μ_{ep}	Electrophoretic mobility
q	Effective molecular charge
r	Effective molecular radius
η	Buffer viscosity
l	Effective capillary length
L	Total capillary length
V	Applied potential
t_{mig}	Migration time
t_0	Migration time of an uncharged compound
μ_{eo}	Electroosmotic mobility
ϵ	Dielectric constant of the separation buffer
ζ	Zeta potential at the internal capillary wall
t_{rel}	Relative migration time
μ_{rel}	Relative electrophoretic mobility
μ_x	Actual electrophoretic mobility

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JOURNAL OF CHROMATOGRAPHY A

Determination of critical micelle concentration by capillary electrophoresis. Theoretical approach and validation

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Abstract

The aim of this study was the determination of the critical micelle concentration (CMC) of the most commonly employed anionic surfactant in micellar electrokinetic chromatography, sodium dodecyl sulphate (SDS), using capillary electrophoresis, i.e., under the operating conditions of the electrophoretic separation (pH, ionic strength, temperature, etc.). The effective electrophoretic mobility of a neutral compound, resulting from the solvophobic and micellar contributions, appeared to be a well adapted parameter for the study of the micellization process of anionic surfactants. In fact, the theoretical treatment of the evolution of this parameter as a function of the total surfactant concentration allowed the identification of a sharp change in slope at the cmc, and therefore to establish capillary electrophoresis as a new analytical tool for the determination of critical micelle concentrations. In the experimental case of an electrolytic solution consisting of 5 mmol l^{-1} borax, the observed value of the cmc of SDS (5.29 mmol l^{-1}) was in total agreement with the literature data when the sodium concentration in the solution was the same.

1. Introduction

The optimisation of the analytical conditions in micellar electrokinetic chromatography (MEKC) has been an important field of research since 1984 and has allowed the resolution of a number of diverse organic matrices. Most of these studies dealt with the optimization of the operating conditions (nature and concentration of the electrolytic salt, nature and concentration in organic solvent) concerning the relative interactions of the solutes between the micellar and the aqueous phases. However, few authors examined the influence of these operating parameters on the evolution or the existence of the micellar phase. As the study of the micellization process is a key parameter in the optimization of the analytical conditions in MEKC, the determination of the critical micelle concentration under electrophoretic conditions proves to be essential.

Taking into account the complexity of the electrolytic media used in MEKC, the different physico-chemical properties used for the determination of the critical micelle concentration (cmc) (surface tension, conductivity, etc.) appear to be not well adapted or even inappropriate. The micellar solubilization, which can be easily accessible using capillary electrophoresis,

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seems to be an appropriate method for the study of micellar systems as it is essentially due, like micellization, to the hydrophobic effect. The solubility in water of a hydrophobic molecule is strongly improved in the presence of a surfactant above its critical micelle concentration.

This micellar solubilization method for the determination of critical micelle concentrations is based on the measurement of the concentration of a poorly water soluble compound in the presence of increasing concentrations of surfactant. Below the cmc, the sample solubility will remain virtually the same as without surfactant. Above the cmc, one will observe a tremendous increase in the amount of solubilized additive with increase in the micelle concentration [1]. Moreover, this study can be done very simply with a UV–visible spectrophotometer if the solute studied contains a chromophore.

The inherent defaults of this micellar solubilization technique are linked with the use of an additive in the water–surfactant pseudo-biphasic system which can play the role of a catalyst of the micellar process, e.g., as an impurity of the surfactant does. Indeed, the cmc values obtained with this technique are known to be lower than those obtained with techniques that do not require an additive, e.g., measurement of the surface tension. Nevertheless, this systematic error can be minimized if the concentration of the additive is negligible, as in capillary electrophoresis, for example.

However, the principal interest in this technique is its universality, with regard to the nature of the studied surfactant (anionic, cationic, nonionic) or the nature of the aqueous phase (presence of neutral salts, of organic solvents, etc.).

2. Theoretical

Considering we are in the presence of the aqueous phase, the micellar pseudo-phase and the capillary wall, which represents a solid phase on which surfactant molecules are adsorbed, three equilibrium constants can be established: K_{mic}, the equilibrium constant of the solute between the aqueous phase and the micelles (micellar solubilization constant); K_{ads}, the equilibrium constant of the solute between the aqueous phase and a stationary phase constituted of surfactant molecules adsorbed on the capillary wall; and K_{solv}, the equilibrium constant of the solute between the aqueous phase and the monomeric surfactant molecules (solvophobic partition constant). Under these conditions, Fig. 1 shows schematically the exchanges involved in MEKC.

