Colloid Polym Sci 274:1089–1093 (1996)

SHORT COMMUNICATION

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The aggregation of *n*-dodecanephosphonic acid in water

Received: 1 February 1996
Accepted: 1 May 1996

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Abstract Several techniques were employed to study the aggregation of *n*-Dodecanephosphonic Acid (DPA) in water. At 22 °C, the solubillity of DPA increases, probably due to the formation of small premicellar aggregates. The CMC is $(5.4 \pm 2.4) \times 10^{-4}\ \mathrm{mol \cdot dm^{-3}}$ and the solubility reaches the CMC value at 26 °C. At 30 °C and at a concentration of about $9 \times 10^{-3}\ \mathrm{mol \cdot dm^{-3}}$, a lamellar mesophase appears. Both micelles and liquid crystal lamellae are almost uncharged. Their polar heads have strong hydrogen bonds between them. The ionization of DPA molecules in micelles and mesophase structures is strongly reduced in comparison with monomerically dissolved molecules.

Key words Micelles – critical micelle concentration – dodecanephosphonic acid

Introduction

Alkanephosphonic acids are amphiphile compounds whose polarity is similar to that of fatty acids [1–3]. Their aggregation behavior in water has been scarcely studied [4, 5]. Since *n*-alkanephosphonic acids are weak acids, their micelles must have a pronounced nonionic character. This situation is interesting from the point of view of the theories about micelle formation [4, 5]. In addition, phosphonic acids and their salts have many technical applications as collectors [9], corrosion inhibitors [10] and ligands in analytical chemistry [11].

In this laboratory we have studied catanionic systems with *n*-dodecanephosphonic acid as one of the components. This led us to investigate the micellar properties of this acid; this provides important data for the interpretation of the properties of cationic-anionic surfactant mixtures.

Experimental

The synthesis and the purification of *n*-dodecanephosphonic acid (DPA) have been described elsewere [1]. The DPA was carefully purified by repeated recrystallization in petroleum ether.

The solutions were prepared by weighing the solid acid in vials and adding the appropriate amount of double-distilled CO_2-free water. Then the vials were hermetically sealed and heated to 90 °C for about 20 min. Finally, they were left to rest for 2 days before being used. Care was taken to avoid CO_2 contamination.

The statistical treatment of data was performed by the least-squares method, using Student's **t**-distribution and a confidence level of 0.90.

The microscopic observations were performed in a Leitz Westlar crystallographic microscope.

Conductivity measurements were performed with an immersion cell and an automatic conductimeter, namely an Antares II from Instrumentalia.

To perform dye solubilization measurements, sealed tubes with Sudan III and DPA solutions of different concentration were left for a week in a constant temperature bath, with periodic stirring. Then the tubes were centrifuged and the supernantant absorbance was measured with a Spectronic-20 UV–Vis spectrophotometer at 488 nm.

The surface tension measurements were performed with a Du Noüy (Krüss) tensiometer.

HDP^- ion-selective measurements were performed with an ion-selective electrode made by precipitation of disodium *n*-dodecanephosphonate with $CaCl_2$ solution. The solid calcium *n*-dodecanephosphonate was washed with double-distilled water and then dried and pulverized. 0.3 g of this salt was suspended in 10 mL of tetrahydrofuran +0.06 g of dibutylphtalate (plasticiser). 0.3 g of PVC were added, and the suspension was left to evaporate in a Petri dish, covered by a filter paper. The elastic film obtained was glued to a PVC tube with tetrahydrofuran. The inner electrode was Ag/AgCl, and the tube was filled with NaCl $0.001\ \mathrm{mol \cdot dm^{-3}}$ + monosodium dodecanephosphonate (NaHDP) $0.001\ \mathrm{mol \cdot dm^{-3}}$ solution. Some crystals of AgCl were added to ensure saturation. All measurements were performed against a calomel saturated electrode and a CRIBABB pH-meter and millivoltmeter. The electrode was checked by measurements on NaHDP solutions, giving results in agreement with literature [12].

H^+ determinations were made with an Orion glass electrode and a CRIBABB pH-meter and millivoltmeter.

