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Low-concentration aqueous solutions of undecenoic acid and sodium undecenoate

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Abstract The behaviors of low-concentration aqueous solutions of 10-undecenoic acid and its sodium salt were studied by several techniques. The acid does not have a critical micelle concentration, but gives an emulsion of very small droplets at (0.8–1) × 10^{-4} mol dm^{-3}. The emulsion was clearly visible by eye at 0.002 mol dm^{-3}. The sodium salt has a stepwise aggregation process, giving premicellar aggregates at 0.023 ± 0.008 mol dm^{-3}, which grow to form micelles at 0.117 ± 0.007 mol dm^{-3}. The compositions of the solution and the micelles were also studied.

Key words Polymerizable surfactant · Micelles · Undecenoic acid · Sodium undecenoate · Critical micelle concentration

Introduction

Surfactant molecules with chemically active groups have received increased attention in recent years. Since these materials can often be polymerized or oligomerized, a wide range of uses can be foreseen. Polymerizable surfactants can be polymerized to yield polysoaps, which can form hydrophobic microdomains having properties similar to surfactant micelles [1, 2]. They may also be copolymerized with water-soluble or water-insoluble monomers [3–5]. The polymerized structures may be micelles [6, 7], vesicles [8–10], monolayers [11, 12], bilayers [13, 14], liquid crystals [15, 16], and microemulsions [17–19].

Knowledge of the phase behavior of polymerizable surfactants is of fundamental importance to design polymerization experiments. Several studies have been made on this subject [20–23].

The polymerizable surfactant sodium 10-undecenoate [SUD; $CH_2{=}CH\text{-}(CH_2)_8COONa$] can be polymerized to produce low-molecular weight SUD oligomers after irradiation by γ-rays [24–26] or by chemical methods [15, 21, 27]. The potassium salt was employed in copolymerization with methyl methacrylate in microemulsions [28].

The critical micelle concentration (cmc) of SUD has been reported as being 0.4 mol dm^{-3} in some works [21, 28–31]; however, a much lower value (0.04 mol dm^{-3}) has been reported in other works [24, 25]. Other authors reported values of about 0.12 mol dm^{-3} [29–31]. The difference is too large to reflect independent determinations of the same phenomenon. To elucidate the discrepancy, we studied the cmc of SUD using different techniques.

Experimental

10-Undecenoic acid (HUD) was obtained from Aldrich and its sodium salt was prepared by addition of the stoichiometric amount of sodium hydroxide and was then purified by recrystallization from methanol solution.

Surface tension measurements

Surface tension measurements were carried out with a Du Noüy ring tensiometer (Krüss).

Ion-selective electrode measurements

Na^+ determinations were carried out with an Orion Na^+ ion-selective electrode. UD^- determinations were made with an UD^-

ion-selective electrode. This electrode was made with a poly (vinyl chloride) (PVC) film containing barium undecenoate as a carrier, fixed at one end of a PVC tube. The electrode had a Ag/AgCl inner electrode immersed in a 0.001 M NaCl + 0.001 M SUD aqueous solution, saturated with AgCl. The UD^- ion-selective membrane was made by suspending 0.3 g finely powdered carrier in 10 cm^3 tetrahydrofuran with 0.06 g dibutylphthalate (plastiziser) and 0.3 g PVC. Then the solution was allowed to evaporate in a Petri dish covered by a filter paper. The elastic film obtained was glued to the PVC tube with tetrahydrofuran. Both ion-selective electrodes were used against a saturated calomel electrode. A CRIBBAB pH meter and millivoltmeter was employed in all potentiometric determinations. Details about the treatment of the potentiometric data may be found in the literature [32, 33].

When a surfactant forms dimers and other premicellar aggregates, the slope of the E–log c curve below the cmc is not a Nernstian one [34]. This is because the electrode response depends on the monomer activity, which is less than the nominal total activity. If the electrode response is supposed to be Nernstian to the monomer activity, and S_e and S_N are the experimental and Nernstian slopes, the electrode potential may be written

$$E = E^0 + S_e \log a_T = E^{0'} + S_N \log a_m \ , \tag{1}$$

in which a_T and a_m are the total or nominal activity and the true monomer activity, respectively. E^0 and $E^{0'}$ may or may not be equal. Using concentrations instead of activities, the change, dE, in the potential due to changes in the total and monomer concentrations is given by