The adsorption of cationic surfactant molecules on the fused-silica capillary wall is a very important phenomenon, as it has been shown to be responsible for an inversion of the electroosmotic flow [2]. Nevertheless, in the case of anionic surfactants, it seems that the ionic repulsion between the hydrophilic moieties of the surface-active molecules and the silanol groups is strong enough to prevent any adsorption, and the zeta potential remains constant [3].

In the framework of our study, which involved sodium dodecyl sulphate (SDS), the only equilibria present were therefore the partition of the solute N between the aqueous phase and the monomeric surfactant molecules S on the one hand (Eq. 1), and the partition of the solute between the aqueous phase and the micellar pseudo-phase M on the other (Eq. 2). Under these conditions, two equilibria appear to be sufficient to describe the system fully, as we can omit the study of the partition of the solute between the micellar pseudo-phase and the monomeric surfactant molecules:

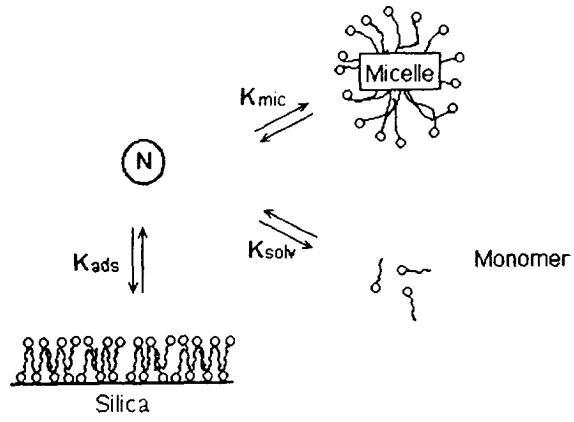

Fig. 1. Illustration of equilibria occurring in MEKC.

$$N + S \rightleftharpoons NS \qquad K_{solv} = \frac{x}{(1-x-y)[S]} \tag{1}$$

$$N + M \rightleftharpoons NM \qquad K_{mic} = \frac{y}{(1-x-y)[M]} \tag{2}$$

where x is the molar fraction of the solute associated with the monomeric surfactant through solvophobic interactions and y is the molar fraction of the solute in the micellar pseudo-phase. The micelle concentration [M] is expressed in moles of micelles per litre whereas [S] is expressed in moles of monomeric surfactants per litre. The total concentration C_T of surfactant introduced in the solution is therefore

$$C_T = [S] + n[M] \tag{3}$$

where n is the micellar aggregation number.

To be precise, an activity coefficient should have been introduced in Eqs. 1 and 2 to take into account the non-ideality inside these micellar aggregates. This introduction would nevertheless be only formal, as no data are available on the interaction between the solute and the surfactant in the micellar core [4].

Even though the partition involving the monomeric surfactant molecules is only rarely taken into account in the literature [5], this partitioning should not be neglected in the framework of a study on the effect of surfactant concentrations near or below the cmc. Under such conditions, the study by MEKC of the electrophoretic behaviour of chosen neutral molecules should lead to the elucidation of the micellization process.

The apparent mobility μ_{app} of a neutral solute will therefore be defined as the sum of the mobilities of the three components of the considered system (aqueous phase of mobility μ_{e0}, micellar pseudo-phase of mobility μ_{mic} and "solvophobic complex" of mobility μ_{solv}) weighted by the molar fraction of the solute in each of these "phases", i.e.,

$$\mu_{app} = (1-x-y)\mu_{e0} + x(\mu_{e0} - \mu_{solv}) + y(\mu_{e0} - \mu_{mic}) \tag{4}$$

or

$$\mu_{eff} = \mu_{e0} - \mu_{app} = x\mu_{solv} + y\mu_{mic} \tag{5}$$

where μ_{eff} is the effective electrophoretic mobility of the neutral solute, i.e., the mobility of the solute which is due only to the hydrophobic interactions with the surfactant molecules, whatever their nature (monomers or micelles).

