrophotometrically the decrease of the absorption due to  $\text{S}^+$  (265 nm) and the increase of the absorption due to the addition product (340 nm). The results of the reaction series were examined throughout with respect to the molar ratio of water to HTAB,  $R$ . Since the rate and equilibrium constants of the bimolecular reaction are affected by the method in which the concentrations of reactants are defined or by fixing the extent of reaction space, the water pool is assumed to be the sole reaction space and the rate and equilibrium constants in the water pool,  $k_{2w}$  and  $K_w$ , which are based on the modified concentrations of the reaction species, have been evaluated. It is found that terms of  $k_{2w}$  and  $K_w$ , the smaller the value of  $R$ , the more the addition reaction is enhanced. From the relationships between  $K_w$  and  $k_{2w}$  vs. temperature, the standard and activation enthalpies of reaction,  $\Delta H^\circ$  and  $\Delta H^\ddagger$ , respectively, have been calculated. The behaviour of  $\Delta H^\circ$  and  $\Delta H^\ddagger$  as well as  $K_w$  and  $k_{2w}$  is found to differ in reactions which have  $R$  below and above ca. 3. To explain the enhancement of the reaction due to the specific field effect of the water pool and the retardation of the reaction due to electrostatic interactions among  $\text{S}^+$  ions, the involvement of  $\text{CN}^-$  and HTAB ions is proposed. The differing behaviour in the reactions is more clearly manifested in the thermodynamic and kinetic diagrams of enthalpy vs. entropy, which give separate plots corresponding to  $R$  both below and above ca. 3. In addition, the effect of varying the  $\text{CN}^-$  ion concentration is discussed and is found to be consistent with the situation described above.

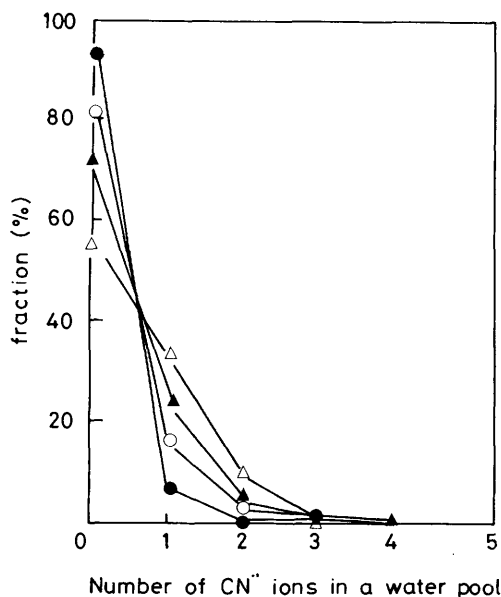
It is well known that water in reversed micelles gives a specific reaction field for reactants which is different from the bulk water field.<sup>1</sup> Since the evaluation of the rate and equilibrium constants of unimolecular reversible reactions is not in principle affected by the method in which the extent or volume of the reaction space—which defines the concentration of each reactant (population/volume)—is fixed, the results of such a reaction in a reversed-micellar system can be compared with those in bulk water without any correction for the concentration of reactant. Sunamoto and his co-workers have investigated various unimolecular reactions in reversed-micellar systems and have interpreted the micro-environmental effects of the water pool in the micelles in terms of multiple field assistance. In order to elucidate further the nature of the water pool, however, a variety of reactions must be examined. We have therefore studied some bimolecular reactions in the reversed micelles formed by cationic and anionic surfactants. In previous work,<sup>3</sup> in which hexadecyltrimethylammonium bromide (HTAB) and sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulphonate (AOT) were used as surfactants, we found that the reversed micelle formed by a cationic surfactant, HTAB, not only enhances the addition reaction of cyanide ( $\text{CN}^-$ ) ion to *N*-methyl-3-carbamoylpyridinium ( $\text{S}^+$ ) ion, especially at lower water concentrations in the micelle, but also stabilizes the product, 4-cyano-1,4-dihydro-*N*-methylpyridine-3-carboxamide (P), which is thermodynamically unstable in an aqueous medium.<sup>4</sup> It was also confirmed that the addition reaction of ionic species is affected remarkably by the electric field inside the micelle and is sensitive to the polarity of the medium.

However, a detailed thermodynamic discussion is not attempted in this paper, which only treats the similar, but somewhat simplified experimental systems introduced in the preceding work. In that paper, the water pool was assumed to be the sole reaction space and the rate and equilibrium constants of the bimolecular reaction, addition of  $\text{CN}^-$  ion to  $\text{S}^+$  ion, were evaluated on the basis of the effective concentrations of reactants in the water pool. These corrected values,  $k_{2w}$  and  $K_w$ , respectively, were obtained for the reactions under various conditions: varying the molar ratio of water to HTAB, the concentration of  $\text{CN}^-$  ion, and the temperature. From this work, two kinds of mechanism or environment for the reaction in the water pool of HTAB reversed micelles were postulated.

### Experimental

**Materials.**—*N*-Methyl-3-carbamoylpyridinium chloride (S), sodium cyanide, HTAB, chloroform and iso-octane were the same as those used in the previous paper.<sup>3</sup> The water used was distilled in an all-glass apparatus.

