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Critical micelle concentration of surfactants in aqueous buffered and unbuffered systems

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Abstract

Critical micelle concentration (CMC) of sodium dodecyl sulphate (SDS), lithium perfluorooctanesulfonate (LPFOS), hexadecyltrimethylammonium bromide (HTAB), tetradecyltrimethylammonium bromide (TTAB), and sodium cholate (SC), surfactants commonly used as pseudostationary phases in micellar electrokinetic chromatography (MEKC), have been determined by means of three different methods: MEKC, spectrophotometry, and conductometry. Determinations have been performed in water, and also in different concentrations of phosphate buffer at pH 7.0. CMC values ranging from 8.08 (water) to 1.99 (50 mM phosphate buffer) mM for SDS, from 7.16 (water) to 2,81 (30 mM phosphate buffer) mM for LPFOS, from 3.77 (water) to 1.93 (20 mM phosphate buffer) mM for TTAB, from 0.91 (water) to ∼0.34 (20 mM phosphate buffer) for HTAB, and around 13 mM (20 mM phosphate buffer) for SC, are obtained. The effect of the electrolyte concentration on the CMC, as well as the linear relationship between the electrolyte counter-ion concentration and the CMC are discussed. This linear relationship provides an easy way for users to estimate the CMC of a MEKC system, at a given electrolyte concentration. A comparison between experimental methods, as well as a discussion about the suitability of a given method for the determination of the CMC for a given surfactant system is also provided.
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1. Introduction

Micellar media have been widely used in separation science due to the properties of micelles to dissolve highly hydrophobic analytes, or alter the selectivity of chromatographic systems. Examples of separation techniques related to micellar phases are liquid–liquid extraction, micellar liquid chromatography and micellar electrokinetic chromatography (MEKC). One of the most significant parameters working with micellar phases is the surfactant critical micelle concentration (CMC) i.e. the concentration above which micelles start to form. Many factors such as addition of electrolytes [1–3], buffer pH [4], temperature [5,6], addition of organic modifiers [2,3,7,8], ionic strength of the aqueous solution [5,9,10], presence of additives [11], etc., make this value different from that determined in pure water.

Among the separation techniques, MEKC is one of the most powerful since it allows the separation of mixtures of both ionized and neutral compounds. The separation is achieved due to the different solvation of analytes between the aqueous and micellar phases [9,12,13]. The aqueous phase requires the presence of an electrolyte and, therefore, the CMC of the surfactant in the running solution becomes dependent of the experimental electrolyte concentration. Thus, to select the MEKC working conditions it would be very useful to know the variation of CMC of the commonly used surfactants with the electrolyte concentration.

Moreover, it is well known that a usual way to reverse electro-osmotic flow in capillary zone electrophoresis is the addition of quaternary amines, such as an alkylammonium salt, to the running buffer. These salts are able to form micelles and to be effective in this instance they should be used at

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concentration lower than its CMC in the running solution [9]. Even here it is necessary to know the variation of CMC of these cationic surfactants with the electrolyte concentration of the aqueous solution.

While CMC values of some of the most popular surfactants such as sodium dodecyl sulfate (SDS) can be found in a wide range of conditions, literature shows a lack of data for other useful surfactants such as fluorinated compounds like lithium perfluoro-*n*-octanesulfonate (LPFOS), cationic surfactants or bile salts. In this paper, several surfactants commonly used in MEKC have been selected and its CMC at various phosphate buffer concentrations determined by means of a variety of techniques. Conductometry [2,14–16], spectrophotometry [2,6,14,15] and capillary electrophoresis [15,17–19], two different methodologies for the latter, have been employed. The use of different methods has permitted to obtain complementary and comparative results and allowed a discussion about advantages and disadvantages of each methodology.

As pointed out before, micelles formation mechanism can be highly altered by the addition of electrolytes. Not only the concentration of electrolyte counter-ion is important in this process, but also other factors such as the nature of the counter-ion, and its hydrophobicity, hydrated size, and valence. Several studies show the effect of counter-ions on micellization process [20,21]. In this work we will study the relationship between the electrolyte counter-ion concentration and the CMC for several surfactants.

