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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 $1000(\mathrm{d}\kappa/\mathrm{d}C)$ was computed as an average of three different numerical computation methods: (a) $1000(\mathrm{d}\kappa/\mathrm{d}C) = 1000(\kappa_1 - \kappa_0)/(C_1 - C_0)$;

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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$_3$H$_2$	R-PO$_3$HNa	R-PO$_3$Na$_2$	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) $1000(\mathrm{d}\kappa/\mathrm{d}C) = 1000(-\kappa_2 - 4\kappa_1 - 3\kappa_0)/2(C_1 - C_0)$ and (c) $1000(\mathrm{d}\kappa/\mathrm{d}C) = 1000(3\kappa_2 - 4\kappa_1 + \kappa_0)/2(C_1 - C_0)$ as a function of the average concentration $C_{\text{average}} = (C_1 + C_0)/2$ [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:

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

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$_3$H$_2$ group may be computed as 9.62 Å^2 from data of adsorption of phosphonic acids on solid substrates in literature [22]. Then,

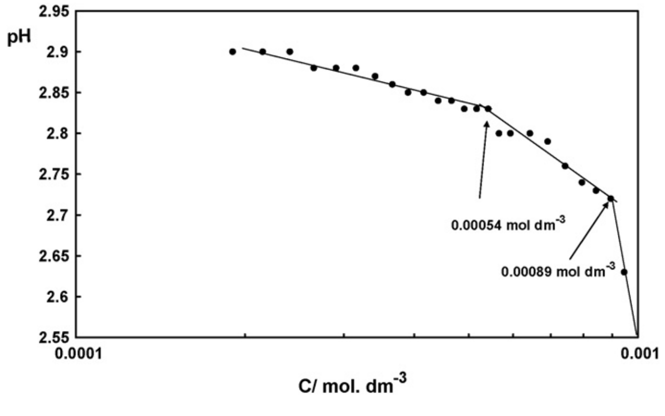

Fig. 1. pH vs. concentration plot for aqueous n-tridecane phosphonic acid at 30 °C.