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Comparison of microstructures of microemulsion and swollen micelle in electrokinetic chromatography

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ABSTRACT

Recently, 1-butanol modified MEKC was proven to be similar to MEEKC in separation performance. In the present work, typical microemulsion containing 0.8% n-octane/3.3% SDS/6.6% 1-butanol/20 mM borax buffer and corresponding swollen micelle without n-octane were used to compare their microdroplet structures including hydrodynamic radius, electrokinetic potential ζ and charge density at the hydrodynamic shear surface, as well as microenvironment polarity in the interior of the microdroplets. Three kinds of corticosteroids were separated with MEEKC and 1-butanol modified MEKC to assess their separation performances. The experiment results showed that both microstructure and separation performance in microemulsion and in swollen micelle systems were alike, no matter whether oil phase n-octane was present. The environment polarity in the core of swollen micelle was slightly higher than in the microemulsions, and both of them were higher than in n-octane medium. Furthermore, the influences of SDS and 1-butanol concentration on microstructures were measured in details. Increasing the amount of SDS, hydrodynamic radius decreased in microemulsion but increased in swollen micelle. On the contrary, ζ and shear surface charge density changed in the reverse trends. With increment of 1-butanol concentration, the hydrodynamic radius increased dramatically in microemulsions, whereas decreased slightly in swollen micelle. Even though using n-octane as oil core was not a key factor, microemulsions and swollen micelle as pseudostationary phase in EKC should not be exactly the same.

1. Introduction

Microemulsions are defined as macroscopically homogenous and optically transparent fluids that have more than one liquid phase. They are formed automatically by mixing lipophilic organic solvents, surfactants and/or cosurfactants in aqueous buffers whenever these components are in an appropriate ratio [1–3]. Microemulsions used in microemulsion electrokinetic chromatography (MEEKC) are usually oil dispersed in aqueous buffer by adding surfactants and cosurfactants to lower interfacial tension between oil and water phases. The inner oil cores of microdroplets are used as pseudostationary phase in MEEKC, therefore the neutral analytes would be separated by partitioning between pseudostationary phase and aqueous buffer [4–6]. For charged analytes, they would be isolated depending on their own electrophoresis, electrostatic interaction with charged microemulsion droplets, and partitioning between pseudostationary phase and surrounding phase. Compared with micelle in micellar electrokinetic chromatography (MEKC) [7], microemulsions have bigger oil cores, more adjustable parameters such as type and concentration of oil and cosurfactant, larger solubilization capacity for highly hydrophobic analytes, therefore MEEKC would provide better selectivity, higher separation efficiency, and could be more suitable to separate water-soluble and fat-soluble compounds simultaneously [8–13]. However, lack of stability may be the biggest problem, since microemulsions would demulsify easily due to dilution with water or addition of excessive amounts of organic solvent. In fact, it is restricted to vary composition of microemulsion to improve the selectivity in MEEKC.

Organic solvents such as 1-butanol, isopropanol, acetonitrile and methanol had been added to sodium dodecyl sulfate (SDS) micelle to improve MEKC separation selectivity by optimizing mass distribution ratio of analytes [14]. It was referred to as solvent modified micelle, or swollen micelle. Recently, 1-butanol modified MEKC was proven to be similar to MEEKC in performance with respect to both separation selectivity and separation efficiency [15–21]. Wen [22] had compared MEEKC with solvent modified MEKC on rapid separation of heroin, amphetamine and their basic impurities. Microemulsions composed of 0.9% n-octane/3.3% SDS/6.0% 1-butanol/89.8% 5 mM borax pH9.5 and swollen micelle