$$dE = S_e dc_T/c_T = S_N dc_m/c_m \ . \tag{2}$$

On the other hand, the total concentration is

$$c_T = c_m + 2K_{dim}c_m^2 \ , \tag{3}$$

in which K_{dim} is the dimerization constant, $K_{dim} = c_{dimers}/c_m^2$. Then,

$$dc_T = (1 + 4K_{dim}c_m)dc_m \tag{4}$$

and by substituting Eqs. (3) and (4) in Eq. (2) and rearranging

$$K_{dim}c_m = c_{dimers}/c_m = \frac{S_N - S_e}{4S_e - 2S_N} \ , \tag{5}$$

which enables one to obtain the concentration ratio of dimers to monomers before the cmc.

pH measurements

pH measurements were performed with an Orion glass electrode. To interpret the hydrolysis behavior of surfactants, Stainsby and Alexander [35] postulated a theory in which the dependence of the degree of hydrolysis, $\beta = [OH^-]/c_T$, upon c_T is explained on the basis of the solubilization by micelles of the acid (HUD) produced by hydrolysis of the amphiphile carboxylate salt. HUD formed by hydrolysis dissolves partially in micelles, and the distribution constant K_D between micelles and intermicellar aqueous solution may be found from

$$K_D = \frac{4\delta\beta_{max}}{K_{hyd}} = \frac{[HUD_M]}{[HUD_S]} \ , \tag{6}$$

in which δ is the micelle density, β_{max} is the value of β at the maximum degree of hydrolysis, and K_{hyd} is the hydrolysis constant. $[HUD_M]$ is the concentration of acid in the micelles, and $[HUD_S]$ is that in the intermicellar aqueous solution. The value of K_{hyd} may be obtained from the hydrolysis curve before the cmc, and δ may be computed from literature data. The micellized HUD to micellized UD^- ratio, R, may be computed with

$$R = \frac{[HUD_M]}{[UD_M^-]} = \frac{K_D V (K_{hyd}[UD_S^-])^{1/2}}{1000} \ , \tag{7}$$

where V is the partial molar volume of micellized surfactant.

The value of the cmc may be obtained as half the concentration at the maximum degree of hydrolysis i.e. cmc $\approx c_{max}/2$.

The concentration at which the hydrolyzed molecules start to form premicellar aggregates is found from

$$c_F = K_h/\beta_{min} \ , \tag{8}$$

in which β_{min} is the minimum value of β.

Conductivity measurements

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

Dye solubilization measurements

Dye solubilization measurements were performed in sealed tubes with Sudan III or Sudan Black B and surfactant solutions of different concentration. The tubes were left for week in a constant-temperature bath with periodic stirring. Then they were centrifuged and the absorbance of the supernatant was measured with a Hewlett-Packard diode-array HP84 52A spectrophotometer at 488 nm (Sudan III) or 600 nm (Sudan Black B).

Turbidity

Turbidity measurements were performed on surfactant solutions without added dye with a Hewlett-Packard diode-array HP84 52A spectrophotometer at 480 nm.

Modification of dye color and fluorescence

Changes in color and fluorescence in Rhodamine 6G were detected by eye, by adding a drop of dilute Rhodamine 6G solution to tubes with surfactant solutions at different concentrations to detect micelle formation [36–39]. All measurements were performed at 35.0 °C.

Confidence intervals were computed with a confidence level of 0.9.

Results

10-Undecenoic acid

The dependence of pH on the concentration of HUD is shown in Fig. 1. Two changes may be seen, one of them at 0.0001 mol dm^{-3} and the other at 0.002 mol dm^{-3}. The surface tension versus concentration curve, showing changes at 0.0001 and 0.001 mol dm^{-3}, is shown in Fig. 2. Sudan III solubilization measurements showed a sudden increase in absorbance at 0.0002 mol dm^{-3}. The same increase was observed at 480 nm in solutions without dye. The absorbance of solutions without added dye increased between 0.0002 and about 0.003 mol dm^{-3}, and decreased at higher concentrations. Solutions with concentrations above 0.002 mol dm^{-3}

