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ORIGINAL CONTRIBUTION

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The effect of surfactant charge on micellization behavior

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Abstract The influence of the surfactant charge on micellization was studied on sodium *n*-dodecanephosphonates, varying the charge of the surfactant ion from 0 to 2. The effects on the cmc, hydrolysis, micelle composition, and micelle ionization degree were studied. The increase of one *e* unit in the charge of the surfactant species reduces the cmc by about one order of magnitude.

Key words Micelle charge – alkanephosphonates – cmc – micellization – micelle composition

Introduction

Alkanephosphonates are surfactants which have been scarcely studied. They are salts of a diprotic acid, which enables a study to be made of the effect of increasing the charge of the headgroup between 0 and 2. However, *n*-alkanephosphonic acids are weak [1–3] and the hydrolysis of their salts complicates the interpretation of data. The theoretical interest in the study of these characteristics is evident. Phosphonates have increasing importance in industry as detergent additives [4], inhibitors of corrosion [5], ligands [6], metal extactors [7, 8] and agents of flotation [9]. Therefore, a knowledge of their properties is of great practical interest.

Only a few measurements of the cmc of alkylphosphonates have been reported in literature, limited to the cmc value determined by a single method, such as conductivity or surface tension. However, the phenomena that take place at the cmc have not been investigated in detail, except in a very few cases.

Experimental

The preparation and purification of *n*-dodecanephosphonic acid (H_2DP) has been described elsewhere [10].

Mono and disodic *n*-dodecanephosphonate (HNaDP and Na_2DP) solutions were made by taking a weighed amount of solid acid and neutralizing by the appropriate amount of NaOH solution in double-distilled water. Surface tension measurements were made using a ring-tensiometer (Krüss). Conductivity measurements were performed with an immersion cell and an automatic conductimeter, namely, an Antares II of Instrumentalia. Sealed tubes with Sudan Black B in surfactant solutions of different concentration were left for 1 week in a constant temperature bath, with periodic stirring. Then the tubes were centrifuged and the supernatant absorbance was measured with a Hewlett-Packard Diode Array HP84 52A spectrometer at 600 nm. OH^- determinations were made with an Orion glass electrode and pH-meter. To determine Na^+ ions, a Na^+ ion-selective electrode Metrohom EA 109 vs. SCE was employed. To determine HDP- and DP2- ions, a membrane electrode was made, whose description and performance are described elsewhere [11]. The potentiometric data were analyzed by the usual method described in literature to determine the free and micellized ion concentrations and the micelle ionization degree [12].

Several tubes with different concentration of HNaDP in water were prepared. The Krafft point was determined by recording the temperature at which the surfactant solid dissolved on heating.

When straight lines were obtained, they were treated by the least-squares method. Averages were obtained with the minimum variance linear unbiased estimation method [13]. A confidence level of 0.90 and the Student's t distribution function were employed in all error estimations.

Results

Monosodium *n*-dodecanephosphonate

Figure 1 shows the HNaDP solubility in water as a function of temperature. The Krafft point obtained from this data was 65 °C. That of monosodium *n*-decanephosphonate is 29.3 ± 1.1 °C [14]. On the basis of the Krafft point, the other experiments were run at 66 °C.

From the dependence of the surface tension of solutions of HNaDP on the concentration, the determined cmc was $(6 \pm 0.2) \times 10^{-3}$ mol dm^{-3}.

The concentrations of free Na^+ and HDP^- ions at different total concentrations (C_T) of the surfactant in water are shown in Fig. 2. The cmc value was $(6.0 \pm 0.4) \times 10^{-3}$ mol dm^{-3} (HDP^- electrode) and $(4 \pm 0.2) \times 10^{-3}$ mol dm^{-3} (Na^+ electrode).

