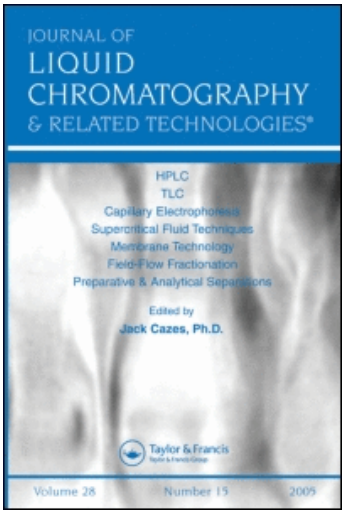

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Micellar Electrokinetic Chromatography Estimation of Critical Micellar Concentration of Sodium Dodecyl Sulphate Systems in Saline Media

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MICELLAR ELECTROKINETIC CHROMATOGRAPHY ESTIMATION OF CRITICAL MICELLAR CONCENTRATION OF SODIUM DODECYL SULPHATE SYSTEMS IN SALINE MEDIA

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ABSTRACT

Micellar Electrokinetic Chromatography was applied to the estimation of the critical micellar concentration of sodium dodecyl sulphate in saline media of different nature (2-(N-cyclo-hexylamino)-ethanesulphonic acid and Ammonium Acetate) and concentration. The linear variation of the capacity factor for two series of compounds (11 benzene and naphthalene derivatives and 17 1,4-dihydropyridines) as a function of sodium dodecyl sulphate concentration in the electrolytic solution allowed this estimation.

INTRODUCTION

The introduction of a surfactant at a concentration above its critical micelle concentration (c.m.c.) in the electrolyte solution in Capillary Electrophoresis has given rise to the Micellar Electrokinetic Chromatography (MEKC).[1-4] In this technique, solutes are distributed between the aqueous and micellar phases according to their association constants with the micelles. If an anionic surfactant is employed, micelles which have an anodic electrophoretic mobility will migrate to the cathode if a strong enough electroosmotic flow exists towards the cathode.

This means that if a neutral solute is introduced in the system, it will elute from the separation capillary at a time somewhere between the migration time of the electroosmotic flow marker, t_0, and the migration time of the micelle, t_m. From these two parameters, the capacity factor (k') of a solute in MEKC can be defined as follows: [1,2]

$$k' = (t_r - t_0) / t_0 [1 - (t_r / t_m)] \quad (1)$$

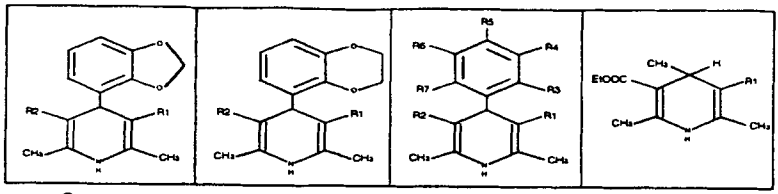
where t_r is the migration time of the solute.

If the micellar concentration in the buffer is low, the solute capacity factor of a solute can be related to the total surfactant concentration in the buffer using the following equation:[2,5]

$$k' = (K_2 + v) (C - c.m.c.) \quad (2)$$

where K_2 is the solute-micelle association constant per surfactant monomer, v is the molar volume of the micelle, and C is the total concentration of surfactant in the buffer. From eq. (2), it can be observed that the c.m.c. of the micellar system can be estimated from the intercept/slope ratio of the straight line of the variation of the capacity factor of a solute in MEKC as a function of the total concentration of the surfactant in the electrolyte solution.[5] Despite this possibility, MEKC has seldom been used in order to determine c.m.c. values in this manner.

Another method of applying MEKC to the estimation of the c.m.c. of a micellar system is to measure the variation of the effective electrophoretic mobility of a neutral compound as a function of the total concentration of surfactant in solution. By this method, the c.m.c. of sodium dodecyl sulphate (SDS) in a electrolytic solution 0.005 M in borax was achieved[6] by using naphthalene as a test solute and SDS concentrations ranging from 0.003 to 0.008 M.