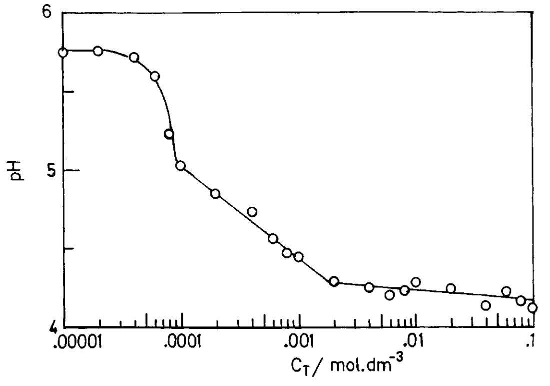

Fig. 1 Dependence of pH on total concentration of 10-undecenoic acid (*HUD*) in aqueous solution

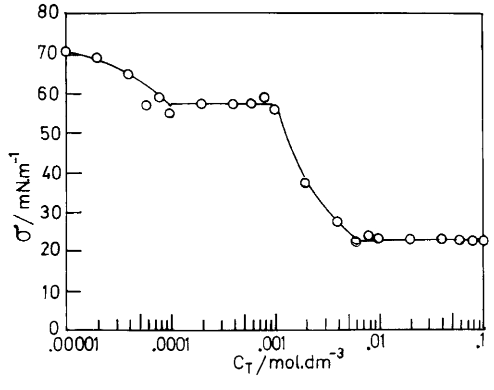

Fig. 2 Surface tension of HUD aqueous solutions

have a turbid appearance, and by microscopic observation droplets of undissolved acid were seen. After ageing for several months some small emulsion droplets were seen in solutions with concentrations between 0.0002 and 0.002 mol dm^{-3}; these droplets were not detected in freshly prepared solutions. The response of the UD$^-$ ion-selective electrode versus the total concentration of HUD is shown in Fig. 3.

Sodium 10-undecenoate

The Sudan Black B and Sudan III solubilization measurements showed an increase in solubility at 0.01 mol dm^{-3}, followed by a larger increase at 0.1 mol dm^{-3}. Rhodamine 6G solubilization measurements showed changes in color and fluorescence at 0.1 mol dm^{-3}. No changes in absorbance were detected without dye.

The response of the Na$^+$ ion-selective electrode is shown in Fig. 4. The break is at 0.13 mol dm^{-3}. The low-concentration slope was 57 mV/decade (which is the Nernstian slope at 35 °C). The potential of the UD$^-$ ion-selective electrode, whose low-concentration slope was 47.2 mV/decade, is shown in Fig 5. The break was at 0.11 mol dm^{-3}.

A plot of the surface tension versus the logarithm of the total concentration c_T, showing two breaks at 0.03 and 0.11 mol dm^{-3}, is given in Fig. 6.

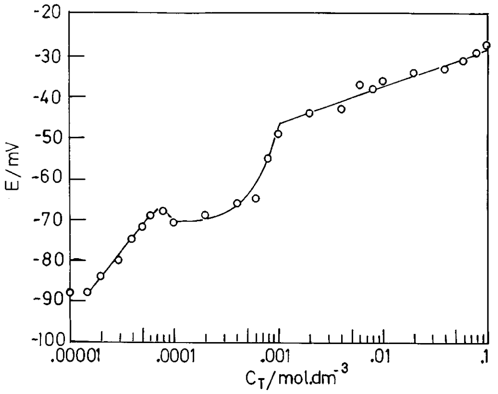

Fig. 3 Response of the UD$^-$ ion-selective electrode versus the total concentration of HUD in water

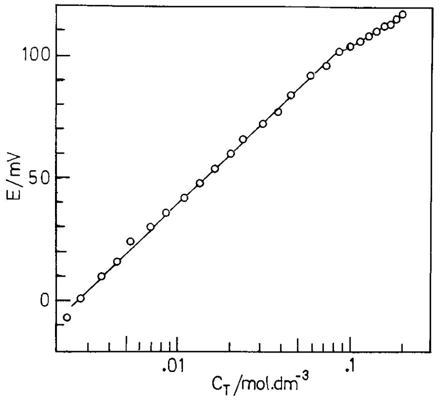

Fig. 4 Response of the Na$^+$ ion-selective electrode versus the total concentration of sodium 10-undecenoate in water