2. Experimental

2.1. Reagents and chemicals

Sodium dihydrogenphosphate monohydrate (G.R.), disodium hydrogen phosphate (G.R.), sodium hydroxide (G.R.), SDS (>99%), methanol (for chromatography), and 4-nitroanisole (handled with activated charcoal and crystallized from acetone–water) were from Merck. Sodium cholate (SC) (>97%), LPFOS (25% in water), *n*-tetradecyltrimethylammonium bromide (TTAB) (>98%), *n*-hexadecyltrimethylammonium bromide (HTAB) (>99%), naphthalene (>99.7%), anisole (>99%), and 2-nitroanisole (>98%) were from Fluka. 4-Ethylnitrobenzene (>99%), butyrophenone (99%), 2-naphthalenemethanol (99%), chlorobenzene (99.99%), and phenylundecylketone (98%) were from Aldrich. *N*,*N*-diethyl-4-nitroaniline (98%) was from Frinton Laboratories.

2.2. Instrumentation and procedure

For conductometric measurements, a Radiometer CDM83 conductometer with a Radiometer conductivity cell was used. Solutions were kept at $25 \pm 0.1\,^{\circ}C$ using a thermostated cell. Conductivity cell was calibrated measuring by triplicate the conductivity of KCl solutions at different concentrations [22]. Experiments were carried out by adding different amounts of a stock surfactant solution to a determinate volume of buffer and measuring the conductivity. The range of concentrations measured for each surfactant varies in order to obtain enough points before and after the change of slope in the conductivity–surfactant concentration plots.

Spectroscopic measurements were done in a Perkin-Elmer Lambda-19 spectrophotometer, with 10 mm quarz cells (Hellma), electronically thermostated at 25 °C. Data was acquired with a computer connected to the spectrophotometer via serial port. The slit width was 0.2 nm, the scan rate was 60 nm min^{-1}, and the acquisition was every 0.1 nm. A holmium oxide filter was used to calibrate the spectrophotometer. Test solutes were solved in water or aqueous phosphate buffer at pH 7.0, at an appropriate concentration in order to obtain maximum absorbances about 0.5 for the peaks of interest. These probe solutions were used to dissolve the corresponding amount of surfactant to prepare 100 mM (SDS, SC, and LPFOS) and 50 mM (HTAB) surfactant stock solutions. In case of anionic surfactants (SDS, SC, and LPFOS), several solutions at different surfactant concentrations in the range 1–100 mM were prepared by diluting the appropriate volume of the 100 mM stock solution with the corresponding probe solution. In some cases also 150 mM surfactant solutions were separately prepared. In case of the cationic surfactant (HTAB), the range of concentration of the solutions prepared by dilution of the 50 mM stock solution was 0.1–50 mM. All spectra were registered by triplicate [23].

MEKC experiments were performed with a Beckman P/ACE System 5500 with an UV diode array detector. A fused silica capillary (from Polymicro Technologies) of 40 cm of effective length (47 cm total length) × 50 μm i.d. was used. It was conditioned as described in a previous work [24]. Retention measurements were made at 25 °C, +15 kV (anionic surfactants) or −15 kV (cationic surfactant) and detection was at $\lambda = 214$ nm. Separation buffers of several surfactant concentrations were prepared by solving the surfactant in phosphate buffer at pH 7.0. The test solutes were solved in methanol at ca. 100 mg L^{-1} and phenylundecylketone, used as micellar marker, was solved at ca. 1000 mg L^{-1}. All solutions were filtered through a 45 μm nylon syringe filters (Albet). Samples were introduced into the capillary by pressure, at 0.5 p.s.i. during 1 s.

3. Results and discussion

3.1. CMC determination

When the conductivity of solutions with increasing concentration of surfactant is measured, the specific conductivity–surfactant concentration plots show two straight lines with different slope. The first one corresponds to the concentration range below the CMC, when only monomers of surfactant exist in solution. At higher concentrations of surfactant, micelles start to form and a change of slope appears because the conductivity increases in a different manner. The intersection of these two straight lines is taken as the

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