The hydrolysis degree $\beta = [OH^-]/C_T$ was plotted in Fig. 3 against the total concentration of the surfactant. The cmc determined in this plot was $(7.0 \pm 0.2) \times 10^{-3}$ mol dm^{-3}. From pH measurements, cmc = $(6.7 \pm 0.4) \times 10^{-3}$ mol dm^{-3}.

In Fig. 4 the equivalent conductivity vs. $\sqrt{C_T}$ is shown. The cmc determined on the basis of these data is

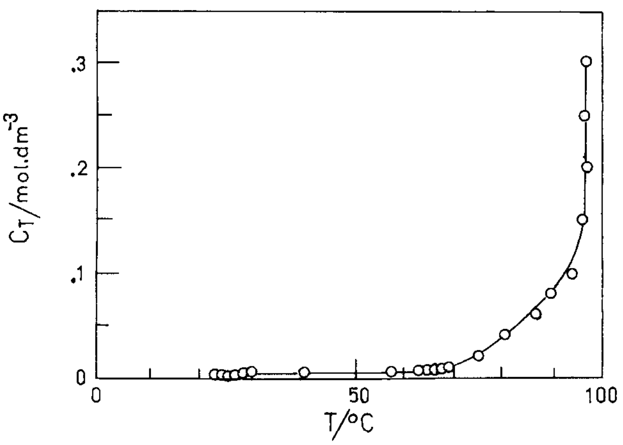

Fig. 1 Solubility of HNaDP in water vs. temperature

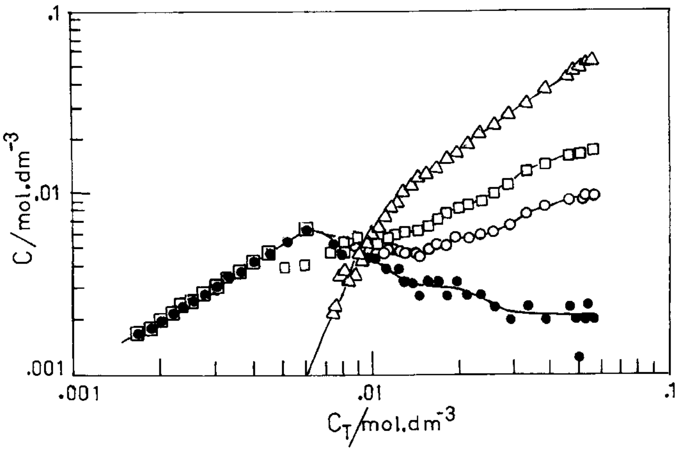

Fig. 2 Concentration of □: free Na^+ ions, ●: free HDP^- ions, △: micelles (on a monomer basis), and ○: ionic strength vs. total concentration of HNaDP in water at 66 °C

