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Critical micelle concentration of tridecane, tetradecane and hexadecane phosphonic acids and their mono- and disodium salts

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ABSTRACT

The critical micelle concentration (CMC) of tridecane, tetradecane and hexadecane phosphonic acids and their mono- and disodium salts were determined with a battery of methods. The CMC values for all the studied species follow the general trend of those of the lower homologos of the series. The values of the Gibbs free energy of micellisation are interpreted on the basis of the micelle structure in salts and acids. The monolater formed by acids at the air/water interface at the CMC is compact, which may be explained by the union among the polar head groups by hydrogen bonds. Monsodium salts show premicellar formation of acid soap-like compounds. The micellisation of disodium salts is accompanied by strong hydrolisis.

1. Introduction

Phosphonic acids and their salts have numerous technological applications such as mineral flotation [1–3], ion extraction [3,4], complex formation [5], polymer production [6], as corrosion inhibitors [7], additives in detergent formulation [8] among others. The number and variety of phosphonate applications are continuously increasing. However, there is scarce information on phosphonate amphiphiles.

Phosphonate surfactants are derivatives of n-alkane phosphonic acids, which are diprotic. This situation allows obtaining a variety of properties derived from its neutralization degree. These properties may be employed in practical applications, and in basic studies relating to the effect of the polar head group charge on surfactant physicochemical properties. This charge may be varied from nearly zero (acting as non-ionic like surfactants) until −2. Several properties of phosphonic surfactants are quite different from those of common mono-charged surfactants. A review on the properties of n-alkane phosphonic acids and their salts may be found in Ref. [9].

Following the studies on phosphonate surfactants performed in this laboratory with the aim to use them in industrial applications, we determined the critical micelle concentration (CMC) of three acids: tridecane ($C_{13}PO_3H_2$), tetradecane ($C_{14}PO_3H_2$) and hexadecane ($C_{16}PO_3H_2$) phosphonic acids and their mono- (R-PO_3HNa) and disodium (R-PO_3Na_2) salts. The C-13 derivative was not previously studied and the other two were only scarcely investigated in literature.

2. Experimental

Tridecane ($C_{13}PO_3H_2$), tetradecane ($C_{14}PO_3H_2$) and hexadecane ($C_{16}PO_3H_2$) phosphonic acids were synthesized with the technique described elsewhere [10].

Salts were made by weighing each acid, which was neutralized with the an appropriate amount of a NaOH aqueous solution and diluted to obtain a concentration four times the CMC estimated from the shorter homologous CMCs, obtained from literature, which are given in Table 1.

Conductivity measurements were performed with an Antares II conductimeter from Instrumentalia and an immersion cell, by titration of water with the concentrated solution of each acid or salt. The device was calibrated with KCl solutions as usual.

To obtain the CMC, the $\Delta\kappa = \kappa_{\text{measured}} - \kappa_{\text{extrapolated}}$ was plotted vs. the surfactant concentration, $\kappa_{\text{extrapolated}}$ being the specific conductivity extrapolated from the data of the more diluted solutions. This procedure enhances the changes in slope enabling a more accurate determination of the break points [11]. Also the differential concentration $1000(d\kappa/dC)$ was computed as an average of three different numerical computation methods: (a) $1000(d\kappa/dC) = 1000(\kappa_1 - \kappa_0)/(C_1 - C_0)$;

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Table 1
Critical micelle concentration of n-alkane phosphonic acids and their mono- and disodium salts (mol dm^{-3}).