To compute the electrode data, the concentration of free HDP^- below the critical micelle concentration (CMC) was calculated with the first-ionization constant $K_1 = 9.33 \times 10^{-5}$ [13]. Since the second-ionization constant is too low ($K_2 = 3.08 \times 10^{-9}$) [13] we did not consider the presence of DP^{2-} ions. We plotted the measured pre-CMC potentials vs. the computed concentration of free HDP^- ions, and used this plot to find the concentration of free HDP^- ions above the CMC with the measured potentials in this zone. The activity correction has been described elsewhere [14].

The charge per micellized molecule was computed by the equation:

$$\alpha = \frac{[H^+]_{\text{micellar ionization}}}{C_0 - [HDP^-]_{\text{free}} - [DPA]_{\text{free}}}, \tag{1}$$

where C_0 is the total concentration, $[HDP^-]_{\text{free}}$ is the concentration of HDP^- in monomeric form, determined with the ion-selective electrode, $[DPA]_{\text{free}}$ is the concentration of DPA in monomerical dissolved molecules, computed with

$$[DPA]_{\text{free}} = \frac{[HDP^-]_{\text{free}}[H^+]_{\text{free}}}{K_1} \tag{2}$$

in which $[H^+]_{\text{free}}$ was obtained with the glass electrode. The concentration of hydrogen ions pertaining to the micellar ionization was computed by:

$$[H^+]_{\text{micellar ionization}} = [H^+]_{\text{free}} - [HDP^-]_{\text{free}}. \tag{3}$$

The first ionization constant of micellized DPA was computed by:

$$K_{1,M} = \frac{([H^+]_{\text{micellar ionization}})^2}{C_0 - [HDP^-]_{\text{free}} - [DPA]_{\text{free}}}. \tag{4}$$

DPA solubility measurements were performed by recording the temperature at which the solid disappeared in tubes with different amounts of DPA and water.

Results

Figure 1 shows the concentration of free H^+ and HDP^- ions and free DPA molecules in water vs. the total concentration of surfactant, obtained from K_1 and the ion-slective electrodes.

Figure 2 shows the solubility curve of DPA vs. temperature, Fig. 3 the solubilization of Sudan III by DPA

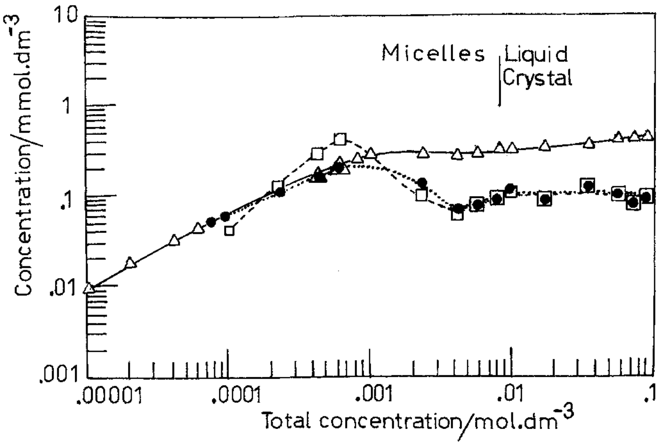

Fig. 1 Concentration of free ● HDP^- and △ H^+ ions, and □ free DPA molecules vs. total concentration in DPA-water systems at 30 °C