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containing 3.3% SDS/5.7% 1-butanol/91.0% 5 mM borax pH9.5 used as separation carriers were compared, the results showed that 17 analytes were separated within 10 min in two systems, and elution orders were also the same. They demonstrated that the inner n-octane organic phase in MEEKC greatly improved the separation resolutions at relative low concentrations of 1-butanol. However, the differences of MEEKC and 1-butanol modified MEKC on separation efficiency became insignificant at high concentrations of 1-butanol. Hansen [23] published a paper entitled "Microemulsion electrokinetic chromatography or solvent-modified micellar electrokinetic chromatography?" He pointed out that solvent-modified MEKC might provide most of the same advantages in selectivity tuning and high separation efficiency without the problem of the possible lack of stability of the microemulsions. In our previous work [24], it was found that variation of type and content of inner oil phase at low concentration had minor influences either on dimension and ζ of microemulsion droplets, or on separation selectivity and efficiency. It appeared whether the lipophilic organic solvents were present in separation carrier was indifferent for separation performance. Did it imply that the microdroplets microstructures were similar whether the lipophilic organic solvent in microemulsion or not in solvent modified micelle?

Most researchers paid attention to compare MEEKC with solvent modified MEKC on separation selectivity, but few of them emphasized on relationship between microdroplet microstructure and separation performance. Fundamentally, microstructures including dimension, surface charge density and environment polarity of the inner core would determine the separation behaviors of the pseudostationary phase. In our previous work, the data about the hydrodynamic radius and ζ of droplets in typical microemulsion were obtained. The target of the present work was to make clear whether the microstructure of the swollen micelle (the composition same as typical microemulsion but lack of n-octane) were the same as that of microemulsions, and whether the tendencies of the hydrodynamic radius and the charge density of microdroplets in the two systems were identical when SDS or 1-butanol concentration varied. The hydrodynamic radius of the microdroplets was measured with dynamic laser light scattering (DLS), which provided hydrodynamic radius, polydispersity index (PDI) and diffusion coefficient [25]. Though it was impossible to determine the surface charge density directly, charge density at the surface of shear could be calculated based on ζ and hydrodynamic radius of the microdroplet [26]. The vibronic band intensities in pyrene monomer fluorescence could be as a probe to indicate the environment polarity [27], thus the polarity in the inner phase of microdroplet could be valuated by relative fluorescent intensity of the first vibronic band to the third one (I_1/I_3). The larger ratio of I_1/I_3 means the higher environment polarity in the inner core of droplets. By comparison the environment polarity in various media, the composition of the inner phase might be estimated. Depending on that, whether solubilized 1-butanol molecules penetrated to the inner core or inserted in the Stern layer could be speculated.

Prednisone, prednisolone and hydrocortisone are molecular structurally similar corticosteroids, shown in Fig. 1. They could not be separated by conventional MEKC. Kuo and Wu [28] had developed a MEKC method using sodium cholate and sodium deoxycholate for the simultaneous determination of six corticosteroids. Wiedmer [29–31] had separated some corticosteroids by MEKC using a mixed micellar solution of SDS and sodium cholate, buffered with 3-(N-morpholino) propanesulfonic acid or 3-[(l,l-dimethyl-2-hydroxyethyl)amino]-2-hydroxypropane sulfonic acid. Cyclodextrin-modified MEKC had also been used to determine eight corticosteroids [32]. To testify and compare the separation efficiency, the three structurally similar analytes were also separated with typical microemulsions and corresponding swollen micelle as separation carriers in electrokinetic chromatography (EKC), respectively.

2. Experimental

2.1. Chemicals

Prednisone, prednisolone and hydrocortisone were purchased from Anpel Scientific Instrument Co., Ltd. (Shanghai, China). Sodium borate, 1-butanol, n-octane, SDS were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All above reagents and chemicals were of analytical grade and used as received.

2.2. Instruments and measurements

The CE-system was a TH-3000 (Baoding, China) equipped with an UV detector and a temperature control device. A 75 cm × 50 μm i.d. un-coated fused silica capillary (Yongnian Photoconductive Fiber Factory, China) was utilized with an effective length of 66 cm. All separation was carried out with a voltage of 20 kV at 20 °C. Between two runs, the capillary was flushed with water, 0.1 M NaOH, and the running buffer for 5 min, each. Samples were injected electrokinetically with a voltage of 20 kV for 3 s. The UV detection wavelength was set at 250 nm.