n_C	T (°C)	R-PO_3H_2	R-PO_3HNa	R-PO_3Na_2	Reference
8	20	0.0035	0.086	0.147	[14]
	25	0.001			[15]
	25		0.138		[16]
	40	0.0035	0.093	0.177	[14]
	40		0.136		[16]
	60	0.0035	0.12–0.13	0.25–0.231	[14,17]
	60		0.132		[16]
	80		0.153	0.294	[14]
9	40	0.0027	0.043	0.103	[14]
	60	0.0027	0.0565–0.056	0.14–0.153	[14,17]
	80		0.069	0.143	[14]
10	20	0.0027		0.053	[18]
	40	0.00166	0.030	0.059	[18]
	60	0.00166	0.0291–0.0368	0.0905–0.094	[14,17]
	60		0.0364		[16]
	80	0.00166	0.0368	0.102	[14]
12	5			0.0069	[16]
	25			0.057	[16]
	26	0.00054 ± 0.00024			[13]
	50			0.050	[16]
	66		0.0058 ± 0.0001		[19]
	25			0.0257 ± 0.0008	[19]
	25			0.0177	[20]
	60	0.00104	0.00563–0.0065	0.0236–0.0221	[14,17]
	60			0.050	[16]
	80		0.0065	0.0221	[14]
13	30	0.00050 ± 0.00005	0.0064 ± 0.0011	0.012 ± 0.001	This work
14	45	0.00042 ± 0.00030	0.0036 ± 0.0004	0.0082 ± 0.0002	This work
16	32	0.000275 ± 0.000090	0.00204 ± 0.00098	0.0021 ± 0.0018	This work
	60	0.00052	0.0013–0.00117	0.0013–0.0014	[15,21]
	80	0.00052	0.0013	0.0013	[15]

(b) $1000(d\kappa/dC) = 1000(-\kappa_2 - 4\kappa_1 - 3\kappa_0)/2(C_1 - C_0)$ and (c) $1000(d\kappa/dC) = 1000(3\kappa_2 - 4\kappa_1 + \kappa_0)/2(C_1 - C_0)$ as a function of the average concentration $C_{average} = (C_1 + C_0)/2$ [12].

Surface tension measurements were made with a ring tensiometer Krüss, using solutions of fixed concentration and beginning with the more dilute one. The tensiometer was calibrated with water and n-hexane.

The measurements of pH were made with a millivoltmeter and pH-meter CRIBABB and a Broade & James glass electrode, by titration of water with the concentrated solution of each acid or salt. The same procedure was followed in the ion-selective electrode measurements, using a Na$^+$-ion-selective electrode Orion 8411 Ross and an homemade surfactant ion-selective electrode, whose description was described elsewhere [13].

3. Results and discussion

The CMC values for the tree acids and their mono- and disodium salts are given in Table 1.

3.1. Acids

For $C_{13}PH_2$ the conductivity increases after micellisation, indicating a strong ionization of micelles. This ionization increase may be seen in Fig. 1 where pH vs. log C is plotted. In this graph another break occurs at $C = 0.00089$ mol dm^{-3}, which probably is due to a micelle structure change.

The surface tension (σ) vs. the logarithm of $C_{14}PH_2$ concentration curve (not shown) has a break in $C = 0.000605$ mol dm^{-3}. The area occupied by an adsorbed head group at the air/water interface may be computed with the Gibbs equation:

$$\Gamma(\text{mol/m}^2) = -\frac{1}{\nu RT} - \frac{d\sigma}{d\log C} \quad (1)$$

where R is the gas constant and T is the absolute temperature. It was assumed that the number of adsorbed species per acid molecule is $\nu = 1$, i.e., that the acid is not significantly ionized below the CMC. With the slope of the straight line immediately before the CMC, $\Gamma = 8.92 \times 10^{-6}$ mol/m^2 = 0.0537 molecule/Å^2. Then, the area per adsorbed molecule was computed as $a_0 = 1/\Gamma = 18.6$ Å^2/molecule. This is the cross-section of a hydrocarbon chain, and means that the air/solution surface is saturated and probably the polar head groups are interconnected by hydrogen bonds. The area occupied by a $-PO_3H_2$ group may be computed as 9.62 Å^2 from data of adsorption of phosphonic acids on solid substrates in literature [22]. Then,