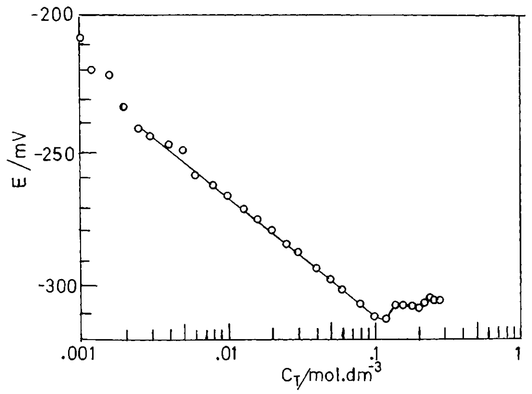

Fig. 5 Response of the UD$^-$ ion-selective electrode versus the total concentration of sodium 10-undecenoate in water

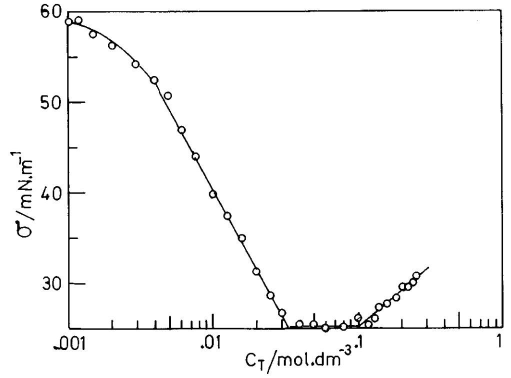

Fig. 6 Surface tension of sodium 10-undecenoate aqueous solutions

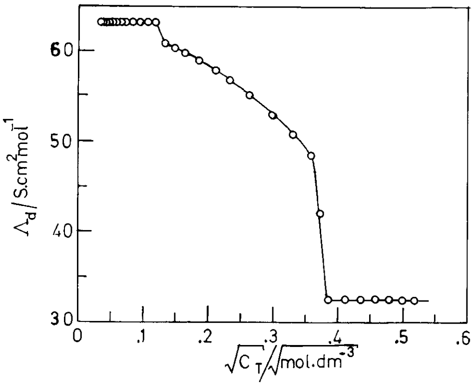

Fig. 7 Differential conductivity of sodium 10-undecenoate aqueous solutions

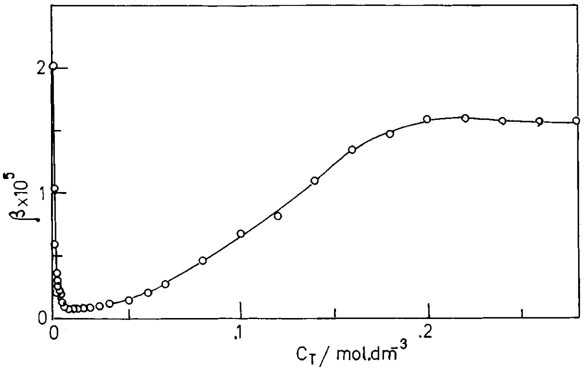

Fig. 8 Degree of hydrolysis of sodium 10-undecenoate aqueous solutions

The specific conductivity versus c_T plot was similar to Fig. 1 of Ref. [21], showing two breaks, one of them at about 0.02 mol dm^{-3} and the other at 0.1 mol dm^{-3}. In Fig. 7 the differential conductivity, $\Lambda_d = d\kappa/dc$, is plotted versus $c_T^{1/2}$.

The degree of hydrolysis, β versus c_T is shown in Fig. 8.

Table 1 Critical concentrations in sodium undecenoate aqueous solutions

Method	First transition (mol dm^{-3})	Second transition (mol dm^{-3})
Rhodamine 6G	–	0.1
Sudan Black B solubilization	0.02	0.13
Sudan III solubilization	0.01	0.12
Sodium ion-selective electrode	–	0.13
Undecenoate ion-selective electrode	–	0.11
Surface tension	0.034	0.11
Conductivity	0.015	0.13
pH (degree of hydrolysis)	0.036	0.105

The concentrations in which transitions were found are given in Table 1.

Discussion

10-Undecenoic acid

From pH measurements at low concentration, the thermodynamic acidity constant (K_a) of HUD was computed as being $(4.2 \pm 0.4) \times 10^{-6}$ (pK_a = 5.38 ± 0.04).