**Procedure.**—HTAB was dissolved in a chloroform–iso-octane mixture (3:2 volume ratio) to 0.2 mol dm<sup>-3</sup>. A small quantity ( $1.0\text{--}9.0 \times 10^{-2}$  cm<sup>3</sup>) of aqueous sodium cyanide was added to 3.0 cm<sup>3</sup> of HTAB solution in a moisture-proof cell. The concentration of sodium cyanide or  $\text{CN}^-$  ion in the aqueous solution to be added,  $[\text{CN}^-]_{\text{aq}}$ , was in the range 0.02–0.2 mol dm<sup>-3</sup>. By stirring the mixture, we obtained a transparent and apparently homogeneous solution, which can be regarded



**Figure 1.** Poisson distribution for  $\text{CN}^-$  in a water pool.  $[\text{HTAB}]_0$ ,  $0.2 \text{ mol dm}^{-3}$ ;  $[\text{CN}^-]_w$ ,  $0.2 \text{ mol dm}^{-3}$ ; ●,  $R = 0.9$ ; ○,  $R = 2.7$ ; ▲,  $R = 4.6$ ; △,  $R = 8.1$ .

as a reversed-micellar system. In the solution, the molar ratio of water to HTAB,  $R$ , was in the range 0.9–8.1. With increasing  $R$ , the concentration of HTAB decreased slightly, from  $0.2 \text{ mol dm}^{-3}$  to a maximum of 3%, but this variation can be ignored in the present work. The quantity of water present was measured on a Karl-Fischer Moisture Automatic Titration Apparatus, Model MK-A, Mitsubishi Chemical Ind.

The reaction was initiated by injecting into the HTAB reversed-micellar solution, containing  $\text{CN}^-$  ion, an aliquot ( $10 \text{ mm}^3$ ) of S in methanol. In the reaction mixture thus formed, the initial concentration of S or  $\text{S}^+$  ion,  $[\text{S}^+]^i$  was in the range  $1\text{--}1.5 \times 10^{-4} \text{ mol dm}^{-3}$  and the methanol content was within 0.4% volume ratio. The absorbance of P and  $\text{S}^+$ , at 340 and 265 nm, respectively,<sup>3</sup> was measured almost simultaneously by means of a Shimadzu UV-265 spectrophotometer thermostatted at various temperatures  $\pm 0.1^\circ\text{C}$ . The above-mentioned procedures were simple by comparison with those required for the previous work<sup>3</sup> and enabled us to carry out a great deal of study on the reactions under various conditions.

## Results and Discussion

*The Rate and Equilibrium Constants Evaluated on the Basis of the Effective Concentrations of Reactants in the Water Pool of the HTAB Reversed-Micelle.*—Firstly, the spatial distribution of each species participating in the reaction was surveyed. As discussed in the preceding work, it can be assumed that the reaction mixture is a reversed-micelle system, in which water pools are dispersed in HTAB reversed-micelles, and  $\text{S}^+$  and  $\text{CN}^-$  ions as well as P are considered to exist mostly in the water pools.<sup>3</sup> We then calculated the average populations of  $\text{S}^+$  and  $\text{CN}^-$  ions in the water pool of each micelle at the start of the reaction by assuming either a random allotment of a Poisson distribution of ions for all water pools present.<sup>5</sup> The calculated distribution of the  $\text{CN}^-$  ions in the water pools of the reaction mixtures with various  $R$  values, and with  $[\text{CN}^-]_{\text{aq}} = 0.2 \text{ mol dm}^{-3}$ , are shown in Figure 1. In the calculation, the aggregation number of the HTAB micelle was assumed to be 20, a rough estimate which is not intended to be accurate and does not account for the influence of  $R$ ; such allowance should not,

however, alter the gist of the discussion. It was found that more than half the water pools are considered to contain no  $\text{CN}^-$  ions, while most of the rest are occupied by only one or two ions. The population of  $\text{S}^+$  is more sparse than that of  $\text{CN}^-$ . In such a situation, there is a good possibility that the addition reaction of  $\text{S}^+$  and  $\text{CN}^-$  ions cannot be localized within a single water pool throughout the whole course of the reaction, but the transfer of ions between water pools is often necessary for the reaction to proceed. The equation would then be whether the transfer plays a significant role in the reaction kinetics.