The hydrodynamic radius of microdroplet was measured on ALV-/DLS/SLS-5022F laser light scattering system (ALV Company, German), equipped with a Ne–He laser at 632.8 nm and a optical detector using a near single mode fiber optical detection system. Light scattering strength was determined at the angle of 90°, and the temperature was maintained at 25 °C during measurement. Viscosity of these solutions was determined with ubbelohde viscometer. Refractive index was measured with Abbemat. Then the data was processed by ALV-WinAlign software to obtain the average hydrodynamic radius.

Microdroplet ζ was determined by ZETASIZER 2000 (Malvern Instruments Ltd., UK). 5 ml of solution was injected into sample cell, then the experiment was performed at 25 °C in replicates of five for every sample. ζ was obtained according to Helmholtz-Smoluckowski equation, and the data were corrected by determining viscosity and dielectric constant of these solution.

Pyrene fluorescence spectrum was measured on RF-5301PC (Shimazu, Japan). Saturated pyrene solution (about 10^{-7} mol l^{-1}) was prepared with triple-distilled water. Microemulsions and swollen micelle were prepared by adding appropriate content of SDS, 1-butanol, and/or n-octane, sodium borate, and diluting with saturated solution of pyrene. Then the mixture solution was sonicated for 15 min and kept overnight. Pyrene fluorescence was obtained at excitation wavelength of 335 nm, and both excitation and emission slit width set at 3.0 nm. The ratio of the first emission peak height to the third one (I_1/I_3) was tested to value the environment polarity of the inner core in microemulsions and swollen micelle.

2.3. Preparation of microemulsions and swollen micelle

The typical microemulsions as MEEKC running buffer were prepared by weighing 1.65 g SDS, 3.3 g 1-butanol and 0.4 g n-octane to a 50 ml volumetric flask, then 20 mM borax buffer (pH 9.2) was added until to 50 ml in volume. The mixture was sonicated for 30 min to obtain optically transparent and highly stable microemulsions. The swollen micelle was prepared in the same procedures as above, but no n-octane added. During the one-factor effect experiment, only one kind of component altered in a narrow range to ensure their stability, the other components were constant. All solutions were

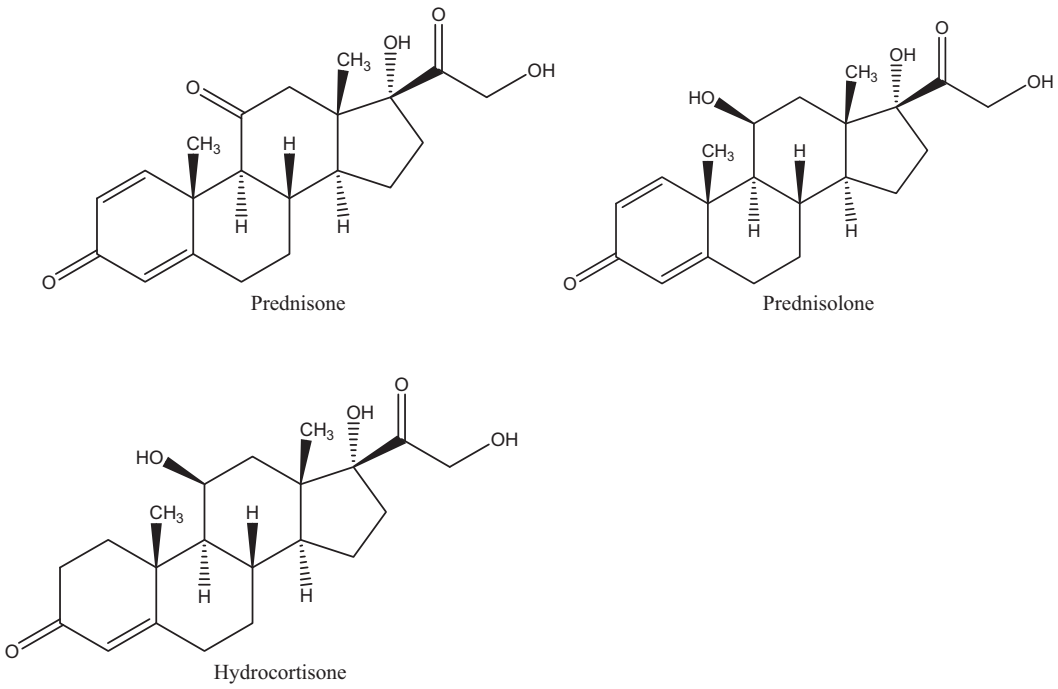

Fig. 1. Molecular structures of prednisone, prednisolone and hydrocortisone.

filtered through a 0.45 μm filter and degassed in an ultrasonic bath prior to use.