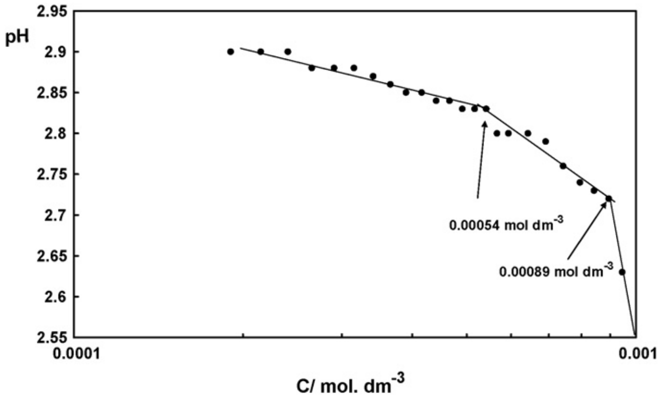

Fig. 1. pH vs. concentration plot for aqueous n-tridecane phosphonic acid at 30 °C.

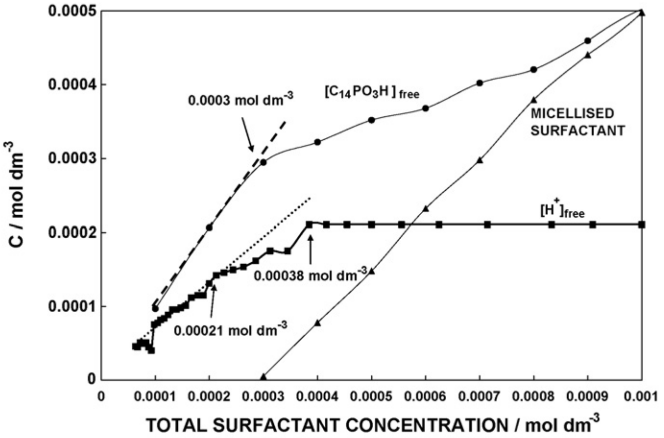

Fig. 2. Concentration of free (unmicellised) surfactant ions, free counterions and micellised surfactant as a function of the total surfactant concentration for aqueous n-tetradecane phosphonic acid at 45 °C.

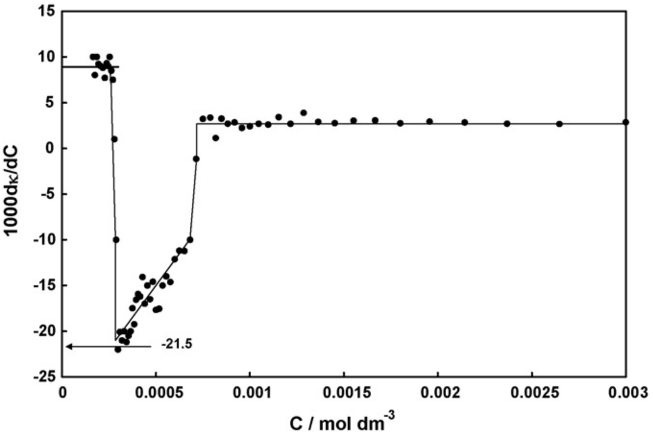

Fig. 3. Differential conductivity of n-hexadecane phosphonic acid in water as a function of surfactant concentration at 32 °C.

a tightly compact monolayer of phosphonic acid molecules must have the cross-section of the hydrocarbon chains. Klose et al. [15] did not compute a_0 for $C_8PO_3H_2$, but they concluded that the interaction between the polar head groups and water at the air/water interface was very strong. A very compact monolayer is not the case in the majority of soluble surfactants adsorbed at the air/water surface. The monolayer reached saturation at $C = 0.000125$ mol dm^{-3}.

The glass electrode is a selective electrode for H^+ ions. The hydrogen ion concentration vs. total surfactant concentration plot (not shown) shows a break at $C = 0.00021$ mol/dm^3. At $C = 0.00038$ mol/dm^3 [H^+] becomes constant. With the surfactant ion-selective electrode, the concentration of free surfactant and that of micellised one were computed and represented in Fig. 2. There is a break at $C = 0.0003$ mol/m^2. The surfactant ion-selective electrode also shows a break at $C = 0.0023$ mol/dm^3.