We found both in this paper and in the preceding one<sup>3</sup> that the time spent on the addition in the HTAB reversed-micellar system is *ca.* 1 min. On the other hand, the transfer of ions between water pools is estimated to be very fast by comparison with the overall reaction, from reports that the exchange of ionic quenchers occurs in a time span of 0.1–10 ms.<sup>6</sup> It can therefore be tentatively concluded that the rate-determining step is the localized reaction of the  $\text{S}^+$  and  $\text{CN}^-$  ions, which encounter in the same water pool *i.e.* the transfer of ions can be neglected in any discussion of the rate constant. The above conclusion was experimentally confirmed by the observation that the rate of reaction was not affected by vigorously stirring the reversed-micellar system over the course of the reaction. Clearly, the ion-transfer process can also be excluded in the discussions of the equilibrium constant of the reaction. The experimental results can thus be analysed in a simplified way, in which the dispersed aqueous phase in the HTAB reversed-micellar system can be treated as a pseudo-continuous phase by ignoring the organic medium and HTAB molecules, which separate water pools from each other.<sup>1</sup>

Since the solubility of  $\text{S}^+$ ,  $\text{CN}^-$ , and P in the exterior of the water pool is *ca.* 0 only the concentrations of these species in the water pools, which will be denoted hereafter as  $[\text{S}^+]_w$ ,  $[\text{CN}^-]_w$ , and  $[\text{P}]_w$ , respectively, must be taken into account in the evaluation of the rate and equilibrium constants. These values can be easily evaluated or estimated, when the volume of a given amount of aqueous solution can be assumed to be independent of the nature of the environment around the solution. According to D'Aprano *et al.*,<sup>7</sup> the apparent molar volume of water is  $17.29$  and  $16.70 \text{ dm}^3 \text{ mol}^{-1}$  in the  $0.196 \text{ mol kg}^{-1}$  AOT reversed-micellar solutions with  $R$  8.31 and 1.23, respectively, showing a relative variation of 3%. We therefore ignore the compressibility of the aqueous solution in the discussion which follows.

Of the above-mentioned concentrations at various stages of reaction, the values for  $\text{S}^+$  and  $\text{CN}^-$  at the start of the reaction,  $[\text{S}^+]_w^i$  and  $[\text{CN}^-]_w^i$ , respectively, can be estimated from the given composition of each reaction system. This is cited in the experimental procedure:  $[\text{CN}^-]_{\text{aq}}$  gives the former quantity and  $[\text{S}^+]^i$  multiplied by the ratio (*ca.* 33–301) of the volume of the reaction mixture to that of the aqueous sodium cyanide solution gives the latter. The values for P at various stages of reaction can be estimated from the absorbance of P at 340 nm,  $A_{340}$ , on the basis of the following observation. Figure 2 shows an example of the plots of  $A_{340}$  *vs.* the almost simultaneously measured optical density at  $\text{S}^+$  at 265 nm,  $A_{265}$ , during the course of the reaction. As the reaction proceeds,  $A_{340}$  increases and  $A_{265}$  decreases with linear relation, according to the stoichiometry of the reaction. In each reaction, we obtained the value of  $A_{340}$  for P in the hypothetical case of the reaction completed by extrapolating  $A_{340}$  at 0  $A_{265}$ , as shown in Figure 2. The extrapolated value is denoted as  $A_{340}^m$  and will be used as the measure of  $[\text{S}^+]_w^i$ , whose value is equal to  $[\text{P}]_w$  at the completion of reaction, with the same proportionality factor to  $A_{340}$  for  $[\text{P}]_w$  at any time. The equilibrium constant for the reaction in the water pool,  $K_w$ , can then be estimated from the experimental results by using equation (1). The superscript, *f*, denotes the state finally

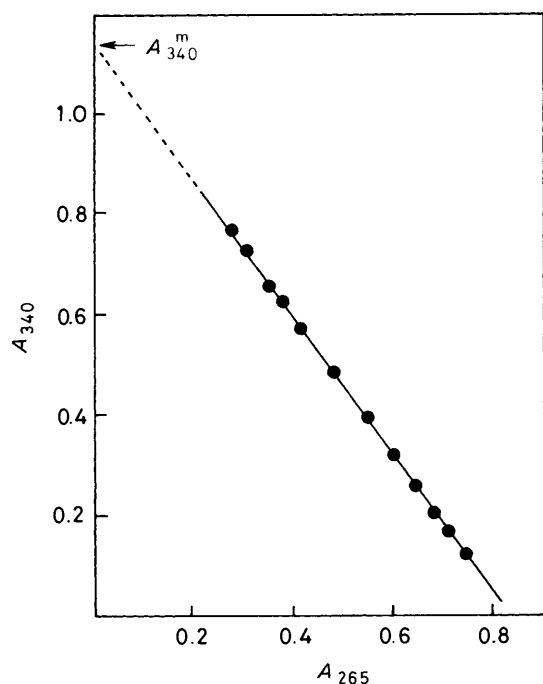


Figure 2. Plots of  $A_{340}$  vs.  $A_{265}$  at 25 °C. [HTAB], 0.2 mol dm<sup>-3</sup>,  $R = 6.3$ ;  $[\text{CN}^-]_w$ , 0.06 mol dm<sup>-3</sup>.