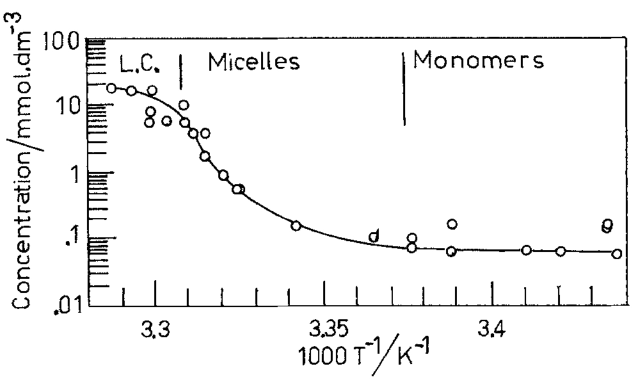

Fig. 2 Total DPA solubility in water as a function of temperature

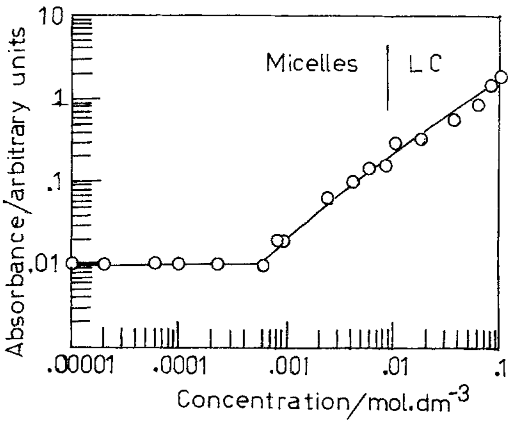

Fig. 3 Sudan III solubilization vs. DPA concentration in water at 30 °C

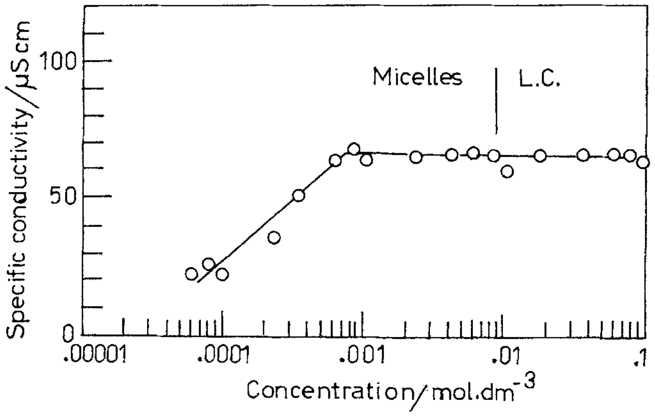

Fig. 4 Specific conductivity of DPA solutions in water at 30 °C

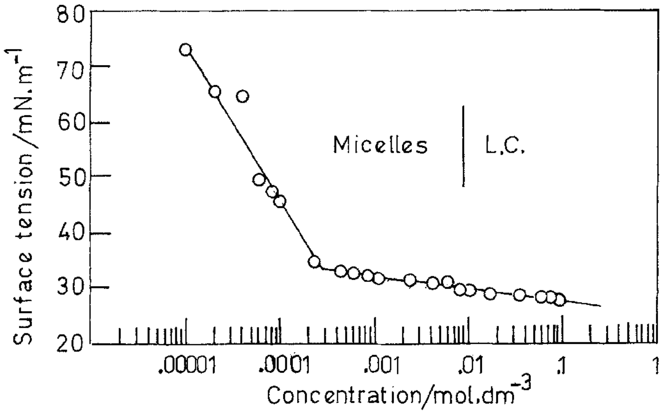

Fig. 5 Surface tension of DPA solutions in water at 30 °C

solutions, Fig. 4 the variation of the specific conductivity vs. concentration of DPA, Fig. 5 the surface tension vs. concentration and Fig. 6 the variation of the $[H^+]/[DPA]$ ratio with concentration.

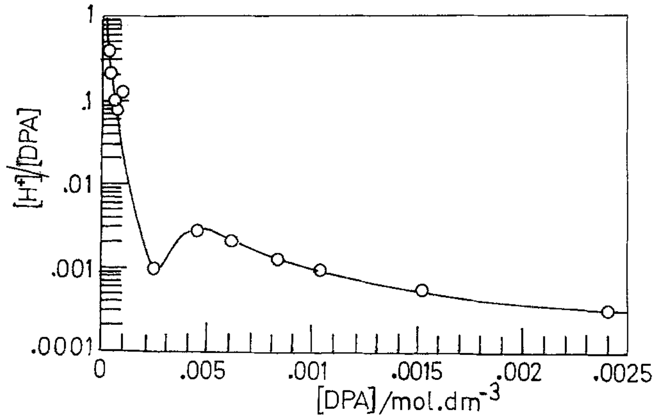

Fig. 6 $[H^+]/[DPA]_{total}$ vs. total concentration of DPA at 30 °C

Table 1 Values of the critical micelle concentration of *n*-dedecanephosphonic acid at 28 °C

Method	CMC/mol·dm^{-3}
Surface tension	2.9×10^{-4}
HDP$^-$ ion-selective electrode	6.2×10^{-4}
Glass electrode	7.8×10^{-4}
Sudan III solubilization	5.5×10^{-4}
Specific conductivity	8.0×10^{-4}
$[H^+]/[DPA]$	2.24×10^{-4}
Average value	$(5.4 \pm 2.4) \times 10^{-4}$

The different values of the CMC obtained from the preceding determinations are summarized in Table 1.