If one expresses this mobility as a function of the equilibrium constants and the concentrations in monomeric and in micellar surfactant (Eqs. 1 and 2), one obtains, considering the two equilibria to be independent as a first approximation, i.e., the molar fraction of the solute associated with the monomeric surfactant, written as

$$x = \frac{K_{solv}[S]}{1 + K_{solv}[S]}$$

and, in an identical manner the molar fraction of the solute in the micellar pseudo-phase, written as

$$y = \frac{K_{mic}[M]}{1 + K_{mic}[M]}$$

Therefore,

$$\mu_{eff} = \frac{K_{solv}[S]}{1 + K_{solv}[S]} \cdot \mu_{solv} + \frac{K_{mic}[M]}{1 + K_{mic}[M]} \cdot \mu_{mic} \tag{6}$$

Therefore, it is possible to analyse the evolution of the effective electrophoretic mobility μ_{eff} of a neutral compound N as a function of the total concentration C_T of surfactant using Eq. 6 and considering three concentrations ranges, as follows.

(a) $C_T <$ cmc: solvophobic solubilization zone. In this case, the total surfactant concentration is reduced to $C_T = [S]$ and the equation for the effective mobility μ_{eff} is

$$\mu_{eff} = \frac{K_{solv}C_T}{1 + K_{solv}C_T} \cdot \mu_{solv} \tag{7}$$

Fig. 2a represents the theoretical evolution of such a mobility for a compound with a partition constant $K_{solv} = 5$ mol^{-1} l when the mobility of the "solvophobic complex" μ_{solv} is fixed at $5 \cdot 10^{-9}$ m^2 V^{-1} s^{-1}, the cmc being arbitrary established as 10^{-2} mol l^{-1} (arbitrary values in the order of experimental magnitudes).

(b) $C_T >$ cmc: "micellar" solubilization zone.

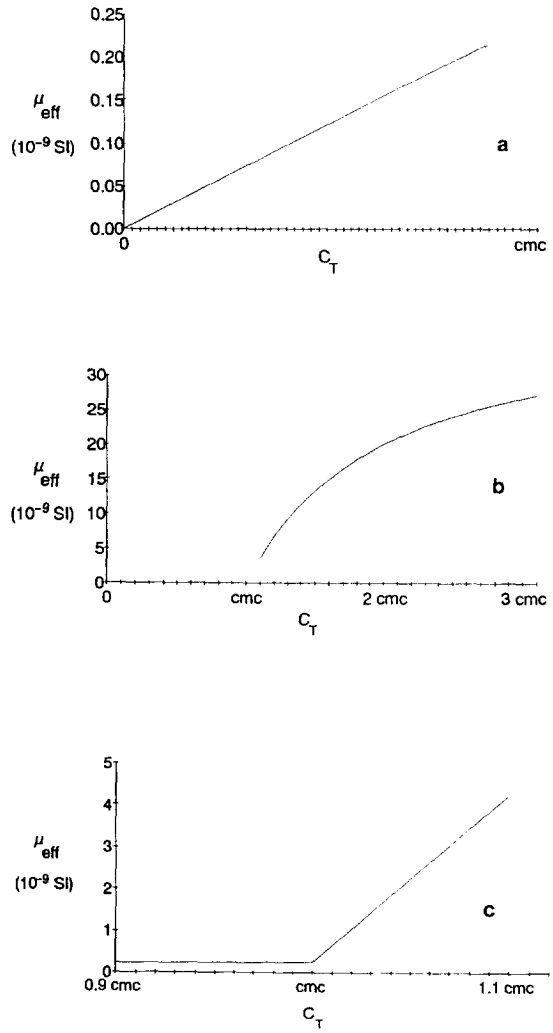

Fig. 2. Theoretical evolution of the effective mobility of a neutral compound as a function of the total surfactant concentration (see text for parameter values adopted for simulation). (a) Surfactant concentration below the cmc; (b) surfactant concentration above the cmc; (c) surfactant concentration near the cmc.

