The Addition of Cyanide Ion to *N*-Alkyl-3-Carbamoylpyridinium Ion in Hexadecyltrimethylammonium Bromide Reversed Micelles: The Effects of Alkyl Chain Length

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The addition of cyanide (CN^-) ion to *N*-alkyl-3-carbamoylpyridinium ion (alkyl derivatives) with various alkyl chains in water pools of the reversed micellar system, water/hexadecyltrimethylammonium bromide (HTAB)/chloroform–iso-octane (3:2, v/v) has been determined spectrophotometrically. The results of the reaction series are examined with respect to the molar ratio of water to HTAB, *R*, and the CN^- ion concentration in the water pool, $[CN^-]_{aq}$, in order to study the effect of the alkyl chain length of the alkyl derivatives on the addition reaction in HTAB reversed micelles. The rate constant, k_{2w}, and the equilibrium constant, K_w, are evaluated on the basis of the dispersed water pools in the micellar system as the space for reaction.

Based on the behaviour of k_{2w} and K_w with *R*, the present results are obtained. The addition reaction proceeds favourably with decreasing *R* and with increasing alkyl chain length of the alkyl derivatives. Furthermore, the reaction tends not to be affected significantly by water content in the reversed micelles with increasing alkyl chain length.

The effect of CN^- ion concentration in water pools on K_w and k_{2w} suggests that the reverse reaction for the longer alkyl derivatives is highly affected by CN^- ion concentration compared to that for the shorter alkyl derivatives.

The behaviour of k_{2w} and K_w with *R* and $[CN^-]_{aq}$ is interpreted mainly on the basis of the different localizations of respective alkyl derivatives in the water pool.

It has been reported in our previous papers [1,2] that the presence of hexadecyltrimethylammonium bromide (HTAB) reversed micelles results in the enhancement of the addition of cyanide (CN^-) ion to *N*-methyl-3-carbamoylpyridinium ion (C_1P^+) in comparison with aqueous media. The enhancement is confirmed in terms of the reaction rate and equilibrium constants, which are evaluated on the basis of the water pool in the micelle as space for reaction.[2] Such a specific reaction field is supposed to be afforded by the water pool, especially at small values of *R* (the molar ratio of water to HTAB). The effect of *R* on the addition is explained mainly by taking into account the non-uniform distribution of CN^- ion and C_1P^+ ion in the water pool and its specific nature.

In this study,[3] we undertake the addition of CN^- ion to *N*-alkyl-3-carbamoylpyridinium ion (*N*-alkyl derivatives, C_nP^+) in order to examine the effect of the modification of C_1P^+ at its methyl residue by more hydrophobic alkyl groups on the addition in HTAB reversed micelles. *N*-Propyl, *N*-hexyl, and *N*-dodecyl-3-carbamoylpyridinium ions (abbreviated hereafter as C_3P^+, C_6P^+, and $C_{12}P^+$, respectively), are employed with C_1P^+. The model in Figure 1 shows schematically the locations of respective *N*-alkyl derivatives in the water pool formed by HTAB reversed micelles. C_1P^+ tends to lie mainly in the centre zone of the water pool due to the electric repulsion between cationic head groups of HTAB and C_1P.[1] With increasing alkyl chain length for alkyl derivatives, they tend to be located near the interface zone of the water pool or within the palisade layer because the hydrophobic interaction between alkyl derivatives and surfactant tends to outweigh the electric repulsion between cationic head groups of HTAB and $C_{12}P^+$.[4,5] The effects of water content and CN^- ion concentration on the addition reaction for alkyl derivatives (C_nP^+) were then studied. It may be of use to study the effects of various examples of respective alkyl derivatives in the water pool on the reaction constants with a view to examining some characteristic fields of the interface zone of the water pool.

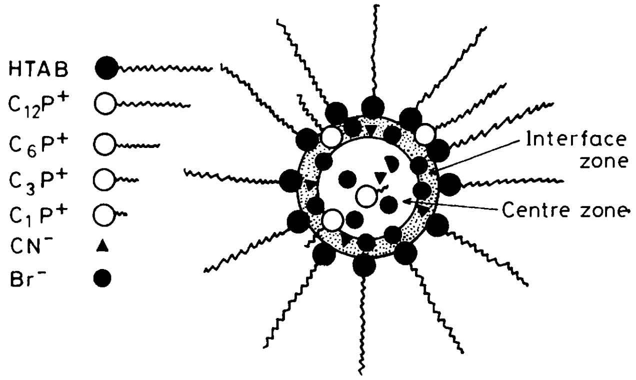

Figure 1. Location of *N*-alkyl-3-carbamoylpyridinium ions in a water pool formed by HTAB reversed micelle.