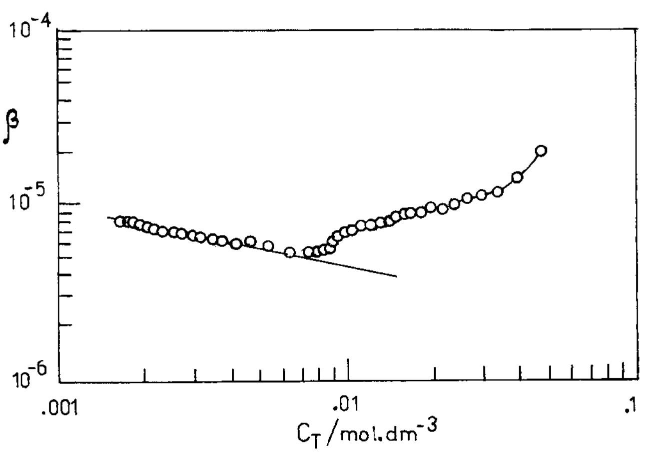

Fig. 3 Degree of hydrolysis of HNaDP vs. concentration in water at 66 °C

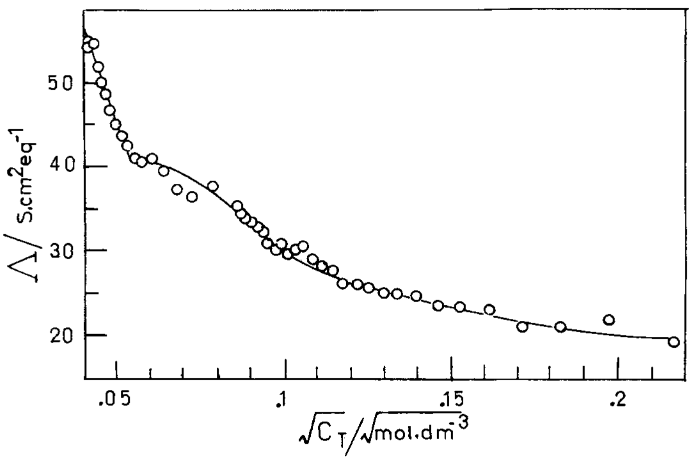

Fig. 4 Equivalent conductivity of HNaDP solutions vs. the square root of total concentration at 66 °C

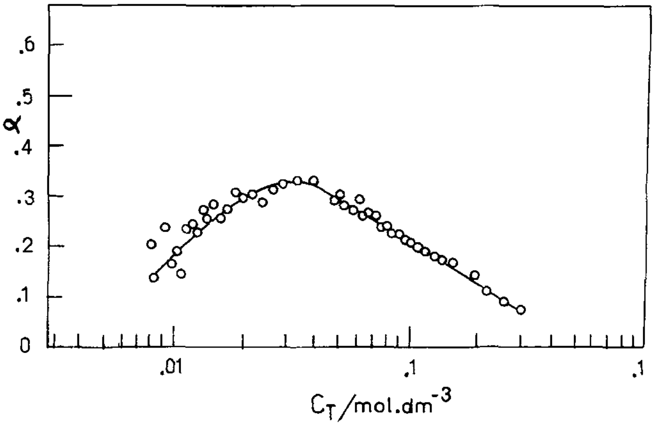

Fig. 5 Micelle ionization degree of HNaDP solutions vs. total concentration at 66 °C

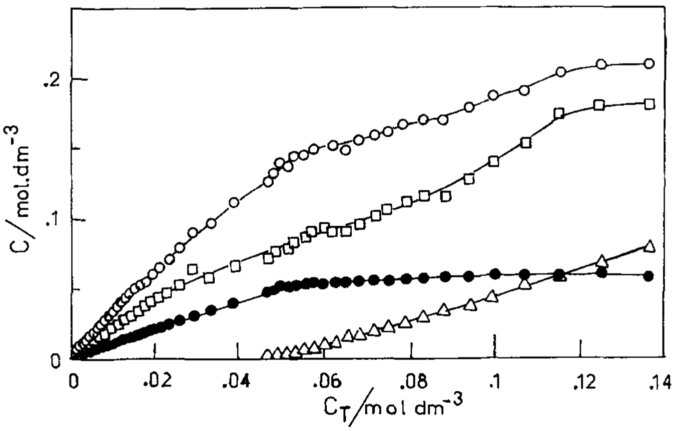

Fig. 6 Concentration of □: free Na^+ ions, ●: free DP^{2-} ions, △: micelles (on a monomer basis), and ○: ionic strength vs. total concentration of Na_2DP in water at 25 °C

$(5.7 \pm 0.4) \times 10^{-3}$ mol dm^{-3}. From specific conductivity, cmc $= (7.3 \pm 0.8) \times 10^{-3}$ mol dm^{-3}. The equivalent conductivity at infinite dilution of NaHDP was $\Lambda_0 = 96.95$ S cm^2 eq^{-1}.

By solubilization of Sudan Black B a value of $(5.9 \pm 0.3) \times 10^{-3}$ mol dm^{-3} for the cmc was found.