For such concentrations above the cmc, the concentration of monomeric surfactants remains approximately constant at the value at the cmc. Hence Eq. 3 can be expressed as $C_T = \text{cmc} + n[\text{M}]$. Under such conditions, the contribution to the effective mobility due to the solvophobic effect will remain constant (μ_{cmc}) as a function of the total surfactant concentration and equal to

$$\mu_{cmc} = \frac{K_{solv} \cdot cmc}{1 + K_{solv} \cdot cmc} \cdot \mu_{solv} \quad (8)$$

The formation of micelles in the electrophoretic medium will correspond to a micellar solubilization, of which the contribution to the effective mobility is translated into

$$\frac{K_{mic}(C_T - cmc)/n}{1 + K_{mic}(C_T - cmc)/n} \cdot \mu_{mic} \quad (9)$$

The effective mobility will therefore be equal to the sum of these two contributions, i.e.,

$$\mu_{eff} = \frac{K_{solv} \cdot cmc}{1 + K_{solv} \cdot cmc} \cdot \mu_{solv} + \frac{K_{mic}(C_T - cmc)/n}{1 + K_{mic}(C_T - cmc)/n} \cdot \mu_{mic} \quad (10)$$

In this surfactant concentration zone, the micellar contribution is much more important than the solvophobic contribution, on the one hand because of the much greater partition constant, but also because of an important micellar mobility. Fig. 2b represents the theoretical evolution of the effective mobility of a compound of which the equilibrium constant K_{mic} is equal to 100 S.I. units while μ_{mic} is fixed at $40 \cdot 10^{-9}$ m^2 V^{-1} s^{-1}. As in Fig. 2a, the equilibrium constant $K_{solv} = 5$ mol^{-1} l when the mobility of the "solvophobic complex" μ_{solv} is fixed at $5 \cdot 10^{-9}$ m^2 V^{-1} s^{-1}, the cmc being arbitrary established at 10^{-2} mol l^{-1} and the micellar aggregation number at 100.

(c) $C_T \approx$ cmc: micellization zone. For such a total surfactant concentration, none of the two terms in Eq. 6 can be neglected. Nevertheless, because of the very low micellar concentration in the solution, the term $K_{mic}[M]$ is negligible compared to 1. In the same way, because of the very low value of the solvophobic equilibrium constant K_{solv}, the term $K_{solv}[S]$ is also negligible compared to 1. Under such conditions, Eq. 6 reduces to

$$\mu_{eff} = K_{solv}[S]\mu_{solv} + K_{mic}[M]\mu_{mic} \quad (11)$$

According to Phillips [6], any property ϕ of the solution expressed as an equation of the form

$$\phi = A[S] + B[M] \quad (12)$$

where A and B are, proportionality constants, has a third derivative, with respect to the total concentration, equal to zero at the cmc and should therefore show, at the cmc, a maximum change in the slope of the curve of the evolution of this property as a function of the total surfactant concentration. This condition is necessary for the evolution of a property of the solution to translate the micellar aggregation as a radical change in the composition of the solution, i.e., the appearance of a new phase in solution.

In such a concentration zone, the effective mobility of a neutral compound then satisfies well the general condition of Phillips, as can be seen in Fig. 2c (the different constants being used for the establishment of this theoretical curve are the same as those used previously).

Hence the evolution of the electrophoretic mobility μ_{eff} of a neutral compound N as a function of the total surfactant concentration C_T in the solution appears to be a new method for the study of the micellization process.

3. Experimental

3.1. Reagents

Buffer and sample solutions were prepared with water purified by reverse osmosis and filtered using a Milli Ro + Milli Q system (Millipore, Molsheim, France). The reagent used as the electrolyte, i.e., borax, was of analytical-reagent grade (99%) from Aldrich (La Verpillère, France). SDS was of 99% purity and purchased from Sigma (Saint Quentin Fallavier, France). The compound used for the validation of the method, i.e., naphthalene, was of 99% purity from Aldrich. For the determination of the electroosmotic flow, we used acetonitrile of analytical-reagent grade from Aldrich.

3.2. Apparatus

All experiments were carried out on a P/ACE 2100 system (Beckman, Fullerton, CA, USA) monitored by a PS/2 computer (IBM, Greenock, UK), using P/ACE software (Beckman). Data collection was performed with the same software.

Samples were loaded by a 1-s pressure injection into a fused-silica capillary (57 cm × 50 μm I.D.). UV detection at 214 nm was performed through the capillary at 50 cm from the inlet. The pH values of the electrolytes were measured using a Beckman Model Φ pH meter at the temperature of the analyses. The separations were performed three to five times for each SDS concentration value studied in order to ensure good reproducibility of the measurements.

3.3. Buffer preparation

Stock solutions of borax ($5 \cdot 10^{-3}$ mol l^{-1}) and of surfactant (SDS) $30 \cdot 10^{-3}$ mol l^{-1}) were prepared daily. Different SDS concentrations were then obtained by mixing these two solutions.

