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Zeta potential of dodecyltrimethylammonium hydroxide micelles in water

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Abstract The electrophoretic mobility of dodecyltrimethylammonium hydroxide micelles has been measured at two different concentrations giving values similar to that determined in other surfactants. There is a good agreement between micelle ionization degrees computed from zeta potential measurements and those from ion-selective electrodes experiments. This demonstrates that electrophoresis experiments may be replaced by the simpler ion-selective electrode measurements to determine micelle surface potential. It has also been

concluded that ion-selective electrodes detect only the non-micellised ions, that only free ions contribute to the intermicellar solution ionic strength, and micelles do not affect the result, and that the dependence of the electrophoretic mobility on the soap concentration is due to the reduction of the micelle net charge when the ionic strength of the intermicellar solution arises.

Key words Micelles – zeta potential – micellar electrophoresis – electrophoretic mobility – micelle ionisation degree

Introduction

Electrophoresis measurements on micelles are not common due to experimental difficulties. The tracer electrophoresis method of Hoyer et al. [1] has been employed in some earlier works [1–5], but, in general, there are few experimental data available in literature on this subject. To confirm the high ionization degrees previously determined in an independent experiment on dodecyltrimethylammonium hydroxide (DTAOH) micelles with ion-selective electrodes [6], their electrophoretic mobility was measured. This work is also useful to determine the reliability of ion-selective electrode measurements and some of the suppositions made when this method is used, and provides a simpler alternative to compute the surface potential of micelles.

Experimental

The electrophoretic mobility of dodecyltrimethylammonium hydroxide (DTAOH) micelles was measured using a tracer electrophoresis device modified from the one quoted in literature [1]. It was verified by measuring the electrophoretic mobility of SDS micelles, which is known from literature [7]. Figure 1 shows the modified apparatus.

DTAOH micelles were tagged with Sudan Black B, an oil-soluble dye which is not charged in alkaline solutions. Solution absorbance was measured with a Spectronic 20 UV-Vis spectrophotometer at 600 nm.

Electrophoretic mobilities were computed following the method of Hoyer et al. [1]. To compute the zeta potential (ζ) the following equations were

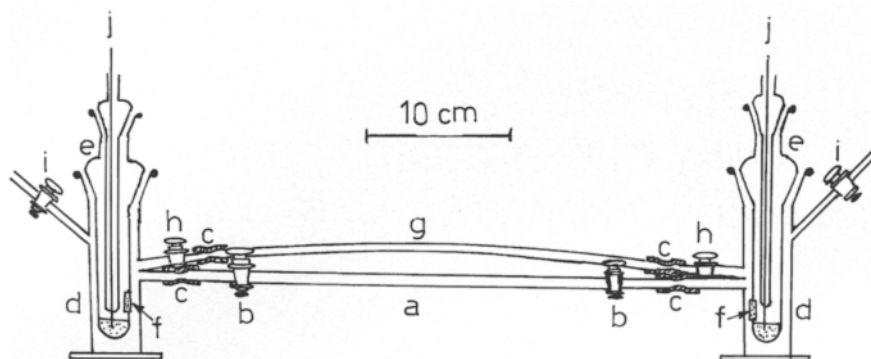


Fig. 1 Tracer electrophoresis cell: a: detachable tube made with a 2 cm³ pipette with two teflon stopcocks (b), c: rubber connection, d: electrode lodging, e: calomel electrode, f: porous plate, g: auxiliary connection with teflon stopcocks (h), i: stopcock, j: connection to the electrophoresis apparatus. Before conducting a run, a was filled with tagged micellar solution between the two stopcocks b, including the stopcock channels which had the same radius as the tube. The excess of tagged solution was carefully eliminated and tube a was connected to d with c. The rest of the apparatus was filled with untagged micellar solution, with stopcocks h and i opened to ensure hydrostatic equilibrium. The calomel electrodes e were put in d, and the cell was immersed in a thermostatic bath. After resting an hour to attain the working temperature, stopcocks h and i were closed and b opened, and the work potential (~500 V) was imposed to the calomel electrodes. The time of the run was regulated in order to obtain migration of about the half of the cell content. At the end of the run, the potential source was switched off, stopcocks b closed and tube a unconnected from the cell. After careful elimination of the remaining solution, the content of the central tube and stopcocks was analysed