From pH data the value of the first ionization constant was computed and represented vs. the total concentration. Extrapolation to $C = 0$ using the linear least squares method gave $K_{a1} = 0.000226 \pm 0.000011$. Then, $pK_{a1} = 3.645 \pm 0.022$, which is a value similar to that obtained for other members of the homologous series ($pK_{a1} = 3.976 \pm 0.001$ for n-decane phosphonic acid [22]; 3.98 for n-dodecane phosphonic acid [23].

The $\Delta\kappa$ vs. concentration plot (not shown) shows a gradual change beginning at $C = 0.00038$ mol/m^2 and the reduction of conductivity becomes linear at $C = 0.00093$ mol/dm^3.

In the light of the precedent results, the CMC was computed as 0.00042 ± 0.00016 mol/dm^3. The critical point at $C = 0.0023$ mol/dm^3 may be due to a structural change.

The differential conductivity plot ($1000(d\kappa/dC)$ vs. C) for $C_{16}PH_2$ is shown in Fig. 3. The central point of the sinusoid is taken as the CMC, whereas the minimum is taken as the micelle molar conductivity. The CMC obtained from conductivity at 45 °C is CMC = 0.00028 ± 0.000090 mol/dm^3, that from literature is 0.00052 mol/dm^3 at 60 °C [14]. The values are of the same magnitude order. The difference may be due to the use of different methods to determine the CMC, to different operational definition of the CMC, or by differences in purity. Since our acid was extremely purified during the synthesis, we believe that our value is correct.

3.2. Monosodium salts

The monosodium n-tridecane phosphonate solutions shows only one critical point, the CMC at $C = 0.0064 \pm 0.0015$ mol/dm^3.

For $C_{14}PO_3HNa$ measurements were made at 45 °C. The σ vs. $\log C$ plot shows a minimum at $C = 0.0024$ mol/dm^3, followed by a plateau which begins at $C = 0.00365$ mol/dm^3. The behavior may be caused by desorption of acid formed by hydrolysis from the air/solution surface captured by micelles. Conductivity confirms that the CMC value is CMC = 0.0036 mol/dm^3.

The analysis of the pH measurements show that there is a break in the pH vs. $\log C$ plot (not shown) at $C = 0.0032$ mol/dm^3. Below this concentration the slope is +1, which accordingly Lucassen [24] corresponds to the formation of acid soap, whilst above this concentration the slope is +1.5. The beginning of acid soap formation was at $C = 0.00118$ mol/dm^3. The same data were used to determine the apparent hydrolysis constant $K_{h,ap} = [OH^-]/(C - [OH^-])$, which represented vs. C (not shown) gave a break at $C = 0.00091$ mol/dm^3 and other at $C = 0.0032$ mol/dm^3 with a large increase in hydrolysis. With the sodium ion-selective electrode, the E vs. $\log C$ plot (not shown) showed a sub-Nernstian slope below the CMC (46.07 mV/decade), which may be due to the formation of a kind of complex which affects the concentration of free sodium ions. This is consistent with the formation of an acid soap as detected by pH measurements. The plot shows a break at en 0.0036 mol/dm^3. The n-alkane phosphonate ion-selective electrode also shows a sub-Nernstian slope and a break at the same concentration.

The conductivity measurements of $C_{16}PO_3HNa$ solutions indicate that CMC = 0.0020 ± 0.0010 mol/dm^3. Above the CMC the conductivity increases, which may be due to an increased hydrolysis. At $C = 0.0088$ mol/dm^3 there is a reduction in conductivity, which may be due to a change in the micelle structure.

3.3. Disodium salts

The $C_{13}PO_3Na_2$ CMC determined by conductivity and pH measurements was CMC = 0.012 ± 0.003 mol/dm^3. The CMC was accompanied by a strong hydrolysis which produces a maximum in the differential conductivity (see Fig. 4).