Experimental

Materials.—*N*-Methyl-3-carbamoylpyridinium chloride and sodium cyanide used as reaction species were as described previously.[1,2] *N*-Alkyl-3-carbamoylpyridinium bromides (alkyl groups = $-C_3H_7$, $-C_6H_{13}$, and $-C_{12}H_{25}$) were prepared from the appropriate alkyl bromide and commercially obtained nicotinamide, and twice recrystallized from methanol–benzene. Hexadecyltrimethylammonium bromide (HTAB) was as used

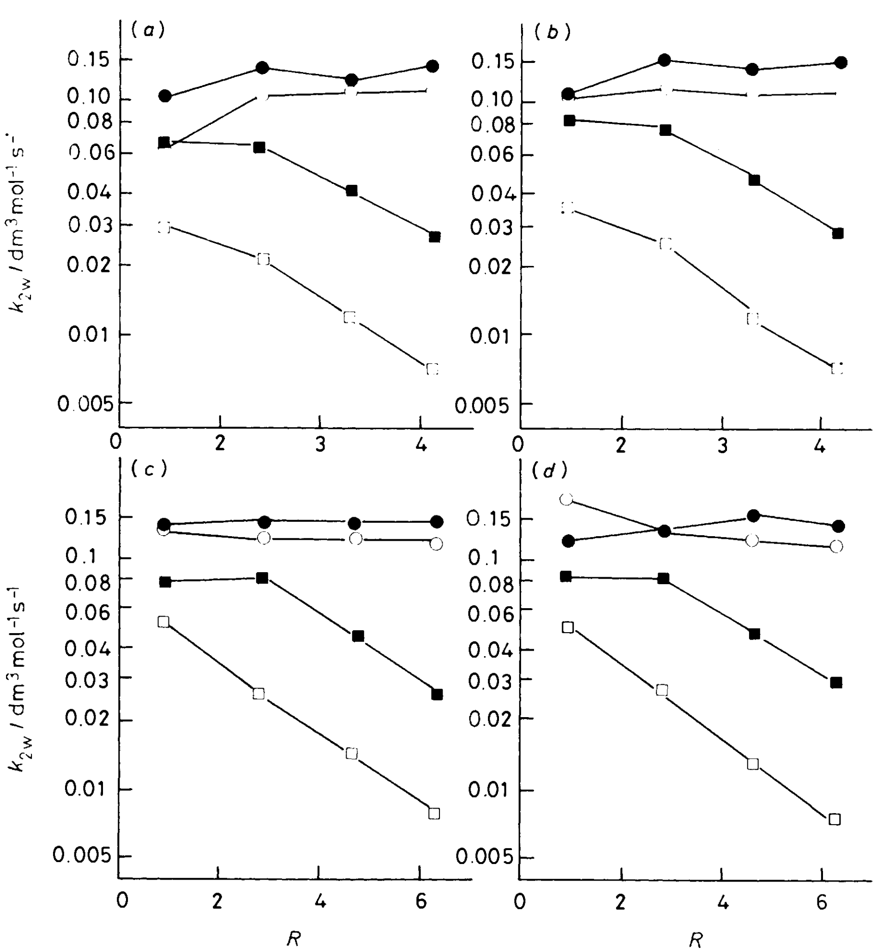

Figure 2. Plots of k_{2w} for *N*-alkyl-3-carbamoylpyridinium ions *vs.* *R*. The concentrations of CN^- ion in water pools; (*a*) 0.04; (*b*) 0.06; (*c*) 0.08; (*d*) 0.10 mol dm^{-3}. ●, $C_{12}P^+$; ○, C_6P^+; ■, C_3P^+; □, C_1P^+.

previously.[1,2] Solvents employed, chloroform and 2,2,4-trimethylpentane (iso-octane) were as used previously.[1,2]