4. Results and discussion

In order to validate the method for the determination of the cmc, several experimental problems had to be solved concerning the nature of the sample and the control of the temperature.

4.1. Problem of the introduction of a neutral compound

The visualization of the evolution of the electrophoretic mobility at very low surfactant concentrations in the electrophoretic media imposes the choice of a neutral and very lipophilic compound. Indeed, the more important the equilibrium constants K_{solv} and K_{mic}, the more dramatic will be the change in the slope of the curve of the electrophoretic mobility as a function of the total surfactant concentration at the cmc, and therefore the easier and more precise will be the determination of this concentration.

Nevertheless, such a compound will be poorly soluble, if not insoluble, in the aqueous phase. This lack of solubility will lead to a low efficiency of the electrophoretic system and to uncertainty

in the measurement of retention times. Moreover, concerning the biphasic system, this lack of solubility will probably result in a shift in the micellization equilibrium and therefore lead to systematic errors in the cmc value.

It was therefore very important to find a compound of low polarity, but not insoluble in water, with a high molar absorptivity in UV–visible spectrophotometry and of sufficiently low residence time in the micellar core that its presence does not interfere with the dynamics of the biphasic system.

With regard to these requirements, different solutes can be considered. Table 1 summarizes the characteristics of a few solutes arranged in lipophilic order.

From Table 1, it is clear that benzene is not lipophilic enough to visualize the evolution of the biphasic system. The use of linear alkylbenzenes which are more lipophilic and with a linear geometric structure close to that of the surfactant molecule, can nevertheless be considered. However, this kind of molecules will not have a high enough molar absorptivity to allow their injection in small amounts, which is a necessary condition to prevent any perturbation of the system. Pyrene and anthracene are compounds of strong lipophilicity and with high molar absorptivities. Nevertheless, their water solubility is very low and they have to be injected in concentrations such that their detection is impossible. Further, biphenyl does not have a high enough molar absorptivity to be detected under its solubility limit in water.

Naphthalene seems to correspond to the ideal solute: it has medium lipophilicity, a high molar absorptivity over a large wavelength range and a low residence time in the SDS micellar core compared with the lifetime of the micelles (1.8–50 ms [9]). Therefore, naphthalene will be the only sample considered further here.

The injection of a 10^{-4} mol l^{-1} solution of naphthalene will probably not perturb the biphasic system, but will still allow the detection of this compound. The amounts injected were nevertheless reduced to the minimum allowed by the instrument, i.e., with the application of a 0.5 bar pressure for 1 s. The hydrodynamic injection mode was preferred here to the electrokinetic mode as it is independent of the nature of the electrophoretic media. The amount injected was therefore not biased when the concentration of bulk salt or surfactant was modified.

4.2. Temperature control problem

According to the instrument's specification, the temperature in the capillary is well controlled and regulated when the power dissipated in the capillary is up to 5 W m^{-1}. However, for security reasons, we adjusted the voltage applied through the capillary so the power did not exceed 2 W/m^{-1}, and the electric field was kept constant for an experimental set. These precautions allowed us to obtain consistent and reproducible results, even with a change in the capillary length.

These two crucial points having been established, we then proceeded to the evaluation of

Table 1
Characteristics of the solutes

Solute	Solubility in water (mol l^{-1})	Residence time in micelles (μs)[a]	$\lambda_{max}(\varepsilon)$ (nm)[b]
Benzene	$2.3 \cdot 10^{-2}$	0.23	204 (8800)
Naphthalene	$2.2 \cdot 10^{-4}$	4	221 (117 000)
Biphenyl	$4.1 \cdot 10^{-5}$	10	201 (46 500)
Pyrene	$6.0 \cdot 10^{-7}$	243	252 (220 000)
Anthracene	$2.2 \cdot 10^{-7}$	59	241 (88 000)

[a] Time taken for a fraction of 63% of the probe molecules to escape the SDS micelles [7].
[b] Wavelength for which the molar absorptivity ε (1 mol^{-1} cm^{-1}) is maximum [8].

the method for the determination of critical micelle concentrations and applied it to SDS.

4.3. Validation of the analytical method

In order to validate the method, we plotted the evolution of the electrophoretic mobility of naphthalene as a function of the SDS concentration. To do so, we used a simple electrolyte which satisfied two conditions: to contain ions in sufficient amounts to conduct the electric current, and to have pH buffer characteristics so as to maintain constant the ionization state of the silanol groups on the capillary wall.