The low-concentration slope of the plot in Fig. 3 is 27 mV/decade. When the data were represented versus the concentration of UD^- computed with the acidity constant, the slope was 58, close to the Nernstian value. With the data of Fig. 3, the K_a value, and the pH measurements, the plot in Fig. 9 was made, showing the concentration of free (unaggregated) H^+ and UD^- ions, free acid molecules, and aggregated acid molecules. The start of aggregation is clearly visible at $c = (0.8–1) \times 10^{-4}$ mol dm^{-3}, and a change in the aggregation mechanism may be noted at about 0.001 mol dm^{-3}. Between these two concentrations, there was an excess of free H^+ ions with respect to free UD^- ions. This difference means that some of the HUD molecules at the surface of the aggregates were dissociated. This situation was probably maintained above 0.001 mol dm^{-3}. However, if the aggregates grow in size, the ratio of HUD molecules at the surface of the aggregates to the total aggregated molecules might drop. This situation would be reflected as a reduction in the difference between free UD^- and free H^+ ions, as can be seen in Fig. 9.

Some carboxylic acids have cmc values. By extrapolation of these cmc values obtained from the literature [40], the cmc of HUD was estimated as 0.0002 mol dm^{-3}. This value is almost the same as that found by surface tension measurements, pH measurements, and dye solubilization; however, it is not the cmc. Upon

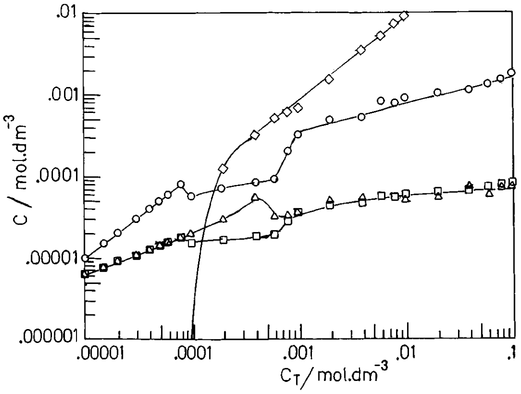

Fig. 9 Composition of aqueous solutions of HUD as a function of the total concentration. △: $[H^+]_{free}$; ○: $[HUD]_{free}$; □: $[UD^-]_{free}$; ◇: aggregated HUD (on a monomeric basis)

ageing these solutions small emulsion droplets formed. It can be concluded that at c_T = (1.5 ± 0.05) × 10^{-4} mol dm^{-3} very small droplets of HUD formed. These droplets were partially stabilized by the charge of aggregated UD^- ions. This explains the turbidity of the solutions between 0.0002 and 0.002 mol dm^{-3}, where the emulsion was clearly visible by eye.

Sodium 10-undecenoate

This system shows two transition concentrations. Many authors have reported systems which have multiple critical concentrations [41–46]. In particular, there is evidence for the formation of premicellar aggregates as dimers [34, 47–49] and larger aggregates [50, 51].

The average first transition concentration was c = 0.023 ± 0.008 mol dm^{-3}. Its meaning will be discussed latter.

The potentiometric data clearly show that substantial aggregation occurred at c = 0.11–0.13 mol dm^{-3}. This value was confirmed by the equivalent conductivity plot. The interpretation of the degree of hydrolysis versus c curve, following the theory of Stainsby and Alexander, indicates that the cmc is about half the concentration of the β maximum, i.e. 0.21/2 = 0.105 mol dm^{-3}. The Rhodamine 6G experiments indicated that micelles existed above 0.1 mol dm^{-3}, but not below this concentration. This allowed us to interpret the second transition as the cmc, in which large aggregates formed, including counterions. The average value of the cmc was 0.117 ± 0.007 mol dm^{-3}. Using vapor pressure osmometry at 37 °C, Larrabee and Sprague [30] found the cmc to be 0.094 ± 0.005 mol dm^{-3} and an aggregation number of 17 ± 3. Durairaj and Blum [52] reported cmc values ranging from 0.128 mol dm^{-3} at 10 °C to 0.114 mol dm^{-3} at 30 °C. Other authors reported values of ca. 0.12 mol dm^{-3} [29–31].

The differential conductivity plot (Fig. 7) shows two transitions: one at c = 0.015 mol dm^{-3} and the other at 0.13 mol dm^{-3}. The decreasing region between the two changes means that the premicellar aggregates formed at the lower concentration decreased their molar conductivity. This may occur by increasing their size and/or decreasing their charge. Small aggregates dissolving uncharged undecylenic acid may be formed. The premicellar aggregates did not capture a significant amount of sodium ions, because this capture was not detected by the Na^+ ion-selective electrode.