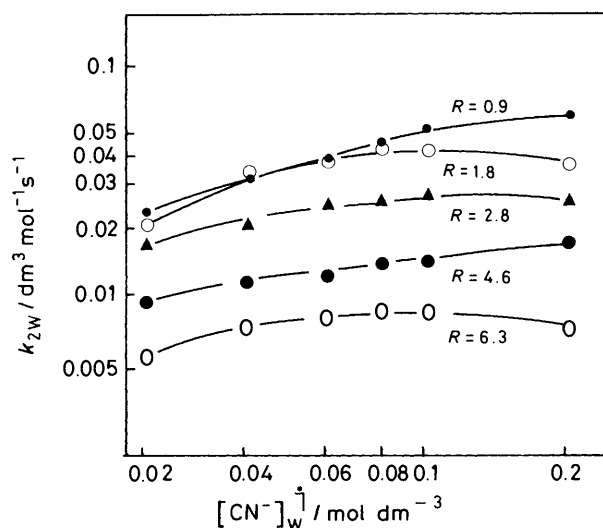


Figure 3. The variation of  $k_{2w}$  at various values of  $R$  with  $[\text{CN}^-]_w$  at 25 °C.

$$K_w = \frac{A_{340}^f / \{(A_{340}^m - A_{340}^f)[\text{CN}^-]_w^f\}}{A_{340}^f / \{(A_{340}^m - A_{340}^f)([\text{CN}^-]_w^i - [\text{S}^+]_w A_{340}^f / A_{340}^m)\}} \quad (1)$$

observed after sufficient time has elapsed, although it is theoretically concerned with the equilibrium state of the reaction.

To describe the bimolecular reaction in this work, we adopted two kinds of rate equations which give the same reaction rate,  $-d[\text{S}^+]_w/dt$  or  $\tau$ . One is a theoretical equation taking into account both forward and backward steps, equation (2), where

$$\tau = k_{2w}[\text{S}^+]_w[\text{CN}^-]_w - k_{bw}[\text{P}]_w \quad (2)$$

$k_{2w}$  is the second-order rate constant in the water pool to be evaluated with priority and  $k_{bw}$  is the rate constant of the

backward step in the water pool. Equation (3) is a kind of

$$\tau = k_{\text{obs}}\{[\text{P}]_w^f - [\text{P}]_w\} \quad (3)$$

practical equation with an apparent rate constant,  $k_{\text{obs}}$ , which can be obtained at any time,  $t$ , as the negative slope of  $\ln \{A_{340}^f - A_{340}\}$  vs.  $t$ , where  $A_{340}^f$  and  $A_{340}$  represent  $[\text{P}]_w^f$  and  $[\text{P}]_w$ , respectively.<sup>3</sup> By combining equations (2) and (3) we derive equation (4). Of the quantities in equation (4),  $k_{\text{obs}}$ ,

$$k_{2w} = k_{\text{obs}}(1 - [\text{S}^+]_w^f/[\text{S}^+]_w) / \{[\text{CN}^-]_w + (1 - [\text{S}^+]_w^f/[\text{S}^+]_w)/K_w\} \quad (4)$$

$[\text{S}^+]_w$ , and  $[\text{CN}^-]_w$  are functions of  $t$ , although the value of  $k_{\text{obs}}$  hardly varied, especially in the intermediate-stage reaction. For simplicity, we adopted the above set of values at the 'relaxation time', at which  $[\text{S}^+]_w$  becomes  $[\text{S}^+]_w^f/e$ , where  $e$  is the base of Napier's logarithm. The other choice of  $t$  seems to affect significantly the final value of  $k_{2w}$ . Estimation of  $K_w$  and  $k_{2w}$ , performed thus from the results of each series of measurements with three or four runs was reproducible within ca. 3.0 and 2.5%, respectively.

*The Dependence of  $k_{2w}$  and  $K_w$  on  $R$  and  $[\text{CN}^-]_w^i$ .*—Figures 3 and 4 show the plots of  $k_{2w}$  and  $K_w$ , measured at 25 °C in the HTAB reversed-micellar systems (with various values of  $R$ ) vs.  $[\text{CN}^-]_w^i$ . It seems that circumstances change at a critical value of  $R$  between 2.8 and 4.6. As will be discussed later, the critical value,  $R_c$ , was estimated to be ca. 3.

Before proceeding further, we ought to comment on the physical meaning of  $R$  with respect to the water pool of the HTAB reversed-micelle. For an accurate discussion, we need an exact knowledge of the aggregation number of the HTAB micelle; this was tentatively assigned the value 20 earlier. However, we have little knowledge of micelles with varying  $R$  values. In spite of this, we can safely presume that the aggregation number increases—or at least remains constant—with increasing  $R$ . From this, it can easily be inferred that the size of the water pool increases more or less with increasing  $R$  in a similar way to the case of the AOT reversed-micelle, which has been extensively studied.<sup>8-13</sup> We then treat  $R$  as a qualitative measure of the size of the water pool rather than a quantitative measure. It must be noted here that there is the possibility of a drastic change in the nature of the HTAB micelle, e.g. micellar structure, at  $R_c$ . In this work, however, we ignore this and attribute the effect of  $R$  to the environmental behaviour of the water pool through its size.