GROUP 1	-R_1	-R_2
1	-$COOCH_2$- (1)	-$COOCH_3$
2	-$COOCH_3$	-$COOCH_3$
3	-$COOCH_2CH_2OCH_3$	-$COOCH_2CH_2OCH_3$
5	-$COOCH_2CH_3$	-$COOCH_2CH_3$
6	-$COOCH_2CH_2OCH_3$	-COOIsp
10	-$COOCH_2CH_3$	-$COOCH_3$
14	-COOIsp	-$COOCH_3$

(1)

GROUP 2	-R_1	-R_2
4	-$COOCH_2CH_3$	-$COOCH_3$

GROUP 3	-R_1	-R_2	-R_3	-R_4	-R_5	-R_6	-R_7
7	-$COOCH_2CH_3$	-$COOCH_3$	-H	-NO_2	-H	-H	-H
8	-$COOCH_2CH_3$	-$COOCH_3$	-OCH_2OCH_3	-H	-H	-H	-H
9	-$COOCH_2CH_3$	-$COOCH_3$	-H	-OCH_3	-H	-OCH_3	-H
11	-$COOCH_2CH_3$	-$COOCH_3$	-H	-H	-H	-H	-H
12	-$COOCH_2CH_3$	-$COOCH_3$	-H	-OCH_3	-OCH_3	-H	-H
13	-$COOCH_2CH_3$	-$COOCH_3$	-OCH_3	-OCH_3	-H	-H	-H
17	-COOIsp	-$COOCH_2CH_2OCH_3$	-H	-NO_2	-H	-H	-H

GROUP 4	-R_1	-R_2	-R_3
15	-$COOCH_3$	-$COOCH_2CH_3$	-H
16	-$COOCH_2CH_3$	-$COOCH_2CH_3$	-H

Figure 1. Structures of 1,4-dihydropyridines and their identification numbers.

In this work, MEKC has been used to estimate the c.m.c. of SDS in saline media which consisted of two buffers, 2-(N-cyclo-hexylamino)-ethanesulphonic acid (CHES) (pH = 10) (at three different concentrations) and Ammonium Acetate pH = 9). Data for the capacity factors of these two groups of solutes (11 benzene and naphthalene derivatives and 17 1,4-dihydropyridines) previously measured for different SDS concentrations in solution[7,8] have been used.

EXPERIMENTAL

Figure 1 shows the structure of the 1,4-dihydropyridines studied and the identification numbers used throughout this paper. The benzene and naphthalene derivatives were the following: 1) benzene, 2) benzyl alcohol, 3) benzamide, 4) toluene, 5) benzonitrile, 6) nitrobenzene, 7) 2-phenylethanol, 8) chlorobenzene, 9) phenylacetonitrile, 10) naphthalene, 11) 1-naphthylamine.

Experimental micellar electrokinetic chromatographic data used in this work was previously determined to obtain solute-micelle association constants of the compounds studied as indicated in References.[7,8]

Briefly: a) For the benzene and naphthalene derivatives, a P/ACE System 2050 capillary electrophoresis (Beckman, Fullerton, CA, USA) with UV detection (214 nm) and 25 μm I.D. capillaries (Polymicro Technologies, Phoenix, AZ, USA) were used. Ammonium Acetate (pH 9) and 2-(N-cyclo-hexylamino)-ethanesulphonic acid (CHES) (pH = 10) buffers were used. Sudan III or benzo(a)pyrene and dimethylformamide were used to determine micelle migration time and electro-osmotic flow time respectively. The washing routine employed for the capillary prior to each injection, in order to determine solutes capacity factors, was the following: Milli-Q water for 3 min, 0.1 M sodium hydroxide for 3 min, Milli-Q water for 2 min and separation buffer for 3 min. Working temperature was 25 °C and the electrical field strength applied was 15 kV.

b) For 1,4-dihydropyridines, the instrument used consisted of a Prince programmable injector, a Lambda 1000 UV-detector (238 nm) and a high voltage power supply, all purchased from Lauer Labs (The Netherlands). The integrator employed was a HP3394 from Hewlett Packard (Avondale, PA, USA). A 25 μm I.D. capillary (Polymicro Technologies, Phoenix, AZ, USA) was employed. CHES (pH 10) buffers were used. Sudan III and dimethylformamide were used to determine micelle migration time and electro-osmotic flow time respectively. The washing routine employed was the following: Milli-Q water for 2 min, 0.1 M sodium hydroxide for 2 min, Milli-Q water for 2 min and separation buffer for 2 min. Working temperature was 31 °C and the electrical field strength applied was 15 kV.