Procedure.—HTAB was dissolved in a chloroform–iso-octane mixture (3:2 volume ratio) to 0.2 mol dm^{-3}. A small quantity of aqueous sodium cyanide (1.0–9.0 × 10^{-2} cm^3) was added to HTAB solution (30 cm^3) in a moisture-proof cell. The concentration of added sodium cyanide or CN^- ion in the aqueous solution, $[CN^-]_{aq}$, was in the range 0.02–0.2 mol dm^{-3}. By stirring the mixture, we obtained a transparent and apparently homogeneous solution, which can be regarded as a reversed-micelle system. In the solution, the molar ratio of water to HTAB, *R*, was in the range 0.9–8.1. The quantity of water present was measured as described in the previous paper.[1]

The reaction was initiated by injecting into the HTAB reversed-micellar solution containing CN^- ion, an aliquot (10 mm^3) of C_nP^+ in MeOH. In the reaction mixture thus formed, the initial concentration of C_nP^+ was in the range 1–1.5 × 10^{-4} mol dm^{-3}. The kinetic constant and equilibrium constant were measured at 25.0 ± 0.1 °C by the same method reported in the previous paper.[2] The equilibrium constant for the reaction in the water pool, K_w, was obtained by using

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

equation (1).[2] $A_{340}{}^m$ is the value of A_{340} for the 4-cyano adduct (4-cyano-1,4-dihydro-*N*-alkylnicotinamide) in the hypothetical case of the completed reaction. $[C_nP^+]_w{}^i$ and $[CN^-]_w{}^i$ represent the values for C_nP^+ and CN^- ions at the start of the reaction, respectively. The superscript, f, denotes the state finally observed after sufficient time has elapsed. Although $[C_nP^+]_w$ and $[CN^-]_w$ are functions of time, *t*, in the intermediate-stage reaction, we adopted the above set of values at the relaxation time, as was described previously.[2]

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

Results and Discussion

The second-order rate constants, k_{2w}, and the equilibrium constants, K_w, were measured for *N*-propyl, *N*-hexyl, and *N*-dodecyl derivatives. The reaction constants were evaluated on the basis of the water pool in the micelle being the reaction space, as reported in the measurement of C_1P^+.[2] Here, their reaction constants must be apparent because they were determined on the basis of the concentration of reaction species in the water pools, while the reaction species could be unevenly distributed or localized in water pools, as shown in Figure 1. Figure 2 shows the plots of the values of k_{2w} *vs.* *R* at 0.04, 0.06, 0.08, and 0.10 mol dm^{-3} of CN^- ion concentration in water pools, $[CN^-]_{aq}$. The plots of the values of k_{2w} for C_1P^+ reported in the previous paper,[2] are simultaneously included in the respective figures. The values of k_{2w} tend to increase over the