From the inspection of  $k_{2w}$  at various  $R$  values in Figure 3, taking into consideration the fact that the second-order rate constant for this reaction in the bulk water was estimated to be 0.016 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> with sufficient  $[\text{CN}^-]_w^i$ ,<sup>4</sup> it might be presumed that the water pool of the reversed-micellar system affects the kinetic behaviour of reactants in different ways at  $R$  values below and above  $R_c$ . The enhancement of the addition reaction  $< R_c$  is considered to be attributable to the specific effect of the water pool.<sup>3</sup> For the retardation  $> R_c$ , there must exist at least two factors, which act counter to each other on  $k_{2w}$ , because by increasing  $R$  far above  $R_c$ , the value of  $k_{2w}$  can be expected to reverse to the value in the bulk water, where  $R \rightarrow \infty$ . One factor is the effect of the water pool itself, mentioned above. As for the other, we suppose this to be due to electrostatic interaction between ions and surfactant ion: the attraction between  $\text{CN}^-$  ion and HTAB cation and the repulsion between  $\text{S}^+$  ion and HTAB cation, resulting in the separation of  $\text{CN}^-$  and  $\text{S}^+$  ion from each other. The lower the concentration of  $\text{CN}^-$  ion, the more effective would be the above separation, as recognized in Figure 3, which shows the decline of  $k_{2w}$  with

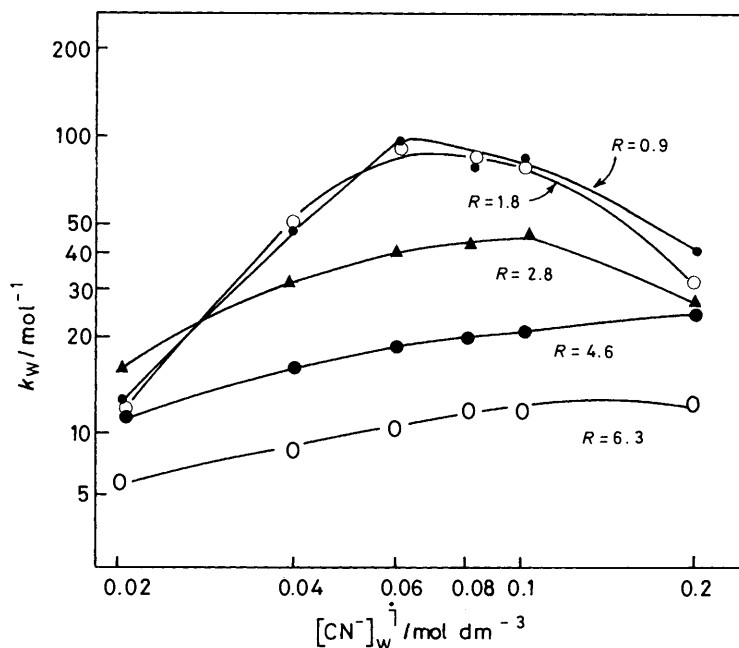


Figure 4. The variation of  $K_w$  at various values of  $R$  with  $[\text{CN}^-]_w$  at 25 °C.

Table 1. Gibbs energy values for the addition reaction in HTAB-reversed micellar systems ( $\text{kJ mol}^{-1}$ ).

| $R$ | $[\text{CN}^-]_w$ 0.06 mol $\text{dm}^{-3}$ |                     |                                      | $[\text{CN}^-]_w$ 0.2 mol $\text{dm}^{-3}$ |                     |                                      |
|-----|---|---------------------|--------------------------------------|--|---------------------|--------------------------------------|
|     | $\Delta G^\circ$                            | $\Delta G^\ddagger$ | $\Delta G^\ddagger - \Delta G^\circ$ | $\Delta G^\circ$                           | $\Delta G^\ddagger$ | $\Delta G^\ddagger - \Delta G^\circ$ |
| 0.9 | -10.8                                       | 80.0                | 90.8                                 | -9.9                                       | 80.9                | 90.8                                 |
| 1.8 | -10.8                                       | 80.9                | 91.7                                 | -8.8                                       | 80.9                | 89.7                                 |
| 2.8 | -9.5  | 81.9                | 91.4                                 | -8.0                                       | 81.8                | 89.8                                 |
| 3.7 | -8.5  | 82.8                | 91.3                                 | -8.1                                       | 83.0                | 91.1                                 |
| 4.6 | -7.7  | 83.3                | 91.0                                 | -7.6                                       | 83.4                | 91.0                                 |
| 5.5 | -7.1  | 83.6                | 90.7                                 | -6.2                                       | 85.2                | 91.4                                 |
| 6.3 | -6.7  | 84.2                | 90.9                                 | -5.1                                       | 84.8                | 89.9                                 |
| 8.1 | -5.5  | 84.7                | 90.2                                 | -5.1                                       | 82.7                | 87.8                                 |

decreased  $[\text{CN}^-]_w$ . The fact that the declining tendency mentioned above was also found  $< R_c$  suggests the existence of electrostatic interactions over the whole range of  $R$  values, whose negative contribution to the reaction kinetics compensates for the positive contribution due to the specific effect of the water pool exactly at  $R_c$ , owing to the different variation between the two kinds of contributions with the change of  $R$ . The contribution due to the specific effect of the water pool should monotonously increase with a decrease in  $R$ . On the other hand, the negative contribution of the electrostatic interaction should reach a maximum value with the change of  $R$  from infinite to zero. At sufficiently large  $R$  values the ratio of  $\text{CN}^-$  ion attracted by HTAB cation to  $\text{CN}^-$  ion in the interior of the water pool must be negligible and so because of the effect of ionic separation (at small  $R$ )  $\text{CN}^-$  and  $\text{S}^+$  ions will be closely situated with respect to each other, nullifying the effect of the ionic separation, even if it did, in fact, remain.