Discussion

The average CMC value $(5.4 \pm 2.4) \times 10^{-4}$ mol·dm^{-3}, which is below the value found in the literature: 0.00104 mol·dm^{-3} from conductivity data [4]. The curve of DPA solubility in water shows that solubility reaches the CMC at about 26 °C (Fig. 2). Since the plot is curved and not formed by straight lines, it may be concluded that DPA solubilization in water is a complex phenomenon. Below about 29 °C, there are hydrated crystals of "waxy" texture in equilibrium with isotropic solution (Fig. 7). These crystals have a partially fused hydrocarbon network and the polar network is interconnected by hydrogen bonds [15]. The type of solubilization changed at about 22 °C, probably by formation of dimers or other small aggregates [14, 16] which grew and became true micelles at about 26 °C. At temperatures above 29 °C and concentrations above 0.009 mol·dm^{-3}, a lamellar liquid crystal appeared, as can be seen in Fig. 8, in which typical myelin

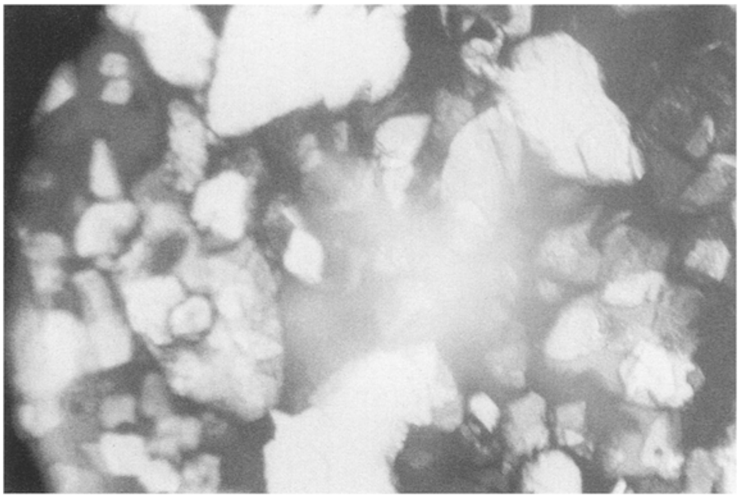

Fig. 7 Waxy crystals of DPA in water at 20 °C. Crossed polaroids × 100

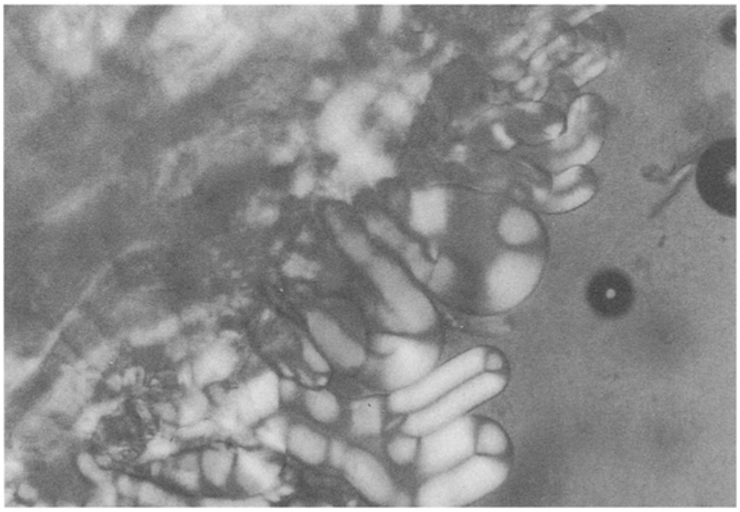

Fig. 8 Myelin figures by peripheral dilution of DPA crystals with water at 30 °C. Crossed polaroids and retardation plate, × 100

figures grew from the crystals in contact with water. This liquid crystalline phase was studied elsewhere [15].

The surface tension plot shows the very high surface activity of DPA, with a slope in the pre-CMC zone of $-119.000\ \mathrm{mN \cdot m^{-1}/mol \cdot dm^{-3}}$, similar to that of the literature [17, 18]. The surface tension above the CMC is about $30\ \mathrm{mN \cdot m^{-1}}$, which is larger than that found by Klose et al. [5] in octyl- and nonylphosphonic acids. Klose et al. said that their phosphonic acids were not extremely pure, and this may be the reason for the discrepancy.