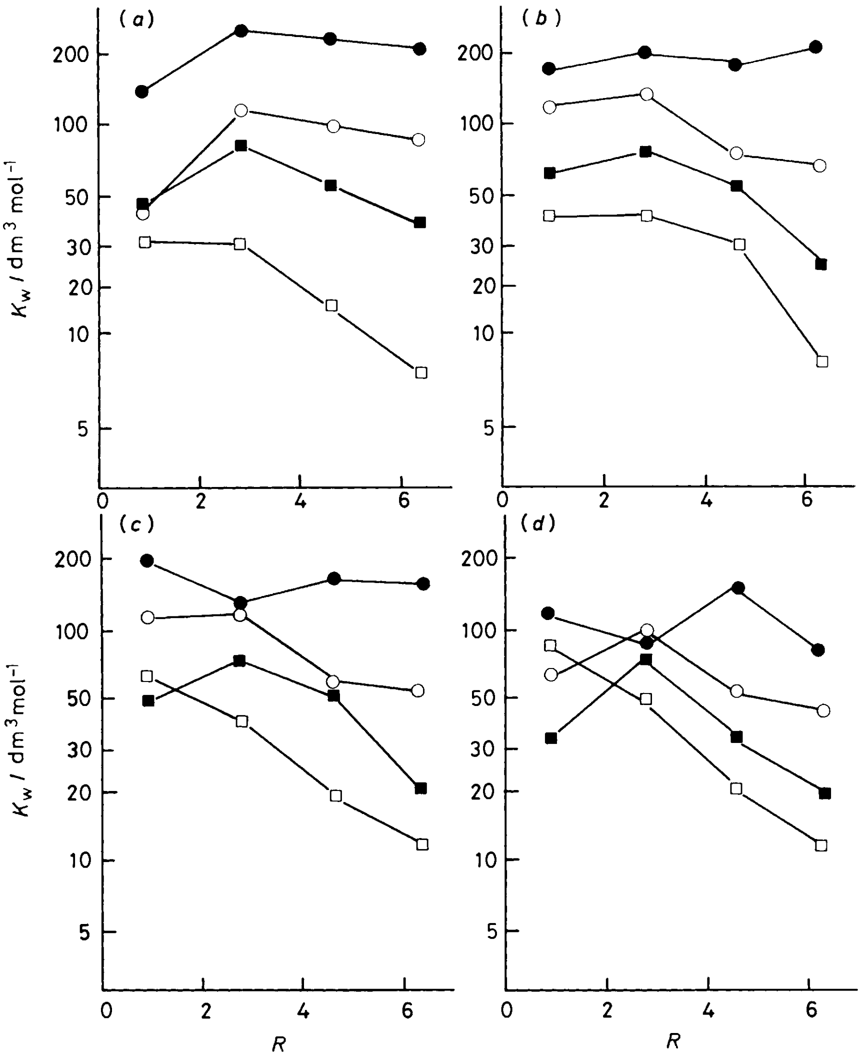

Figure 3. Plots of K_w for N-alkyl-3-carbamoylpyridinium ions vs. R. The concentrations of CN^- ion in water pools; (a) 0.04; (b) 0.06; (c) 0.08; (d) 0.10 mol dm^{-3}. ●, $C_{12}P^+$; ○, C_6P^+; ■, C_3P^+; □, C_1P^+.

overall range of concentrations of CN^- ion with increasing alkyl chain length. Such a tendency is well observed with increasing R, though the values of k_{2w} for C_6P^+ are similar to those for $C_{12}P^+$. In other words, k_{2w} for the longer alkyl derivatives become less dependent on R.

Figure 3 shows the plots of the values of K_w vs. R, where the concentrations of CN^- ion in water pools, $[CN^-]_{aq}$ are equal to those in Figure 2. Pyridinium ion having a longer alkyl chain tends to give a higher K_w value in the overall range of CN^- ion concentration, especially at large R.

The results of Figures 2 and 3 are summarized as follows. First, both values of k_{2w} and K_w for respective alkyl derivatives tend to increase more or less with decreasing R. Secondly, the addition reaction tends to proceed favourably as alkyl chain length increases in the overall range of CN^- ion concentration and R. Third, the addition reaction tends not to be affected significantly by the water content in the reversed micelles with increasing alkyl chain length for alkyl derivatives.

The factors responsible for this phenomenon are qualitatively discussed. It is well known that addition of water results in a rapid increase of the average aggregation number and the size of the water pool.[6a] For example, in the reversed-micelle system of sodium bis(2-ethylhexyl)sulphosuccinate(AOT)–cyclohexane, the aggregation numbers are 36 and 114 at 2 and 8 for R, respectively, and the radii of the water pool are 0.81 and 1.8 nm at 2 and 8 for R, respectively.[6b] The size of the water pool increases with increasing R.[6] No attempts have been made to measure the size of water pools formed by HTAB reversed micelles, though it is reported that the aggregation number of HTAB reversed micelle in chloroform at $R = 0$ is ca. 3 measured using vapour pressure osmometry.[7] However, the dependence of the size of the water pool on R in the HTAB system was assumed to be similar to that found in the AOT system. The water molecules present in water pools may be divided into two types according to the two-phase model.[8a] The water in the HTAB–chloroform reversed-micelle system is also thought to be divided in the two types of water based on measurements of near-infrared spectra and NMR spectra.[8b]