By comparison with the behaviour of  $k_{2w}$  vs.  $R$  and  $[\text{CN}^-]_w$ , that of  $K_w$  showed two conspicuous features, as seen in Figure 4: over the whole range of  $R$  values, the values of  $K_w$  in the reversed-micellar systems were always higher than those in the bulk water. This was estimated to be  $0.238 \text{ dm}^3 \text{ mol}^{-1}$  with sufficient  $[\text{CN}^-]_w$ ,<sup>4</sup> and the profiles of  $K_w$  vs.  $[\text{CN}^-]_w$  plots at  $R < 2.8$  had maxima and were different from those  $> 4.6$ , which

were monotonous curves similar to the case of  $k_{2w}$ . Since  $K_w$  is the quantity  $k_{2w}/k_{2b}$  mentioned earlier, the different features of  $K_w$  as compared with  $k_{2w}$  should be reduced to the behaviour of  $k_{2b}$ , i.e. the reactivity of P or in other words, its stability, in the reversed-micellar systems. Then, as regards the behaviour of  $K_w$  vs.  $R$ , we attribute this to the stability of P, which is caused by the reversed-micellar system or, more specifically, probably by HTAB. The reasoning for which we assigned the stability of P to HTAB rather than to the water pool was the invariability of  $k_{2b}$  with  $R$ ; this will be qualitatively treated in the thermodynamic discussion which follows. The fact that the values of  $K_w$  in the reversed-micellar systems were always higher than those in the bulk water was thought to suggest that the contribution of HTAB to  $k_{2b}$  or the stability of P overwhelms the negative contribution of the electrostatic interactions among ions in the water pool to  $k_{2w}$ , which makes a significant contribution below  $R_c$ . The irregular behaviour of  $K_w$  vs.  $[\text{CN}^-]_w$  below  $R_c$  suggests that the variability of the activity coefficient of P is due to the coexisting ions and/or the effect of the water structure on the hydrophobicity of P.

#### Thermodynamic Parameters Concerned with the Equilibrium and Rate of Reaction.

From the values of  $K_w$  and  $k_{2w}$ , the standard Gibbs energy of reaction,  $\Delta G^\circ$ , and the activation Gibbs energy,  $\Delta G^\ddagger$ , respectively, can be obtained according to thermodynamics and Eyring's absolute rate theory. These quantities at 25 °C with  $[\text{CN}^-]_w = 0.06$  and  $0.2 \text{ mol dm}^{-3}$  are shown in Table 1. Since the steady decline in both values with a decrease in  $R$  could be attributed to the specific effect of the water pool in a similar way to that described in the discussion on  $K_w$  and  $k_{2w}$ , this conclusion was not considered. The value of  $k_{2b}$ , to which we referred in the preceding discussion, should be studied in the form  $\Delta G^\ddagger - \Delta G^\circ$ . As seen in Table 1,  $\Delta G^\ddagger - \Delta G^\circ$ , or the backward activation Gibbs energy of P, was not influenced by  $R$  or the size of the water pool and was only slightly affected by a change in  $[\text{CN}^-]_w$ . The cause of the above-mentioned situation has already been described in the discussion of  $k_{2w}$  in terms of the stability of P. However, we can add the following remarks. It can be presumed that the Gibbs energy of the reactants,  $\text{S}^+$  and  $\text{CN}^-$ , must be affected by the