Figure 5 shows the effective charge per micellized molecule vs. the total concentration of surfactant.

Disodium *n*-dodecanephosphonate

Figure 6 shows the dependence of the free Na^+ and DP^{2-} ions on the total concentration of the surfactant. The cmc was $(2.6 \pm 0.2) \times 10^{-2}$ mol dm^{-3} (Na^+ electrode) and $(3.0 \pm 0.2) \times 10^{-2}$ mol dm^{-3} (DP^{2-} electrode).

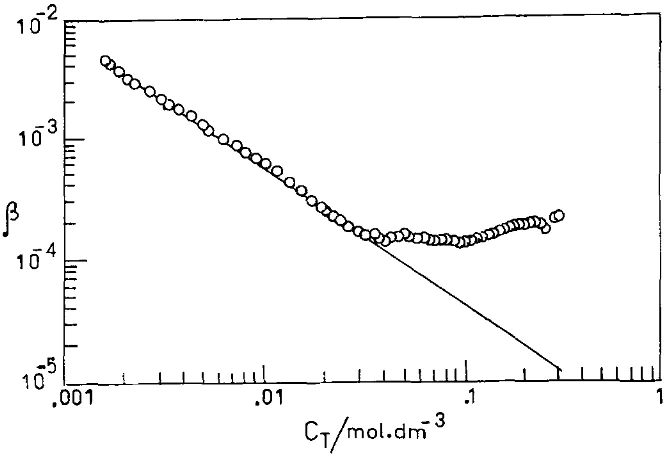

Fig. 7 Degree of hydrolysis of Na_2DP vs. concentration in water at 25 °C

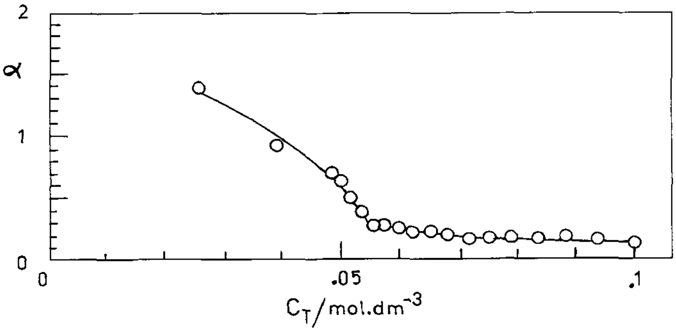

Fig. 8 Micelle ionization degree of Na_2DP solutions vs. total concentration at 25 °C

In Fig. 7 the hydrolysis degree of Na_2DP was plotted vs. the total concentration. From this plot, cmc $= (3.5 \pm 0.2) \times 10^{-2}$ mol dm^{-3}. From $[OH^-]$ vs. concentration data, cmc $= (3.2 \pm 0.2) \times 10^{-2}$ mol dm^{-3}. Sudan Black B solubilization gave cmc $= (1.1 \pm 0.3) \times 10^{-2}$ mol dm^{-3}. Surface tension measurements gave cmc $= (1.3 \pm 0.2) \times 10^{-2}$ mol dm^{-3}. Specific conductivity measurements gave cmc $= (1.6 \pm 0.8) \times 10^{-2}$ mol dm^{-3}, and the same data, plotted as equivalent conductivity, gave cmc $= (2.3 \pm 0.8) \times 10^{-2}$ mol dm^{-3}.

Figure 8 shows the micellar degree of ionization as a function of concentration. Note that the maximum value of α is 2 for Na_2DP micelles.

Discussion

Monosodium *n*-dodecanephosphonate

From the various methods employed, the cmc average value of monosodium *n*-dodecanephosphonate at 66 °C obtained by the linear unbiased minimum variance estimation method was:

cmc = $(5.80 \pm 0.10) \times 10^{-3}$ mol dm^{-3} .

The literature value is 0.0056 mol dm^{-3} [15] or 0.0065 mol dm^{-3} [16].