employed [8]:

$$\zeta = \frac{\mu\eta}{\varepsilon\varepsilon_0 f(\kappa a)}, \quad (1)$$

where μ is the electrophoretic mobility, η the viscosity of the intermicellar medium, κ the inverse of the Debye distance, ε the relative dielectric constant of the medium, ε_0 the vacuum permittivity, and the function $f(\kappa a)$ is given by

$$f(\kappa a) = \frac{2}{3} \left[1 + \frac{1}{2(1 + 2.5/\kappa a \{1 + 2 \exp(-\kappa a)\})^3} \right] \quad (2)$$

for spherical micelles of radius a [2], and

$$f(\kappa a) = \frac{1}{2} \left[1 + \frac{1}{2(1 + 2.5/\kappa a \{1 - 2 \exp(-\kappa a)\})^2} \right] \quad (3)$$

for cylindrical micelles with radius a [9].

The micelle charge was computed by [10]

$$Q = 4\pi\zeta\varepsilon\varepsilon_0 a(1 + \kappa a). \quad (4)$$

Measured electrophoretic mobilities were $(3.94 \pm 0.08) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at the total concentration $C_T = 0.03197 \text{ mol dm}^{-3}$ and $(2.11 \pm 0.05) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $C_T = 0.08607 \text{ mol dm}^{-3}$.

The confidence intervals were computed with Student's t function at a confidence level of 0.90.

Discussion

The determined values of μ are similar to those obtained at the cmc and 25 °C for other surfactants, as dodecylamine hydrochloride ($3.62 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [3], sodium dodecylsulphate (SDS) ($4.55 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [7] and dodecyltrimethylammonium chloride (DTAC) ($3.5055 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [4].

To compute κ , the concentration of free HO^- and DTA^+ ions at the two total concentrations were obtained from Ref. [6].

The kinetic entity is the hydrated micelle. The radius of the spherical micelle was computed by

$$a = (3V_M/4\pi)^{1/3}, \quad (5)$$

where V_M is the hydrated micelle volume, computed by

$$V_M = n\bar{V}_{m,h}/N_A, \quad (6)$$

n being the aggregation number ($n = 20.5$) [11], N_A the Avogadro's number and $\bar{V}_{m,h}$ the partial molar volume of the hydrated micellized surfactant, obtained by

$$\bar{V}_{m,h} = \bar{V}_m + n_h V_w, \quad (7)$$

where \bar{V}_m is the partial molar volume of micellized surfactant ($\bar{V}_m = 264.80 \pm 0.76 \text{ cm}^3 \text{ mol}^{-1}$) [12], n_h is the micelle hydration number ($n_h = 39 \pm 7 \text{ mol of water per mol of surfactant}$) [13], and V_w is the molar volume of water.

To compute the zeta potential and micelle charge per unit length of rodlike micelles, a micelle whose hydrocarbon core radius is equal to the fully extended surfactant hydrocarbon chain (l) was postulated. To compute l , the following equation was employed [14]:

$$l(\text{nm}) = 0.13n_C + 0.1704, \quad (8)$$

n_C being the number of carbon atoms in the chain. The hydrocarbon core volume per unit length was computed by

$$V = \pi l^2 \quad (9)$$

and the number of surfactant molecules per unit length of a rodlike micelle was computed with

$$n = \pi l^2 / V_{\text{HC}}, \quad (10)$$

where the volume of a micellized hydrocarbon chain V_{HC} was computed with the contribution of the $n_C - 1$ methylene groups (V_{CH_2}) and that of the methyl group (V_{CH_3}) [15]. These volumes were estimated by [16]

$$\begin{aligned} V_{\text{CH}_3} (\text{nm}^3) &= 0.05108 \pm 0.0001311t, \\ V_{\text{CH}_2} (\text{nm}^3) &= 0.02669 \pm 0.0000143t, \end{aligned} \quad (11)$$

where t is the temperature in °C. This gave $n = 26.7$ molecules per nm of micelle length. The volume of this cylindrical section is $nV_{\text{m,h}}$, which gave the radius of the hydrated micelle $a = 2.2 \pm 0.3$ nm.