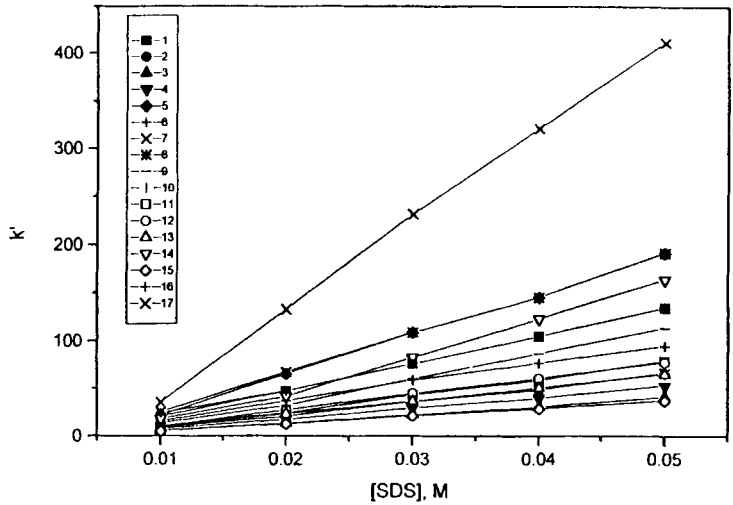


Figure 2. Variation of the capacity factor for a group of 17 1,4-dihydropyridines as a function of the SDS concentration in a 0.05 M CHES buffer (pH=10).

Data Manipulation

A Wilcoxon matched-pair test was carried out using a SOLO Statistical System.[9]

RESULTS AND DISCUSSION

The determination of the variation of capacity factors for a group of benzene and naphthalene derivatives and 1,4-dihydropyridines in a MEKC system as a function of total SDS concentration in the buffer solution[7,8] should enable estimation of the c.m.c. of SDS in different saline media. Such variation is a straight line (eq. (2)) except for very hydrophobic solutes, for which the variation of the capacity factor with the SDS concentration was shown to be not linear, due to the error in the determination of the capacity factor for these compounds whose migration times are very similar to the micelle migration time (eq.(1)).[7] If a straight line is obtained for a solute, the ratio between the intercept and the slope of this straight line should allow for the estimation of the c.m.c. of the micellar system in the buffer employed.

Table 1

Critical Micelle Concentration for SDS Calculated from Benzene and Naphthalene Derivatives Capacity Factors Data in Different Electrolyte Solutions by MEKC

Compound	c.m.c. (0.05 M CHES)	c.m.c. (0.10 M CHES)	c.m.c. (0.05M NH_4OAc)
1	$5.27\ 10^{-3}$	$1.71\ 10^{-3}$	$1.67\ 10^{-3}$
2	$3.82\ 10^{-3}$	$1.01\ 10^{-3}$	$1.25\ 10^{-3}$
3	$5.57\ 10^{-3}$	$1.35\ 10^{-3}$	$1.50\ 10^{-3}$
4	$4.67\ 10^{-3}$	$1.71\ 10^{-3}$	$2.34\ 10^{-3}$
5	$5.01\ 10^{-3}$	$1.75\ 10^{-3}$	$2.78\ 10^{-3}$
6	$4.33\ 10^{-3}$	$1.46\ 10^{-3}$	$2.22\ 10^{-3}$
7	$3.23\ 10^{-3}$	$2.00\ 10^{-3}$	$2.54\ 10^{-3}$
8	$3.52\ 10^{-3}$	$2.04\ 10^{-3}$	$2.37\ 10^{-3}$
9	$4.37\ 10^{-3}$	$2.16\ 10^{-3}$	$2.70\ 10^{-3}$
10	$1.27\ 10^{-3}$	$1.49\ 10^{-3}$	$1.97\ 10^{-3}$
11	$3.54\ 10^{-3}$	$3.14\ 10^{-3}$	$2.52\ 10^{-3}$
c.m.c. $\pm\ \sigma_{N-1}$	$4.05\ 10^{-3} \pm 1.19\ 10^{-3}$	$1.80\ 10^{-3} \pm 5.55\ 10^{-4}$	$2.17\ 10^{-3} \pm 5.07\ 10^{-4}$