Dodecanephosphonic acid has two ionization constants ($pK_1 = 3.98$ and $pK_2 = 8.42$ [17]. In HNaDP aqueous solutions, there are two species in equilibrium, HDP^- and H_2DP. They are related by the hydrolysis equilibrium:

$$HDP^- + H_2O = H_2DP + OH^- \ .$$

The straight line in Fig. 3 corresponds to a normal hydrolysis of an aqueous solution of a weak acid salt. The separation of the experimental data from the straight line indicates the increased hydrolysis at the cmc. Because of the low solubility, *n*-decanephosphonic acid (formed by the HDP^- hydrolysis) dissolves into micelles. In micelles, the unionized -PO3H2 groups intercalate between charged -PO3H-groups. As in H_2DP mesophases [18], the groups in surface must be bound by strong hydrogen bonds. At the same time, the surface charge density is reduced, stabilizing micelles.

The degree of hydrolysis together with the hydrolysis equilibrium, which is applicable to the unmicellized HDP^- ions, enabled us to determinate the composition of micelles. The concentration of free (unmicellized) H_2DP was computed by the hydrolysis constant:

$$[H_2DP]_{free} = \text{Khid}.[HDP^-]_{free}/[OH^-]_{free}$$

and the micellized HDP^- to micellized H_2DP ratio was computed by

$$R = \frac{[H_2DP]_{mic}}{[HDP^-]_{mic}} = \frac{([OH^-] - [H_2DP]_{free})}{(CT - [HDP^-]_{free})} \ .$$

This ratio is plotted in Fig. 9 against total concentration. It is seen that between the cmc and $C_T =$ 0.036 mol dm^{-3}, it is almost constant, with an average value of $(1.03 \pm 0.40) \times 10^{-5}$. The ratio is 3.03×10^{-7} for dodecyltrimethylammonium hydroxide micelles [19] and 2.8×10^{-4} for sodium palmitate micelles [20]. At $C_T > 0.036$ mol dm^{-3}, this ratio rises with increasing concentration. This situation is probably associated with a change in micelle structure. As an example, rod-like micelles have more solubilizing capacity than spherical ones [21]. The transition may be facilitated by formation of strong hydrogen bonds between the headgroups.

The distribution constant of H_2DP molecules between micelles and intermicellar solution may be computed by the equation:

$$K_d = \frac{[H_2DP]_{mic}}{[H_2DP]_w} = \frac{1000R}{V_{m,HNaDP} \cdot [H_2DP]_w} \ ,$$

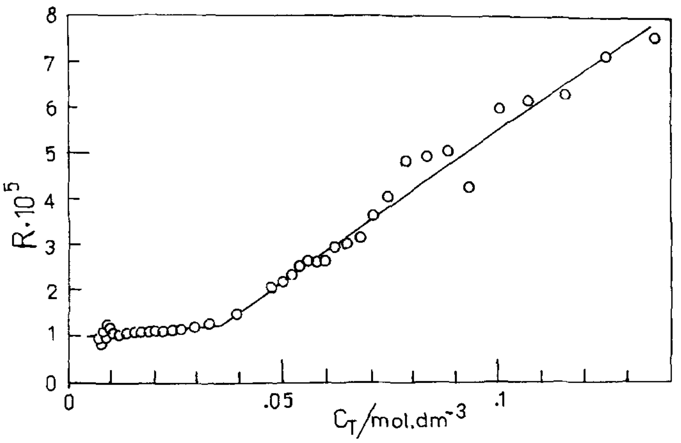

Fig. 9 The micellized H_2DP molecules to micellized HDP^- ions ratio vs. total concentration. HNaDP solutions in water at 66 °C