The dκ/dc value at the cmc is interpreted as the molar conductivity of micelles [53], including their ionic atmosphere, resulting in Λ_M = 32.5 S cm^2 mol^{-1}.

The dye solubilization experiments showed that solubilization started at the lower transition concentration, but increased at the second. Hydrolyzable surfactant solutions which form premicellar aggregates may solubilize hydroinsoluble substances below the cmc [54–56], whereas the non-hydrolyzable amphiphiles only solubilize these substances at the cmc [57].

The surface tension curve shown in Fig. 6 is different to that found by McGrath [21]. In particular the break at 0.004 mol dm^{-3} may be interpreted as the surface saturation [58]. By using the Gibbs adsorption isotherm on the straight line between 0.004 and 0.034 mol dm^{-3}.

$$\Gamma = \frac{1}{2RT}\frac{d\sigma}{d\ln a} , \qquad (9)$$

where a is the activity of the surfactant; the surface area per molecule a_{molec} at the cmc was found to be 0.40 nm^2, a value larger than the cross-section of a hydrocarbon chain (0.18 nm^2) [59]. Values of $a_{molec} \geq 0.40$ nm^2 are commonly found in soluble surfactant monolayers [60, 61]. This is associated with a disordered chain layer and water penetration between surfactant molecules [62]. Figure 6 shows the same shape that Zimmels and Lin found with sodium dodecanoate [47]. This shape is related to a stepwise aggregation [46, 47]. Between 0.034 and 0.1 mol dm^{-3} there is a plateau in which the surface excess of amphiphile ions (Γ) is zero, which means that the surface and bulk concentrations are equal and increase by the same amount with c [58, 63]. This is commonly interpreted as evidence of the existence of micelles, but it is not the only possible interpretation. It may be due to a modification of the structure of the solution affecting the activity coefficients. The other results indicate that some modification which affects the adsorption at the air/solution interface may occur at 0.034 mol dm^{-3}. In particular, the break at 0.034 mol dm^{-3} may be interpreted as the start of premicellar aggregation and that at 0.1 mol dm^{-3} as the cmc [46, 47, 63] where the aggregates have the properties of true micelles.

The desorption at 0.1 mol dm^{-3} was found in other surfactants at the cmc [41, 46, 47, 63]. It may be due to a slight energetic advantage of the micellized state when compared with the adsorbed state. If it is supposed that the state of the polar headgroup does not differ significantly in the micellized and the adsorbed states, the energetic advantage must be due to the hydrocarbon tails. There is some immersion of the hydrocarbon chains in the water layer in soluble monolayers, ranging from 10 to 30% of the total chain length [62, 64]. Taking into account the probable contact of the terminal end of the chain with the water surface (because double bounds have some affinity with water [65]) the hydrocarbon–water contact may be larger than that in SUD monolayers. Micellization probably reduces this hydrocarbon–water contact, even if some double bonds remain at the micelle surface. This may be origin of the energetic advantage.

From the plot of the degree of hydrolysis (Fig. 8) $c_{\min} = 0.01$ mol dm^{-3}, $\beta_{\min} = 7 \times 10^{-6}$, $c_{\max} = 0.21$ mol dm^{-3}, and $\beta_{\max} = 1.6 \times 10^{-5}$. The partial molar volume of micellized SUD may be computed using that of sodium undecylate, $V = 193.3$ cm^3 mol^{-1} [66] by adding the group contributions of the C=C (20.51 cm^3 mol^{-1}) group and the three hydrogen atoms bound to the π carbons (2.78 cm^3 mol^{-1} each), and by substracting that of the terminal methyl group (19.06 cm^3 mol^{-1}) and the adjacent methylene group (15.80 cm^3 mol^{-1}) [67]. This gives $V_{\mathrm{SUD}} = 187.3$ cm^3 mol^{-1}. Then, the micelle density is $M_{\mathrm{SUD}}/V_{\mathrm{SUD}} = 1.101$ g cm^{-3}. From the acidity constant of undecenoic acid, $K_{\mathrm{hyd}} = (2.4 \pm 0.3) \times 10^{-9}$, and using Eqs. (6) and (8) the following values were found: $K_{\mathrm{D}} = (2.8 \pm 0.3) \times 10^4$ and $c_{\mathrm{F}} = 0.036 \pm 0.004$ mol dm^{-3}. The value of K_{D} is 9×10^5 in SUD micelles [35], due to the difference in solubility with HUD. The K_{D} value in monosodium dodecanephosphonate micelles is 2.3×10^5 [68]. The micellized HUD to micellized UD$^-$ ratio, R, was computed using Eq. (7) giving 0.057 ± 0.002. This means that micelles have 17.6 ± 0.6 UD$^-$ ions per HUD molecule. Taking into account the aggregation number of 17 ± 3 found by Larrabee and Sprague [30], there was about only one HUD molecule per micelle.