The $C_{14}PO_3Na_2$ CMC determined by conductivity and pH measurements was CMC = 0.0082 ± 0.0002 mol/dm^3.

For $C_{16}PO_3Na_2$ the CMC determined by conductivity and pH measurements was CMC = 0.0021 ± 0.0009 mol/m^2.

The three disodium salts did not show other critical points in the explored concentration range.

3.4. The dependence of the CMC with the chain length

Fig. 5 shows the dependence of the logarithm of the CMC on the number of carbon atoms in the surfactant chain length. To plot this figure the values of CMC (in mole fraction) determined in this work were used together with other obtained from literature (see

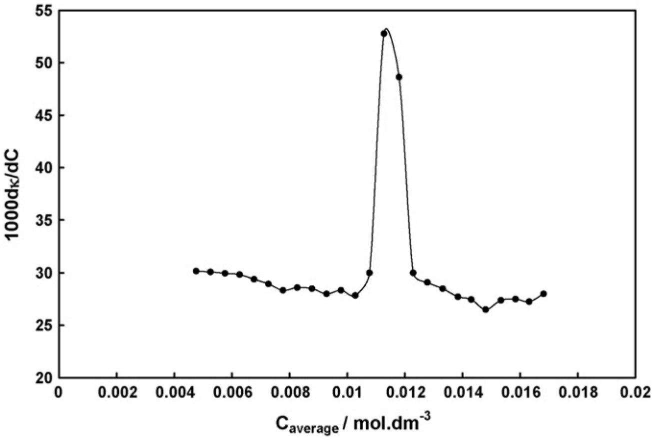

Fig. 4. Differential conductivity of aqueous disodium n-tridecane phosphonate solutions vs. the average concentration.

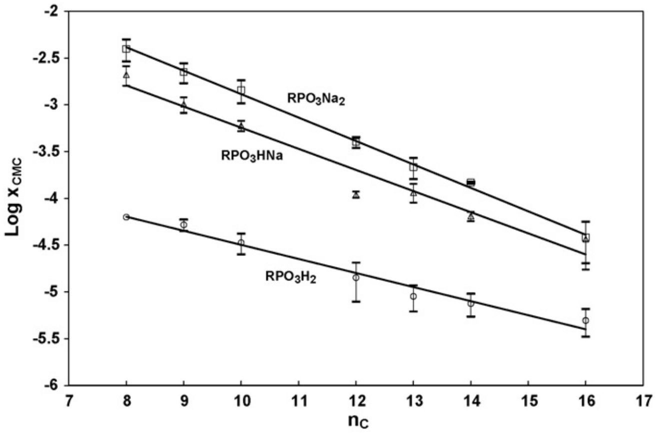

Fig. 5. Dependence of the logarithm of the CMC on the number of carbon atoms in the hydrocarbon chain of (○) n-alkane phosphonic acids, (△) monosodium n-alkane phosphonates and (□) disodium n-alkane phosphonates. Lines are linear least squares fittings.

Table 1). The least squares fitting straight lines equations are:

- Acids:

  $\log x_{\mathrm{CMC}} = -(0.1517 \pm 0.0015)n_{\mathrm{C}} - (2.98 \pm 0.36)$,

  with a correlation coefficient $r = 0.9830$

- Monosodium salts:

  $\log x_{\mathrm{CMC}} = -(0.226 \pm 0.024)n_{\mathrm{C}} - (0.984 \pm 0.038), \quad r = 0.9785$

- Disodium salts:

  $\log x_{\mathrm{CMC}} = -(0.2505 \pm 0.0063)n_{\mathrm{C}} - (0.381 \pm 0.021)$,

  $r = 0.9988$

The dependence of log CMC on n_{C} is related with the free energy of micellisation by the relationship [21]:

$$\log \mathrm{CMC} = \frac{n_{\mathrm{C}}\Phi_{\mathrm{CH_2}}}{2.303k_{\mathrm{B}}T(1+m/n)} + K_0 \tag{2}$$

Table 2
Thermodynamic values of micellisation for n-alkanephosphonic acids and their mono- and disodic salts.