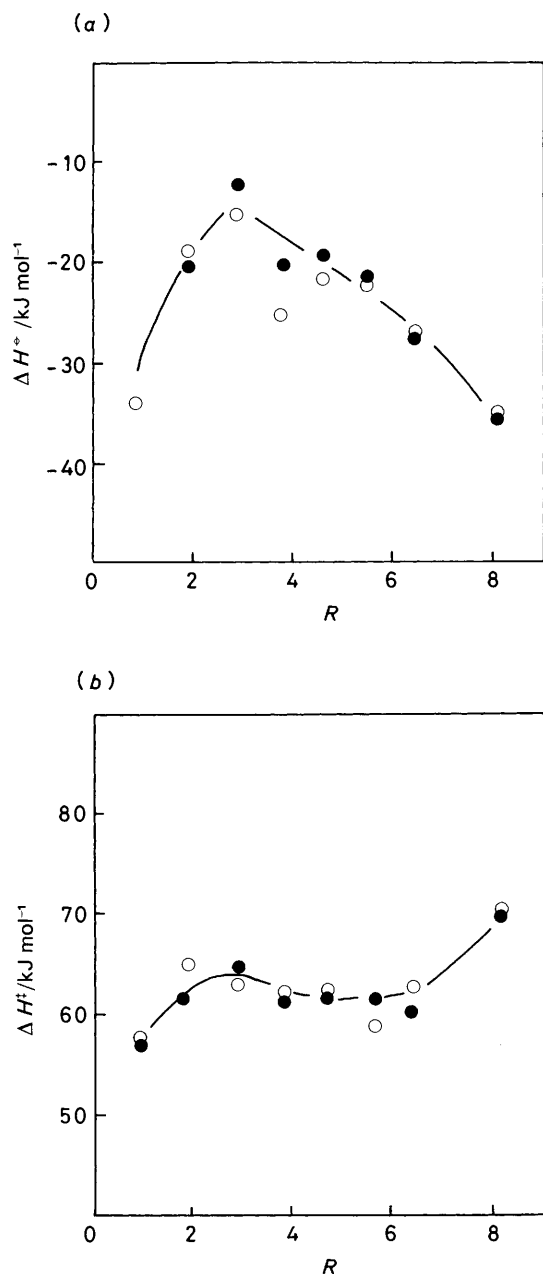


Figure 5. Plots of (a)  $\Delta H^\ddagger$  and (b)  $\Delta H^\ddagger$  for the addition reaction vs.  $R$ . ●,  $[\text{CN}^-]_w 0.06 \text{ mol dm}^{-3}$ ; ○,  $[\text{CN}^-]_w 0.2 \text{ mol dm}^{-3}$ .

water pool through its specific field, the nature of which is essentially electrostatic,<sup>2</sup> or through the greater electrostatic interactions between the reactant ions and the HTAB cation as compared with those of P and the activated complex,  $M^*$  (which has no net electric charge). The variation of  $R$  would then affect the Gibbs energy of the reactants,  $M^*$  and P, in a similar manner. The constancy of  $\Delta G^\ddagger - \Delta G^\circ$  might result from the constancy of the Gibbs energies of  $M^*$  and P or from the change in those energies to the same extent (which would be only slight, if it did in fact occur).

Generally speaking, the behaviour of the Gibbs energy can be better clarified in terms of its components, enthalpy and entropy. The values of enthalpy and entropy can be estimated from a thermodynamic analysis of Gibbs energy vs. temperature plots. We therefore measured the values of  $K_w$  and  $k_{2w}$  at various temperatures from 15 to 40 °C in order to obtain the

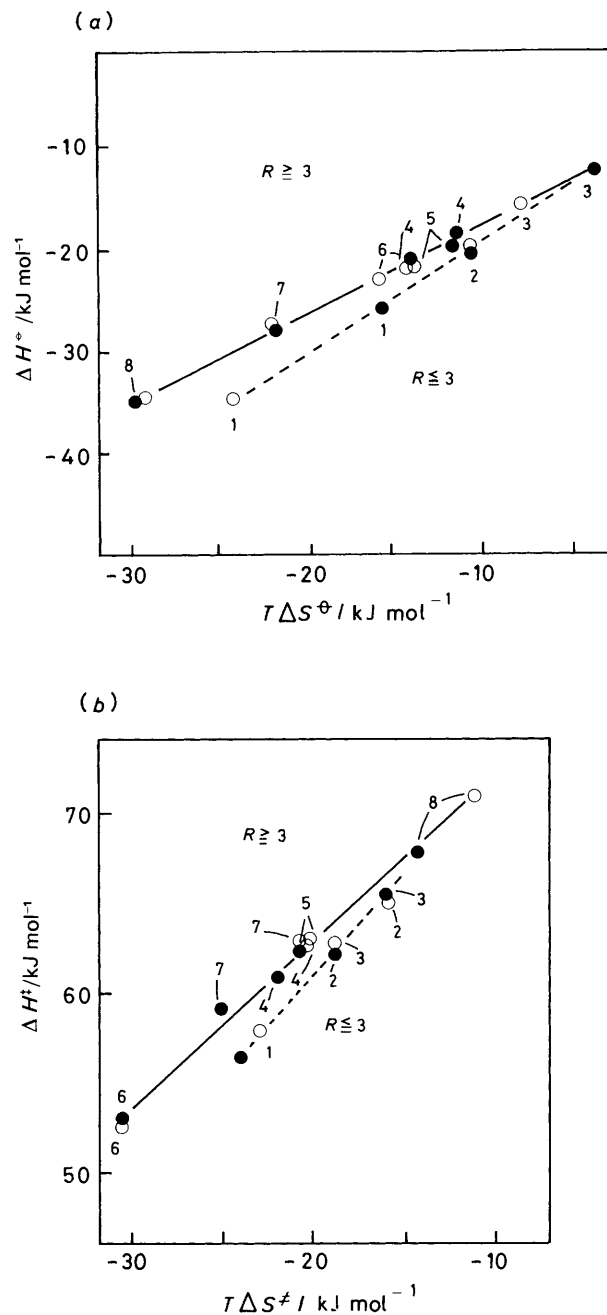


Figure 6. Plots of (a)  $\Delta H^\ddagger$  and (b)  $\Delta H^\ddagger$  vs.  $T\Delta S^\ddagger$  for the reaction at 25 °C. The numbers in the main body of the plots refer to the value of  $R$  as follows: 1, 0.9; 2, 1.8; 3, 2.8; 4, 3.7; 5, 4.6; 6, 5.5; 7, 6.3; 8, 8.1.