We propose that the models of the water pools at large and at small R, is as shown in Figure 4. Type I water represents water molecules residing near the micellar interface and is tightly bound to the ionic head group of surfactants.[9,10] Therefore, the nature of this kind of water is different from that of pure water solution. Type II water represents water molecules present in the centre zone of the water pool and the nature of this kind of water is also regarded as being almost identical to that of pure water solution. The behaviour of surfactant in the water pool is considered to be afforded in the interfacial zone. The size of the water pool at high R is large and its water pool also consists of type I water present in the interfacial zone and type II water in the centre zone. As the interfacial zone becomes occupied with decreasing R, the physical properties of type I water also become favourable, as observed with decreasing R. As described in the previous paper,[1] the micropolarity of the water pools for a low content of water becomes close to that of MeOH for the HTAB reversed micelles.[11] Therefore, it seems reasonable to consider, regardless of alkyl chain lengths, that one of the factors responsible for the enhancement of the addition at small R must be the lowering in micropolarity of water pool that is brought about mainly by type I water.

The effect of unequal distribution of reactants in the water pool must be taken into account. It is ascribed to the electric field produced by the cationic surfactant, HTAB reversed micelle. In the large water pool, CN^- ions are predominantly distributed in the interfacial zone owing to the electrostatic attraction. Therefore, the degree of distribution of CN^- ion is qualitatively assumed in Figure 4. However, a small water pool contains mainly type I water and the distribution of CN^- ion is rather uniform, as shown in Figure 4.

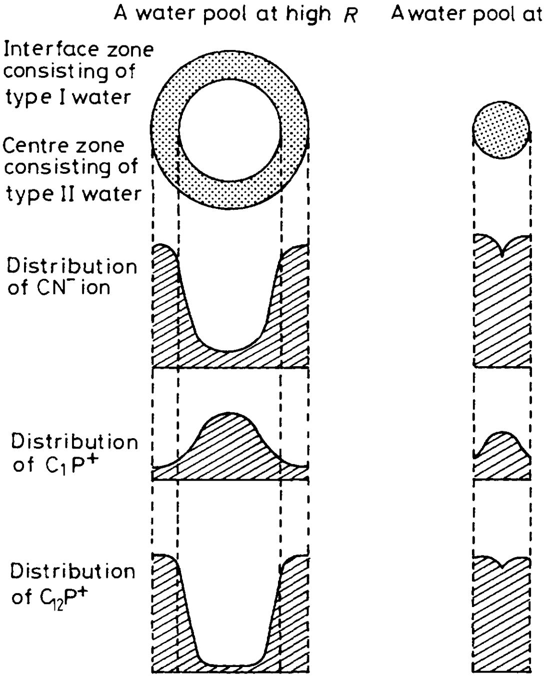

Figure 4. Non-uniform distribution of reactants in a water pool formed by HTAB reversed micelle.

Here, we remark on another reactant, C_1P^+. It is water-soluble[1] and is also distributed mainly in the centre zone due to the electric repulsion, although the hydrophobicity, though small, of C_1P^+ keeps a small quantity in the interface zone.[1,2] The distribution of C_1P^+ tends to be uniform in the small water pool compared to that in the large water pool, as shown in Figure 4. However, pyridinium ion having a long alkyl chain such as $C_{12}P^+$ is distributed mainly in the interface zone in which CN^- ion is concentrated, regardless of the size of water pools, as shown in Figure 4. Therefore, it is likely that the addition reaction for $C_{12}P^+$ proceeds favourably in comparison with that for C_1P^+ and is not affected significantly by any change in R, but that for C_1P^+ proceeds advantageously with small R.

In order to interpret the enhancement of the addition reaction for the longer alkyl derivatives such as $C_{12}P^+$, the electric repulsion between cationic head groups of $C_{12}P^+$ and HTAB should be noted. In other words, since transition state formation results in charge neutralization and, therefore, a decrease in the electric repulsion,[4,5] the reaction for $C_{12}P^+$ which is located in the interface zone, is likely to proceed advantageously compared to that for C_1P^+.

Since both CN^- and Br^- ion are predominantly concentrated in the interface zone of the water pool, as shown in Figure 1, the physical properties of the interface zone must be different to those of the centre zone and it is hence presumed that these ions concentrated in the interface zone significantly affect the reaction, especially for the longer alkyl derivatives.