Property/species	R-PO$_3$H$_2$	R-PO$_3$HNa	R-PO$_3$Na$_2$	Reference
$\Phi_{\mathrm{CH_2}}/k_{\mathrm{B}}T$	-0.6495 ± 0.0062	-0.913 ± 0.099	-1.036 ± 0.026	This work
		-1.020 ± 0.009	-1.020 ± 0.009	[27]
$\Phi_{\mathrm{ph}}/k_{\mathrm{B}}T$	-12.75 ± 0.37	-6.70 ± 0.22	-1.14 ± 0.46	This work

where m/n is the micellised counterions to micelised surfactant ions ratio, $\Phi_{\mathrm{CH_2}}$ is the free energy of micellisation per methylene group, k_{B} the Boltzmann constant and K_0 the micellisation per polar head group (Φ_{ph}) plus the excess of the terminal methyl group ($\Phi_{\mathrm{CH_3}} = -3.74k_{\mathrm{B}}T$ [21]) over that of the methylene one:

$$K_0 = \frac{(\Phi_{\mathrm{CH_3}} - \Phi_{\mathrm{CH_2}}) + \Phi_{\mathrm{ph}}}{2.303k_{\mathrm{B}}T(1+m/n)} \tag{3}$$

The m/n value was determined with the Evans equation [25] using the slope prior (S_1) and after (S_2) the CMC in the specific conductivity vs. surfactant concentration plot:

$$1000S_2 = \frac{\alpha^2}{n^{2/3}}[1000S_1 - \Lambda_{\mathrm{X}}] + \alpha\Lambda_{\mathrm{X}} \tag{4}$$

where n is the aggregation number of micelles which may be any reasonable value because the equation is not strongly dependent on the chosen n value, $\alpha = 1 - (m/n)$ is the ionization degree of micelles, and Λ_{X} is the equivalent conductivity of counterions ($\Lambda_{\mathrm{Na+}} = 50.9\,\mathrm{S\,cm^2\,Eq^{-1}}$ [26].

The obtained values are $m/n = 0.859 \pm 0.001$ for acids, 0.7545 ± 0.025 for monosodium salts and 0.795 ± 0.005 for disodium salts. Then, by application of Eqs. (2) and (3), the thermodynamic values were computed (Table 2). Some literature values for $\Phi_{\mathrm{CH_2}}$ are $-1.0k_{\mathrm{B}}T$ [28], $-1.08k_{\mathrm{B}}T$ [28,29] and $-1.09k_{\mathrm{B}}T$ [28,29]. An average value of $\Phi_{\mathrm{CH_2}}$ obtained from literature CMC data [30] of 30 homologous series including non-ionic, anionic, cationic and zwitterionic surfactants is $(1.34 \pm 0.14)k_{\mathrm{B}}T$. The almost coincident values of $\Phi_{\mathrm{CH_2}}$ for mono- and disodic salts and their coincidence with the average value from other surfactants indicate that the transition of the hydrocarbon chains from the monomer to the micellised state is the same, while that for the acids is different. The value significantly smaller for acids indicates that probably the water–hydrocarbon contact in non-micellised acids is less that that in the non-micellised salts, probably due to the formation of pre-micelles in solutions below the CMC.

The values of Φ_{ph} follow the expected trend: the polar head groups favor micellisation in the order $-\mathrm{PO_3H_2} > -\mathrm{PO_3H^-} > -\mathrm{PO_3{}^=}$.