relations of  $\Delta G^\circ$  and  $\Delta G^\ddagger$  vs.  $T$ . From the results, we estimated the values of  $\Delta H^\circ$  and  $\Delta H^\ddagger$ , which are shown in Figure 5. The values of  $\Delta S^\circ$  and  $\Delta S^\ddagger$  were also calculated using the corresponding Gibbs energies and enthalpies. Although the profiles (Figure 5) became somewhat deceptive owing to the scattered plots, we recognized that the nature of the addition reaction or that of the water pool as a reaction field changes significantly at  $R$  ca. 3, i.e.  $R_c$  is ca. 3. The above transition at this value of  $R_c$  could be more clearly discerned in the  $\Delta H^\circ$  vs.  $T\Delta S^\circ$  and  $\Delta H^\ddagger$  vs.  $T\Delta S^\ddagger$  plots, as shown in Figure 6, especially in the former plots. It is to be noted that with an increase in  $R$  the plots of  $\Delta H^\circ$  vs.  $T\Delta S^\circ$  tend to move in the opposite direction below and above  $R_c$ , although this trend is not readily discernible in the plots of  $\Delta H^\ddagger$  vs.

**Table 2.** Values of  $\beta'$  in various solvents.

| Solvent                                     | $\beta'$ from equilibrium data | $\beta'$ from rate data  |
|---|--------------------------------|--------------------------|
| 0.2 mol dm <sup>-3</sup> HTAB<br>$R \leq 3$ | 1.05 ( $\gamma = 0.99$ )       | 1.12 ( $\gamma = 0.99$ ) |
| 0.2 mol dm <sup>-3</sup> HTAB<br>$R \geq 3$ | 0.85 ( $\gamma = 0.99$ )       | 0.91 ( $\gamma = 0.98$ ) |
| MeOH-H <sub>2</sub> O                       | 0.2 ( $\gamma = 0.99$ )        | 0.82 ( $\gamma = 0.97$ ) |

$T\Delta S^\ddagger$ . This confirmed the above statement that the reaction proceeds under different environmental conditions below and above  $R_c$ .

The slope,  $\beta'$ , of the linear plot as seen in Figure 6 provides a measure of the relative ratio of the enthalpic contribution to the entropic ones.<sup>2b</sup> When the contribution of the enthalpic effect is equal to the contribution of entropic effect,  $\beta' = 1$ . In Table 2 the values of  $\beta'$  for the equilibrium and rate of the reaction both below and above  $R_c$  are listed. With decreasing  $R$ , the enthalpic contribution is considered to tend to predominate in the HTAB reversed-micellar system. As a reference, we measured the addition reaction in the composite solvent, MeOH-water with various compositions from 65 to 100% v/v, and determined several of the thermodynamic parameters concerned. The values of  $\beta'$  in MeOH-water are shown in Table 2. From the results mentioned above, it was concluded that the environment in the water pool at lower  $R$  values has a specific nature<sup>3</sup> and contributes to the addition reaction mainly through enthalpic mechanisms.

## Acknowledgements

The authors thank Professor M. Hayashi for many valuable discussions.

## References

- P. D. I. Fletcher, A. M. Howe, B. H. Robinson, and D. C. Steytler, in 'Reverse Micelles,' eds. P. L. Luisi and B. E. Straub, p. 73, Plenum Press, 1984.
- (a) J. Sunamoto and D. Horiguchi, *Nippon Kagaku Kaishi*, 1980, 475; (b) J. Sunamoto, K. Iwamoto, S. Nagamatsu, and H. Kondo, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2469; (c) J. Sunamoto, K. Iwamoto, M. Akutagawa, M. Nagase, and H. Kondo, *J. Am. Chem. Soc.*, 1982, **104**, 4904.
- A. Goto and H. Kishimoto, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2854.
- R. N. Lindquist and E. H. Cordes, *J. Am. Chem. Soc.*, 1968, **90**, 1269.
- M. Tachiya, 'Kinetics of Nonhomogeneous Processes,' ed. G. R. Freeman, Wiley-Interscience, 1987, p. 575.
- S. S. Atik and T. K. Thomas, *J. Am. Chem. Soc.*, 1981, **103**, 3543.
- A. D'Aprano, A. Lizzio, and V. T. Liveri, *J. Phys. Chem.*, 1987, **91**, 4749.
- J. H. Fendler, 'Membrane Mimetic Chemistry,' Wiley-Interscience, 1982, p. 59.
- B. H. Robinson, C. Toprakcioglu, and J. C. Dore, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 13.
- A. Maitra, *J. Phys. Chem.*, 1984, **88**, 5122.
- M. Kotlarchyk and J. S. Huang, *J. Phys. Chem.*, 1985, **89**, 4382.
- J. Lang, A. Jada, and A. Malliaris, *J. Phys. Chem.*, 1988, **92**, 1946.
- P. L. Luisi, M. Giomini, M. P. Pileni, and B. H. Robinson, *Biochim. Biophys. Acta*, 1988, **947**, 209.

Paper 9/01095E

Received 14th March 1989

Accepted 16th August 1989