Figure 2 shows, as an example, the variation of the capacity factor of a group of 17 1,4-dihydropyridines as a function of the SDS concentration in a 0.05 M CHES buffer (pH = 10).[8] Similar plots were obtained for the other buffer used (0.08 M CHES) and the other group of compounds studied in this work (11 benzene and naphthalene derivatives), in the different experimental conditions studied (0.05 M and 0.10 M CHES and 0.05 M Ammonium Acetate). Good linearity was observed in all cases ($r>0.99$) and this enabled the employment of eq. (2) in order to estimate the c.m.c. values for the SDS micellar systems in the different saline conditions.

Table 1 groups the c.m.c. values obtained for the SDS micelles with the group of 11 benzene and naphthalene derivatives when 0.05 M and 0.10 M CHES buffers (pH=10) and 0.05 M Acetate buffer (pH=9) were used. This table provides the c.m.c. values obtained with each solute as well as the average values (and standard deviation) for the c.m.c. obtained for all solutes in each buffer. Table 2 gives the c.m.c. values obtained with the group of 17 1,4-dihydropyridines and 0.05 M and 0.08 M CHES buffers (pH = 10).

Table 2

Critical Micelle Concentration for SDS Calculated from 1,4-Dihydropiridines Capacity Factor Data in Different Electrolyte Solutions by MEKC

Compound	c.m.c. (0.05 M CHES)	c.m.c. (0.08 M CHES)
1	$3.22\ 10^{-3}$	$2.31\ 10^{-3}$
2	$3.17\ 10^{-3}$	$2.10\ 10^{-3}$
3	$3.88\ 10^{-3}$	$2.27\ 10^{-3}$
4	$4.04\ 10^{-3}$	$1.73\ 10^{-3}$
5	$4.77\ 10^{-3}$	$1.81\ 10^{-3}$
6	$1.46\ 10^{-3}$	$2.33\ 10^{-3}$
7	$3.91\ 10^{-3}$	$1.54\ 10^{-3}$
8	$4.65\ 10^{-3}$	$1.67\ 10^{-3}$
9	$5.88\ 10^{-3}$	$1.83\ 10^{-3}$
10	$2.98\ 10^{-3}$	$2.21\ 10^{-3}$
11	$4.94\ 10^{-3}$	$1.52\ 10^{-3}$
12	3.6310^{-3}	$2.12\ 10^{-3}$
13	$2.97\ 10^{-3}$	$2.21\ 10^{-3}$
14	$6.90\ 10^{-3}$	$1.87\ 10^{-3}$
15	$3.18\ 10^{-3}$	$2.03\ 10^{-3}$
16	$3.22\ 10^{-3}$	$1.31\ 10^{-3}$
17	$5.96\ 10^{-3}$	$2.01\ 10^{-3}$
c.m.c. $\pm\ \sigma_{N-1}$	$4.05\ 10^{-3} \pm 1.35\ 10^{-3}$	$1.93\ 10^{-3} \pm 3.06\ 10^{-4}$

From these tables, it can be observed that all solutes provide similar SDS c.m.c. values for a given buffer, being the highest standard deviation obtained corresponding to the lowest CHES concentration (0.05 M); this is true for the benzene and naphthalenes derivatives as well as for the group of 1,4-dihydropyridines. This result can be observed in Figure 3 which shows the box plot for the SDS c.m.c. values obtained with the two groups of compounds studied in the different experimental conditions.