With the preceding data, we were able to compute the zeta potential and the micelle ionization degree (α) in both models: spherical and rod-like micelles. The values are given in Table 1.

The ζ values are similar to those found by Stigter and Mysels [2] for SDS micelles for similar ionic strengths: $\zeta = 80.9$ mV in 0.03 mol dm^{-3} NaCl and 68.3 mV in 0.1 mol dm^{-3} NaCl, and for alkyltrimethylammonium chlorides ($\zeta = 56.5$ mV for $\text{C}_{10}\text{N}(\text{CH}_3)_3\text{Cl}$ and 75 mV for $\text{C}_{12}\text{N}(\text{CH}_3)_3\text{Cl}$ [4].

In Fig. 2 the computed values of α are compared with those determined with ion-selective electrodes [6]. The agreement is very good. The results are not very sensitive to the micelle structure model (rod-like or spherical micelle). It may be concluded that the use of ion-selective electrodes together with information on micelle structure can replace the more difficult electrophoresis experiments giving essentially the same information.

It can also be concluded that the agreement between the values of α computed by two different methods supports the commonly used supposition that ion-selective electrodes detect only the non-micellised ions in surfactant systems.

To compute free ion concentration from ion-selective measurements, the free ion activity coefficients must be

Table 1 Values of zeta potential and micelle ionization degree

C_T (mol dm^{-3})	Spherical micelles		Rod-like micelles	
	ζ (mV)	α	ζ (mV)	α
0.03197	78 ± 2	0.493 ± 0.002	87 ± 2	0.52 ± 0.02
0.08607	53 ± 1	0.370 ± 0.005	55 ± 1	0.433 ± 0.008

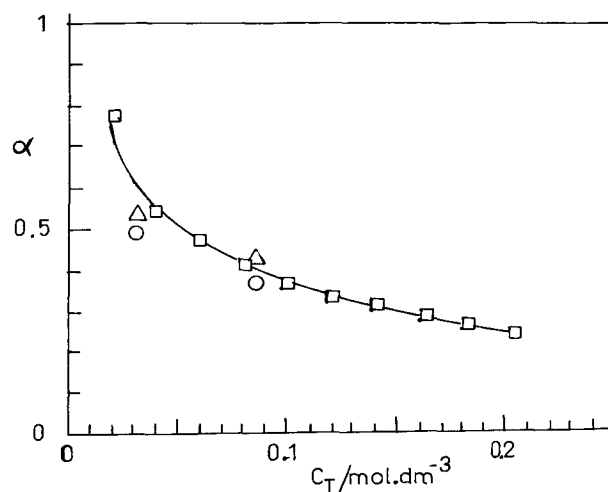


Fig. 2 DTAOH micelle ionization degree at 25°C. \square : from ion-selective electrodes [5], Δ : from ζ potential, rod-like micelles, \circ : from ζ potential, spherical micelles, vs. total DTAOH concentration

estimated. To do this, it is commonly assumed that only free ions contribute to the intermicellar solution ionic strength, and micelles do not affect the result. The coincidence between both estimations of α in this work also supports the preceding suppositions.

Stigter [7] explained the dependence of μ on the soap concentrations as primarily due to the solvent backflow. However, in view of the coincidence of the α values obtained from μ and ion-selective electrodes, it may be concluded that this dependence is due to the reduction of the micelle net charge when the ionic strength of the intermicellar solution arises. The finding of Hoyer and Greenfield [3] of the linear dependence of $\log \mu$ on the logarithm of the ionic strength for various alkylamine hydrochlorides supports this interpretation.

Conclusions

- The use of ion-selective electrodes together with information on micelle structure can replace the more

difficult electrophoresis experiments giving essentially the same information.

- Ion-selective electrodes only detect the non-micellised ions.
- Only free ions contribute to the intermicellar solution ionic strength, and micelles do not affect the result significantly.

- The dependence of μ on the soap concentration is due to the reduction of the micelle net charge when the ionic strength of the intermicellar solution rises.

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