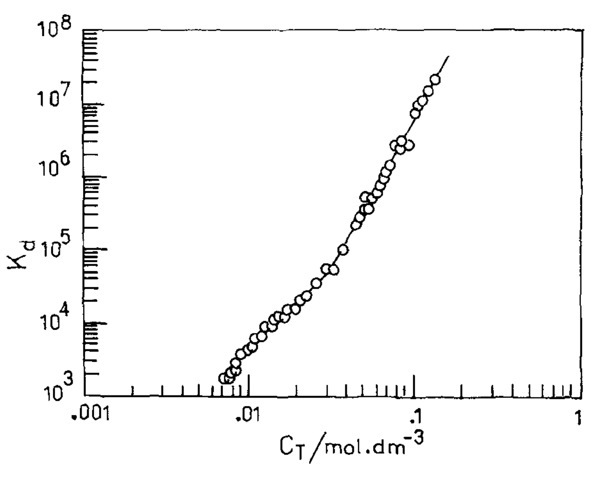

Fig. 10 The distribution constant of H_2DP between HNaDP micelles and water vs. total concentration. HNaDP solutions in water at 66 °C

$V_{m,HNaDP}$ being the partial molar volume of micellized HNaDP. The partial molar volume of micellized Na_2DP is 240.73 ± 0.5 cm^3 mol^{-1} at 21 °C, and its temperature coefficient is 0.001810 ± 0.000011 °C^{-1} [22]. There are no literature data for HNaDP, but a good estimation may be made by substracting the partial molar volume of the Na^+ ion (-5.7 cm^3 mol^{-1}) and adding that of H^+ ion (-4.5 cm^3 mol^{-1}) [23]. This gave $V_{m,HNaDP} = 241.9 \pm 0.2$ cm^3 mol^{-1} at 21 °C, and 261.6 ± 0.2 cm^3 mol^{-1} at 66 °C. The dependence of K_d with the total concentration is shown in Fig. 10. It may be seen that K_d increases with C_T, with a break at $C_T \approx 0.035$ mol dm^{-3}. This behavior shows that the interaction between H_2DP and micelles changes with concentration. The growth of micelles with concentration indicates that the micellized headgroups approach each other, giving better opportunities to the formation of inter-headgroup hydrogen bonds. This may increase the capacity of micelles to solubilize H_2DP molecules.

The shape of the conductivity curve in Fig. 5 may be due to the formation of an excess of strongly conducting OH^- ions by the micellization hydrolysis.

Figure 7 shows that micelles have an ionization degree (α) similar to that of other anionic surfactants near the cmc ($\alpha \approx 0.2$), but differs from them, since α rises with increasing concentration and passes through a maximum ($\alpha \approx 0.35$) at about 0.035 mol dm^{-3}. At higher concentrations the micellar degree of ionization falls which is common in other surfactants. The change in behavior occurs at the same concentration in which both the $[H_2DP]/[HDP^-]_{mic}$ ratio and K_d change their dependence on total concentration. A change in micelle shape, such as a sphere–rod-like transition, must mean that the headgroups approach each other. This situation increases the surface potential and in consequence, more counterions are attached to the micelle Stern layer, thus reducing α.

Disodium *n*-dodecanephosphonate

The average value of the cmc of Na_2DP at 25 °C was

cmc = 0.0257 ± 0.0008 mol dm^{-3}.

Literature values are 0.0177 mol dm^{-3} [24], 0.0238 mol dm^{-3} [15] and 0.0221 mol dm^{-3} [16].

Figure 7 shows that hydrolysis increased at the cmc. However, in this case the product of hydrolysis is the HDP^- ion. This ion is less soluble than DP^{2-}, but much more soluble than H_2DP and solubilizes in micelles. The value of α was high at the cmc (about 1.4) and diminished with increasing concentration because of the high surface potential which captures Na^+ ions in the Stern layer, and the very high ionic strength I (see Fig. 6), which diminishes the Debye length. At $C_T \approx 0.55$ mol dm^{-3}, α reached a more normal value of ~0.2.