According to theories about the contribution of micelles to the total conductivity of the system [19] the almost horizontal plot of the post-CMC conductivity data (Fig. 4), together with the variation of the free ions in the same zone in Fig. 1 indicates that DPA micelles must be almost uncharged. This may be seen in Fig. 9, in which α was plotted vs. the concentration of micellar surfactant. The value of α was extremely low, while the normal value in ionic micelles is about 0.3–0.5. The value of α diminished when the concentration was increased, and became almost constant ($\alpha \approx 1.3 \times 10^{-3}$) in the zone of liquid crystals. This means that DPA micelles are very similar to that of nonionic surfactants, as Klose et al. found with the lower homologous of this series [5].

The micellization process decreased the ionization of DPA (maximum the $[H^+]/[DPA]$ vs. concentration plot (Fig. 6)), and this is probably due to the capture of HDP^- ions by micelles. However, the first ionization constant of DPA in micelles diminished, as can be seen in Fig. 10. $K_{1,M} \approx 10^{-6}$ in micelles, and became about 1.8×10^{-7} in the lamellar mesophase, which had the polar head groups strongly bound among them by hydrogen bonds [15]. This supports the assumption of Klose et al. that the polar head groups in micelles may also be bound in the same

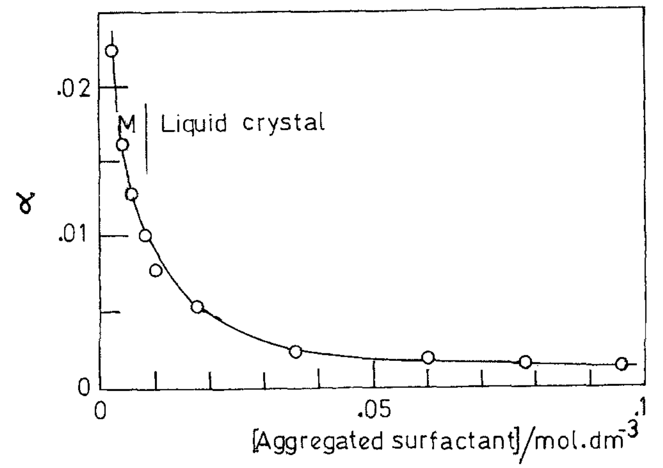

Fig. 9 Dissociation degree (α) of micelles and mesophase lamellae of DPA at 30 °C

way [5]. The hydrogen-bonded network may reduce the ionization constant in micellized DPA by stabilization of H^+ ions between two acidic oxygen atoms in the micellar surface.

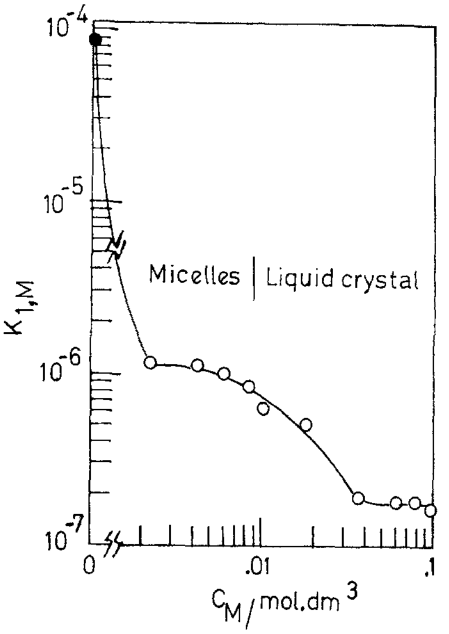

Fig. 10 First ionization constant of DPA: ● in monomerica form, ○ in micelles and mesophase lamellae at 30 °C

Conclusions

* DPA molecules are strongly surface-active.

* At 22 °C, the solubility of DPA increases, probably due to the formation of small premicellar aggregates.

* DPA CMC is $(5.4 \pm 2.4) \times 10^{-4}$ mol · dm^{-3} and the solubility reaches the CMC value at 26 °C.

* At 30 °C and concentration about 9×10^{-3} mol · dm^{-3}, a lamellar mesophase appears.

* Micelles and liquid crystal lamellae are almost uncharged. Their polar heads have strong hydrogen bonds between them.

* The ionization of DPA molecules in micelles and mesophase structures is strongly reduced in comparison with monomerically dissolved molecules.

Acknowledgments One of us (MAM) has a fellowship of the Consejo Nacional de Investigaciones Científicas Y Técnicas de la República Argentina. This work was supported by a grant of the Universidad Nacional del Sur.

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