We note the effects of CN^- ion concentration on the addition reaction. Figures 5 and 6 show the effects of CN^- concentration in water pools, $[CN^-]_{aq}$, on k_{2w} and K_w, respectively, where the values of R are 2.8 and 6.3. The values of k_{2w} for respective alkyl derivatives tend to increase with CN^- ion concentration in the water pools. However, the values of K_w for C_3P^+, C_6P^+, and $C_{12}P^+$ decrease with increasing CN^- ion concentration, but their values for C_1P^+ tend to increase slightly with CN^- ion concentrations. Therefore, the effect of the concentrations of

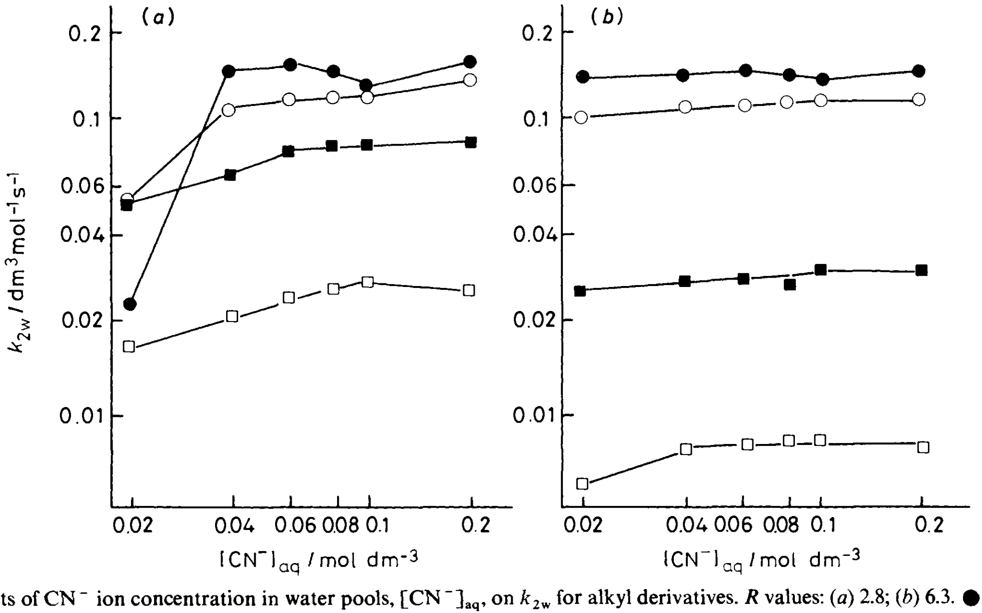

Figure 5. The effects of CN^- ion concentration in water pools, $[CN^-]_{aq}$, on k_{2w} for alkyl derivatives. R values: (a) 2.8; (b) 6.3. ●, $C_{12}P^+$; ○, C_6P^+; ■, C_3P^+; □, C_1P^+.