The micellized HDP^- to $DP^=$ ratio was computed in the same manner as in the preceding section, giving an almost constant value of $R = (2.9 \pm 1.7) \times 10^{-7}$. This value is two orders of magnitude lower than in NaHDP micelles, reflecting the higher water solubility of the product of hydrolysis.

The partial molar volume of Na_2DP micellized molecules was 242.41 ± 0.16 cm^3 mol^{-1} at 25 °C. The distribution constant of HDP^- ions between micelles and intermicellar solution was $K_d = 34 \pm 13$, showing no significant dependence on C_T. It is evident that HDP^- ions have only a slightly higher solubility in micelles over that in water, and the interaction between solubilizate and micelles does not change with concentration. In contrast, H_2DP molecules have a very strong interaction with HNaDP micelles, with K_d ranging from 2×10^3 to 2×10^7 in the studied concentration range.

Effect of charge on cmc and micellization

The cmc values of aqueous solutions of H_2DP, HNaDP and Na_2DP are given in Table 1. Cmc values are only slightly affected by temperature [16], so it may be concluded from the data of Table 1 that cmc increases by about one order of magnitude when the headgroup charge increases by one *e* unit.

Comparison between Figs. 2 and 6 showed that micelles of the 1:1 surfactant are more stable than that of 1:2. At concentrations larger than the cmc, HNaDP micelles grew speedly and the concentration of monomeric surfactant decreased strongly, whereas the concentration of Na_2DP micelles grew slowly and the concentration of the free surfactant was almost constant. On the basis of the theories about factors influencing micelle formation, this result is not surprising [26].

At the cmc, HNaDP micelles were less ionized ($\alpha \approx 0.2$) than Na_2DP ones ($\alpha \approx 1.4$). The behavior of α when the concentration is increased is different: in HNaDP micelles α first rose, passed through a maximum and then decreased, whereas in Na_2DP α decreased monotonically when the total concentration was increased. The latter is the normal behavior of α. The behavior of HNaDP micelles may be associated with the hydrogen-bonded structure of the Stern layer, because other 1:1 common surfactants do not show this phenomenon.

Due to the lower solubility of H_2DP, the distribution constant of this product of hydrolysis is several orders of magnitude higher in HNaDP micelles than that of HDP^- ions in Na_2DP micelles. Solubilization of H_2DP molecules may stabilize HNaDP micelles and "dilute" the surface

Table 1 CMC values of H_2DP and its mono and disodium salts

Surfactant	T (°C)	cmc (mol dm^{-3})	Reference
H_2DP	26	$(5.4 \pm 2.4) \times 10^{-4}$	25
	20–80	0.00104	16
HNaDP	66	$(5.8 \pm 0.1) \times 10^{-3}$	This work
	80	6.5×10^{-3}	16
Na_2DP	25	$(2.57 \pm 0.08) \times 10^{-2}$	This work
	25	0.0177	24
	60	0.0238	15
	60	0.0221	16

charge density, thus releasing some of the Na^+ ions from the Stern layer. If a change in micelle structure occurs at $C_T \approx 0.035$ mol dm^{-3}, such as a sphere-rod transition, the subsequent approximation of the headgroups may cause an increase in the surface charge density and the capture of counterions by the Stern layer. In addition to this phenomenon there is a normal reduction of the Debye length by an increase of the ionic strength (I) in the intermicellar solution, when C_T increases.

The initial value of $\alpha \approx 1.4$ corresponds to a neutralization of about the 30% of the total charge of the micelle ($\alpha_{max} = 2$), whereas in the HNaDP–water system, $\alpha \approx 0.2$ corresponds to the neutralization of about the 80% of the charge ($\alpha_{max} = 1$). The very high value of α in Na_2DP micelles near to the cmc is due to the high ionization of the headgroups and the low HDP^- content in micelles, which could not "dilute" the surface charge. The very rapid decrease of α in the Na_2DP–water system with increasing total concentration is due to the very high value of I.

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