Among the most commonly employed inorganic salts in MEKC, borax (sodium tetraborate) seemed the most appropriate. From very low concentrations ($<10^{-3}$ mol l^{-1}), this salt leads to aqueous solutions of pH 9.2 at 25°C. An aqueous solution of $5 \cdot 10^{-3}$ mol l^{-1} borax allows one to work at constant pH, keeping the ionic strength of the solution low (10 mequiv. l^{-1}).

Fig. 3 shows the general evolution of the electrophoretic mobility of naphthalene as a function of the SDS concentration under these simple electrolytic conditions. The general shape of this graph shows a dramatic change in slope at an SDS concentration of ca. $5 \cdot 10^{-3}$ mol l^{-1}. In order to measure this concentration value with more accuracy, we studied the part of the graph corresponding to surfactant concentrations between $3 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ mol l^{-1} (Fig. 4).

The values of the electrophoretic mobility of naphthalene in this concentration range are given in Table 2. The values given are means calculated from three independent electropherograms for each SDS concentration. From these data, and according to the theoretical representation in Fig. 2c, two linear regression curves were plotted: one for SDS concentrations between $3 \cdot 10^{-3}$ and $5.2 \cdot 10^{-3}$ mol l^{-1}, with the equation $\mu_{eff} = -0.193 \cdot 10^{-9} + 0.189 \cdot 10^{-6}$ [SDS], and for SDS concentrations between $5.4 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ mol l^{-1}, with the equation $\mu_{eff} = -30.048 \cdot 10^{-9} + 5.834 \cdot 10^{-6}$ [SDS]. The intersection of these two lines allows one to evaluate the cmc and the contribution to the electrophoretic mobility of the "solvophobic complex" (μ_{cmc}) at and above this concentration, i.e., cmc = $5.29 \cdot 10^{-3}$ mol l^{-1} and $\mu_{cmc} = 0.807 \cdot 10^{-9}$ m^2 V^{-1} s^{-1}.

The hypotheses made for the theoretical approach for the determination of the cmc using this new technique (Eq. 11) were based on,

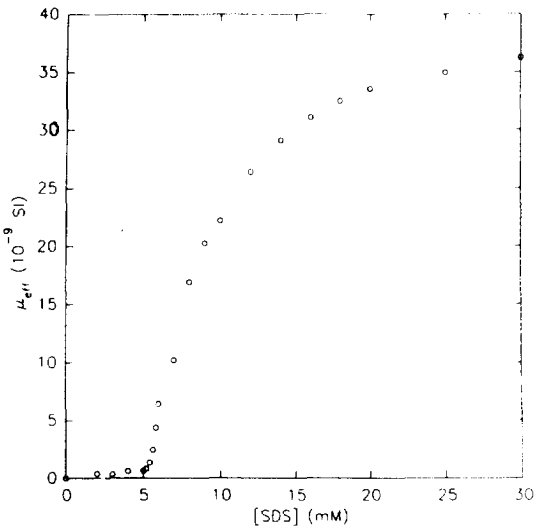

Fig. 3. Graph of the evolution of the electrophoretic mobility of naphthalene as a function of the SDS concentration. Bulk salt: $5 \cdot 10^{-3}$ mol l^{-1} borax.

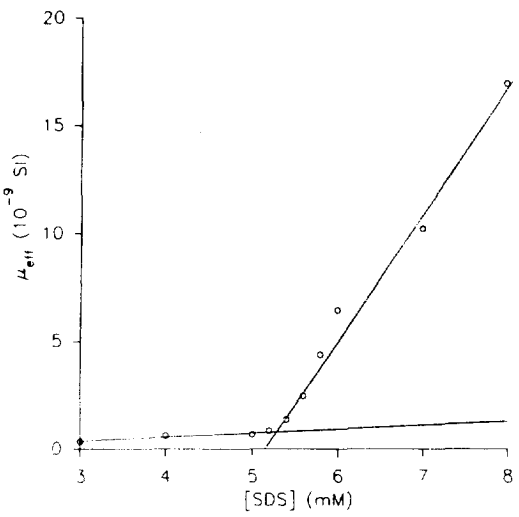

Fig. 4. Graph of the evolution of the electrophoretic mobility of naphthalene as a function of the SDS concentration near the cmc. Bulk salt: $5 \cdot 10^{-3}$ mol l^{-1} borax.