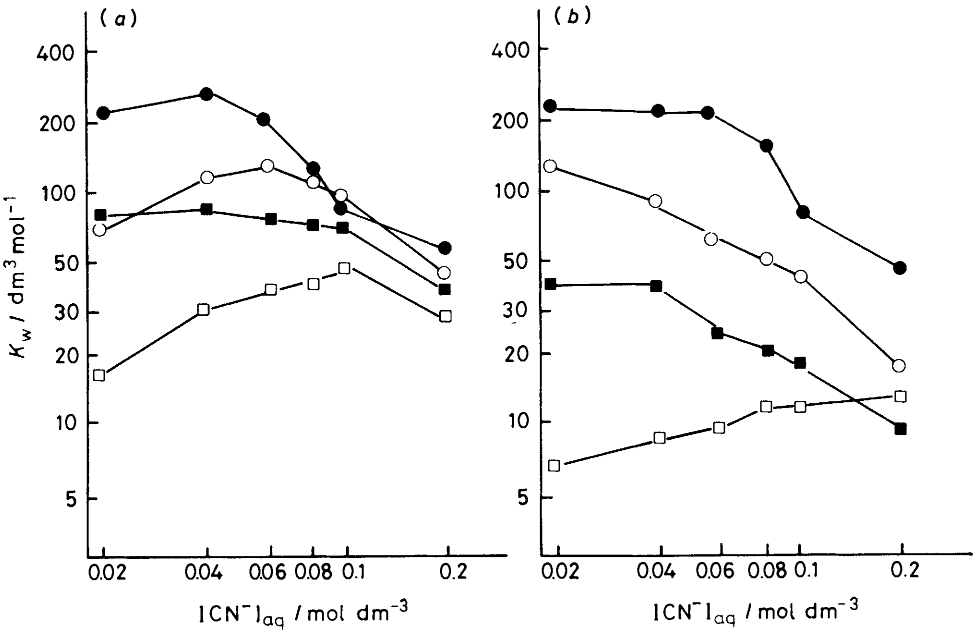

Figure 6. The effects of CN^- ion concentration in water pools, $[CN^-]_{aq}$, on K_w for alkyl derivatives. R values: (*a*) 2.8; (*b*) 6.3. ●, $C_{12}P^+$; ○, C_6P^+; ■, C_3P^+; □, C_1P^+.

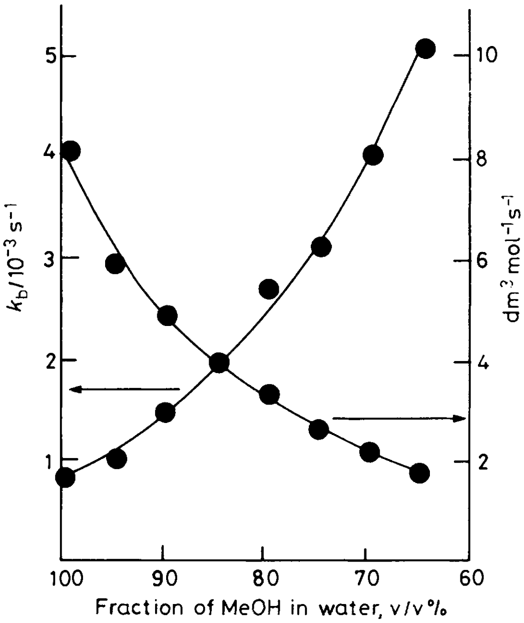

Figure 7. Plots of k_b for *N*-methyl-3-carbamolypyridinium ion against the fraction of MeOH in water with k_f.

CN^- ion on k_{2w} is somewhat different from that on K_w. Since it has been reported that CN^- ion is exchangeable with Br^- ion on the micellar surface in aqueous cationic micelle systems,[4] it is speculated that the effect of the concentration of CN^- ion on the addition reaction is closely related to that of Br^- ion not only in aqueous HTAB micellar systems,[4,5] but also in HTAB reversed-micelle system. The concentration effect of CN^- ion on the addition is also complex.

One of the factors responsible for the effect of CN^- ion concentration is suggested as follows. The above model as represented in Figure 4 might be best applied to the forward reaction, in which C_nP^+ and CN^- ions are invoked as principal species. Some discrepancies in k_{2w} and K_w between the effects of CN^- ion concentration thus suggest that the effect of CN^- ion concentration on the forward reaction is somewhat different from that on the backward reaction, in which it is concerned with the 4-cyano adduct as a sole reaction. Alternatively, it is suggested that the main field of the forward process differs somewhat from that of the backward process, as described in the previous papers.[1,2]

On the basis of the value of the second-order rate constant for the forward reaction, k_f, and the value of the equilibrium constant, K, in the mixed solvent MeOH–H_2O previously reported,[1] the rate constant regarding the backward reaction, k_b, for C_1P^+ was calculated from K and k_f. The values of k_b and k_f were plotted against the fraction of MeOH in the mixed solvent, as shown in Figure 7. As the fraction of MeOH in water decreases *i.e.* the polarity of the medium increases, the values of k_b were found to increase. The backward reaction is likely to be accelerated with increase in micropolarity, in contrast to k_f.

Alternatively, it is presumed that the micropolarity of the interface zone varies with increasing concentration of CN^- ion in the water pools because it is known that the hydration around the ions[11,12] may change any physical properties of the water pools. With respect to the forward reaction, the effect of non-uniform distribution of reactants described above would exceed the microenvironmental effect brought about by CN^- ion. However, the backward reaction might be affected mainly by the microenvironment effect due to CN^- ion. Therefore, it seems also reasonable to assume that the backward reaction for longer alkyl derivatives is likely to be accelerated by CN^- ion concentrated in the interface zone, resulting in a decrease in K_w with CN^- ion concentration.

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