All the experiments described here suggest that at the lower critical concentration, small premicellar aggregates form. This conclusion was also reached by Sprague et al. [29]. These aggregates may be dimers (UD_2^{2-}) or acid soaps [H(UD)$_2$] formed by hydrolysis. The interpretation of the pH–concentration curve made by McGrath [21] following the theory of Lucassen [69] suggests that they may be acid soaps. This may explain the gradual reduction in differential conductivity.

Supposing the small aggregates are dimers, and using Eq. (5), the dimer-to-monomer concentration ratio $c_{\mathrm{dimers}}/c_{\mathrm{m}}$ was computed giving 0.131 before the cmc. Using potentiometric data and this $c_{\mathrm{dimers}}/c_{\mathrm{m}}$ value, the concentration of free monomers $[\mathrm{UD}^-]_{\mathrm{free}}$, free sodium ions $[\mathrm{Na}^+]_{\mathrm{free}}$, free dimers $[\mathrm{D}^{2-}]_{\mathrm{free}}$, and micellized UD molecules (on a monomer basis) [M] may be estimated. These results are shown in Fig. 10. The degree of ionization of the micelles was also computed giving $\alpha = 0.392 \pm 0.007$, which was independent of c_{T}. Using vapor pressure osmometry, Larrabee and Sprague [30] found $\alpha = 0.27$ at 37 °C, and Vikingstad et al. [70] reported a value of $\alpha = 0.28 \pm 0.02$ at 25 °C from electromotive force experiments.

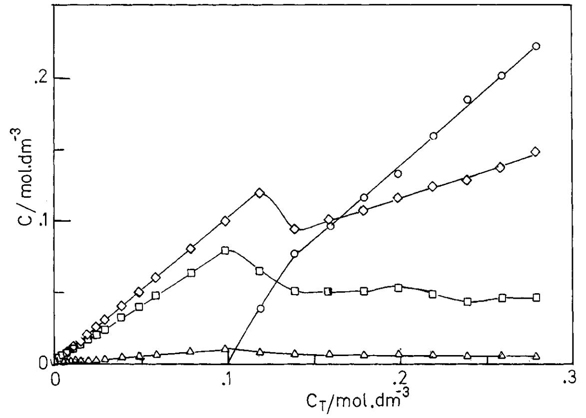

Fig. 10 Composition of aqueous solutions of sodium 10-undecenoate as a function of the total concentration. △: free dimers; □: $[\mathrm{UD}^-]_{\mathrm{free}}$; ◇: $[\mathrm{Na}^+]_{\mathrm{free}}$; ○: micelles (on a monomeric basis)

Concluding remarks

- HUD did not form micelles. An emulsion of very small droplets formed at $c_{\mathrm{T}} = (0.8\text{–}1) \times 10^{-4}$ mol dm^{-3}, which became visible by eye at 0.002 mol dm^{-3}. The acidity constant, K_{a}, was $(4.2 \pm 0.4) \times 10^{-6}$ (p$K_{\mathrm{a}} = 5.38 \pm 0.04$).
- SUD formed premicellar aggregates at $c_{\mathrm{T}} = 0.023 \pm 0.008$ mol dm^{-3}. These premicellar aggregates did not take Na$^+$ counterions, but could solubilize dyes. Premicellar aggregates probably grew in size to give true micelles at the cmc of 0.117 ± 0.007 mol dm^{-3}.
- About one HUD molecule was solubilized per micelle, and the degree of ionization α, was, 0.392 ± 0.007.

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