The box plot is defined in terms of percentiles and gives a quick overview of the median and spread of the data, and also the mean, minimum, and maximum values for the variable studied. The length of the upper and lower lines pertaining to the box shows how stretched the tails of the distribution are.

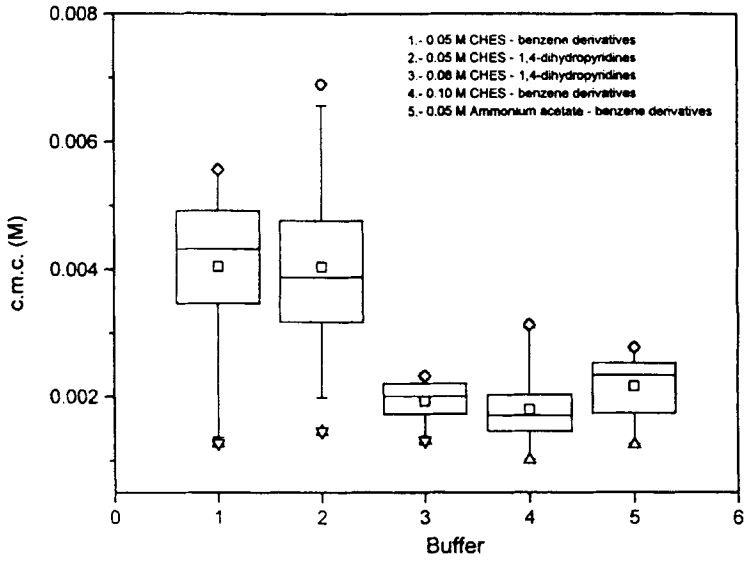


Figure 3. Box plot for the SDS c.m.c. values obtained with the two groups of compounds studied (benzene and naphthalene derivatives and 1,4-dihydropyridines) in different experimental conditions.

All c.m.c. average values obtained for SDS micellar systems were lower than the c.m.c. of this micellar system in pure water ($8 \cdot 10^{-3}$ M),[10] and also lower than the c.m.c. of SDS obtained in a 0.005 M borax buffer ($5.29 \cdot 10^{-3}$ M), by using a MEKC method (variation of the effective electrophoretic mobility of a neutral compound as a function of the total concentration of surfactant in solution).[6] This could be expected because the introduction of a salt in a micellar medium generally decreases the c.m.c. value.[11] Good agreement was obtained for the c.m.c. average value obtained for the same buffer (0.05 M CHES (pH =10)) and the two different groups of compounds studied. Values were statistically similar; Wilcoxon test, prob. 0.8589 for the 11 benzene and naphthalenes derivatives and 1,4-dihydropyridines numbers 1-11.

Figure 3 also shows that the c.m.c. for SDS decreases when increasing the buffer concentration in solution (0.05 M, 0.08 M and 0.10 M CHES buffers). Values were statistically different when comparing 0.05 M and 0.08 M CHES (Wilcoxon test, prob. 0.0044) and when comparing 0.05 M and 0.10 M CHES (Wilcoxon test, prob. 0.0044); values were statistically similar when comparing 0.08 M and 0.10 M CHES for the 11 benzene and naphthalene derivatives and 1,4-dihydropyridines numbers 1-11 (Wilcoxon test, prob. 0.3739).

When comparing the c.m.c. values obtained for a CHES (pH =10) and an Acetate buffer (pH =9) at the same concentration (0.05 M), it can be observed that a minor value is obtained for this last buffer being statistically significantly different (Wilcoxon test, prob. 0.0058).

The c.m.c. value obtained for SDS in a 0.10 M CHES buffer was close to that measured by a spectrophotometric method, which gave a value of 3 10^{-3} M.[12] A similar value was also obtained when the c.m.c. was measured by a conductrimetric method in the presence of another organic buffer (N,N'-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid) at a 0.10 M concentration (pH=7) (3.1 10^{-3} M).[13]

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