The value for $-\mathrm{PO_3H_2}$ (-12.75 ± 0.37) (in $k_{\mathrm{B}}T$ units) indicates that this group highly favors micellisation. We have computed numerous Φ_{ph} values from CMC data of Ref. [30]. The more negative value found was -12.8 for sodium p-1-methyl alkylbenzene sulfonates, followed by that of sodium alkylbenzene sulfonates (-10.6) and saccharose monostearates (-10.1). The value for $-\mathrm{PO_3H^-}$ is -6.70 ± 0.22, which is a more common value. As examples, $\Phi_{\mathrm{ph}} = -6.51$ for sodium-n-alkyl β sulfopropionates, -7.24 for alkylsulfonic acids and -5.89 for sodium n-alkyl sulfoacetates. For $-\mathrm{PO_3{}^=}$ the value for Φ_{ph} is -1.14 ± 0.46. This Φ_{ph} value is similar to that of sodium 3-oxoalkane sulfonates (-1.72) and sodium 1-hydroxy–2-alkylsulfonates (-0.77). The maximum value found with the data given by Ref. [30] was +3.66 for alkyl dimethylamine oxides and +1.75 for N-alkyl N,N dimethylglycines. Nevertheless, other cationic headgroups have negative values: -4.89 for N-alkylamine hydrochlorides and -2.99 for N-alkyltrimethylammonium bromides.

Previous work on aqueous n-alkane phosphonic systems have shown that the micelle polar surface of acids is composed by a hydrogen-bonded layer of phosphonic groups, while the micelles of the salts have a more conventional Stern layer [19,31]. This situation was also found in lamellar liquid crystals formed in more concentrated solutions of $C_8PO_3H_2$ [23] and $C_{12}PO_3H_2$ [31,32] aqueous systems. As it was seen above, the structure of the monolayer at the air/water interface is also probably hydrogen-bonded. This polar layer structure is very different from that of both, the common ionic and non-ionic micelles, and is probably the cause of the different value of Φ_{CH_2} obtained for acids in comparison with that from the salts. If surfactant molecules in solutions below the CMC form hydrogen-bonded aggregates, the change from these pre-micelles to micelles will not produce a large change in the tails methylene groups' environment, which may explain that the value of Φ_{CH_2} of acids is about 50% lower than the value for more conventional surfactants micelles.

4. Concluding remarks

The CMC values for n-tridecane, n-tetradecane and n-hexadecane phosphonic acids and their mono- and disodium salts follow the general trend of those of the lower homologos of the series. The straight lines fitting the log CMC vs. n_C dependence for mono- and disodium salts are almost parallel, giving almost the same value for the Gibbs free energy of micellisation of a methylene group (Φ_{CH_2}), and similar to literature values for other surfactants. This means that the monomer-micelle transition is similar in both sodium n-alkane phosphonates and in other ionic surfactants, i.e., that the structure of ionic micelles is similar irespective of the polar head groups. However, the line for phosphonic acids has different slope indicating that the unmicellised to micellised state transition is different for the acids. The Φ_{CH_2} value for acids is about 50% lower than that for the salts, which means that the transition from unmicellised to micellised state is associated to a smaller change in the chain environment. As long as we know, this situation is unique. Since alkylsulfonic acids behave as common ionic surfactants, this is not caused by the nature of counterions. Moreover, Φ_{ph} for the $-PO_3H_2$ group is a large negative value, but similar to that of some other headgroups whose micelles behave as common surfactant ones. Then, this cannot be the cause of the low value of Φ_{CH_2}. This may be caused by a transition between hydrogen-bonded pre-micelles having less hydrocarbon/water contact than monomers to micelles which also have a hydrogen-bonded polar layer. The monolater formed by acids at the air/water interface at the CMC is compact, which is not the common case in soluble surfactant monolayers, and this behavior may also be explained by the tight union of the polar head groups by hydrogen bonds.

The values of the Gibbs free energy of micellisation of polar head groups follow the expected trend that the larger the polar head charge, the lower the predisposition to micellise.

The micellisation of $C_{13}PO_3H_2$ is accompanied by an increase in ionization, which is not the case in the other acids here studied. Monsodium salts show premicellar formation of acid soap-like compounds.

The micellisation of disodium salts is accompanied by strong hydrolisis.

As a conclusion, micelles of mono- and disodium phosphonates behave as those of other common ionic surfactants, but micelles of the acids show some differences probably caused by the strong tendency of the phosphonic acid headgroups to form intermolecular hydrogen bonds.

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