2.4. Preparation of standard solutions

Standard stock solutions of prednisone, prednisolone and hydrocortisone were prepared in methanol and all of them were 2.5 mg ml^{-1}. The standard solutions of various concentrations were prepared by appropriately diluting the stock solutions with the running buffer and stirred ultrasonically for 5 min before injection.

3. Results and discussion

3.1. Effect of surfactant concentration

In this experiment, the SDS concentration changed in the range of 2.4–4.6%, but the other composition remained. As SDS concentration reduced below than 2.0%, microemulsion became turbid. On the other hand, SDS higher than 4.6% did not make sense in MEEKC, because larger electrophoresis current generated too much joule heat resulting in poor separation efficiency, and the migration time was too long resulting from too large mass distribution ratio. As shown in Fig. 2A, the hydrodynamic radius of swollen micelle were between 90 nm and 110 nm, whereas that of typical micelle is less than 10 nm. It was demonstrated that a large amount of 1-butanol might be solubilized into the micelle. Notably, they were even larger than corresponding microemulsion. With the increase of surfactant concentration, the hydrodynamic radius of microdroplets in swollen micelle became larger; in contrast, microemulsions system had a decreasing trend. In microemulsions, though the content of oil was unchanged in the experiment, added surfactant molecules still should be arranged at the surface of the oil cores. The smaller size and the more number of droplets could enhance specific surface area. Therefore, the droplet size became smaller as increase of SDS concentration. Unlike microemulsions, there was no oil phase in the inner core of micelle. When a large amount of 1-butanol molecules were solubilized into the micelle, they might enter in palisade layer, even permeate into the inner core to swell micelle. In general, 1-butanol content was always excessive, a part of 1-butanol molecules were still outside of the swollen micelle. The remaining portion of 1-butanol had opportunity to swell micelle further as increasing SDS concentration. PDI were also obtained by DLS measurement, shown in Fig. 2B. In microemulsion, PDI were lower than 0.2 except as SDS of 2.4%, indicating that the particle size distribution fell within a narrow range of sizes. With increasing SDS, PDI became smaller, microemulsion system was more stable. Unexpected, in swollen micelle, PDI were larger than 0.3 in the experimental range. From this viewpoint, swollen micelle would not be more stable than microemulsion.

Calculation of ζ from measurement of electrophoretic mobility chooses Helmholtz-Smoluckowski equation, which is valid only when $\kappa a > 100$ (κ = Debye–Hückle parameter and a = particle radius) [33,34]. As experimental results show, hydrodynamic radius of microdroplets both in microemulsion and swollen micelle are approximate 100 nm. In EKC, electrolyte concentration is also high, compressed electric double layer results in very small value of κ^{-1}. So, both two systems used in EKC would accord with the requirement of Helmholtz-Smoluckowski equation. From hydrodynamic radius and ζ, electric charge density at the surface of shear could be calculated with empirical formula [26].

$$\sigma_s = -\varepsilon_r \varepsilon_0 \frac{d\psi}{dx} = \frac{\varepsilon_r \varepsilon_0 \kappa k T}{e} I$$

$$\kappa = \left(\frac{2ne^2}{\varepsilon_r \varepsilon_0 kT}\right)^{1/2} \quad I = 2\sin h\left(\frac{y_s}{2}\right) + \frac{4}{A}\tan h\left(\frac{y_s}{4}\right)$$

$$A = \kappa a \quad y_s = \frac{e\xi}{kT}$$

Where σ_s is the charge density at the surface of shear, ε_r is the relative permittivity of the solution, ε_0 is the relative permittivity of a vacuum, e is the elementary electric charge, k is the Boltzmann constant, T is the absolute temperature, n is the electrolyte concentration, and ζ is the electrokinetic potential at the surface of shear.

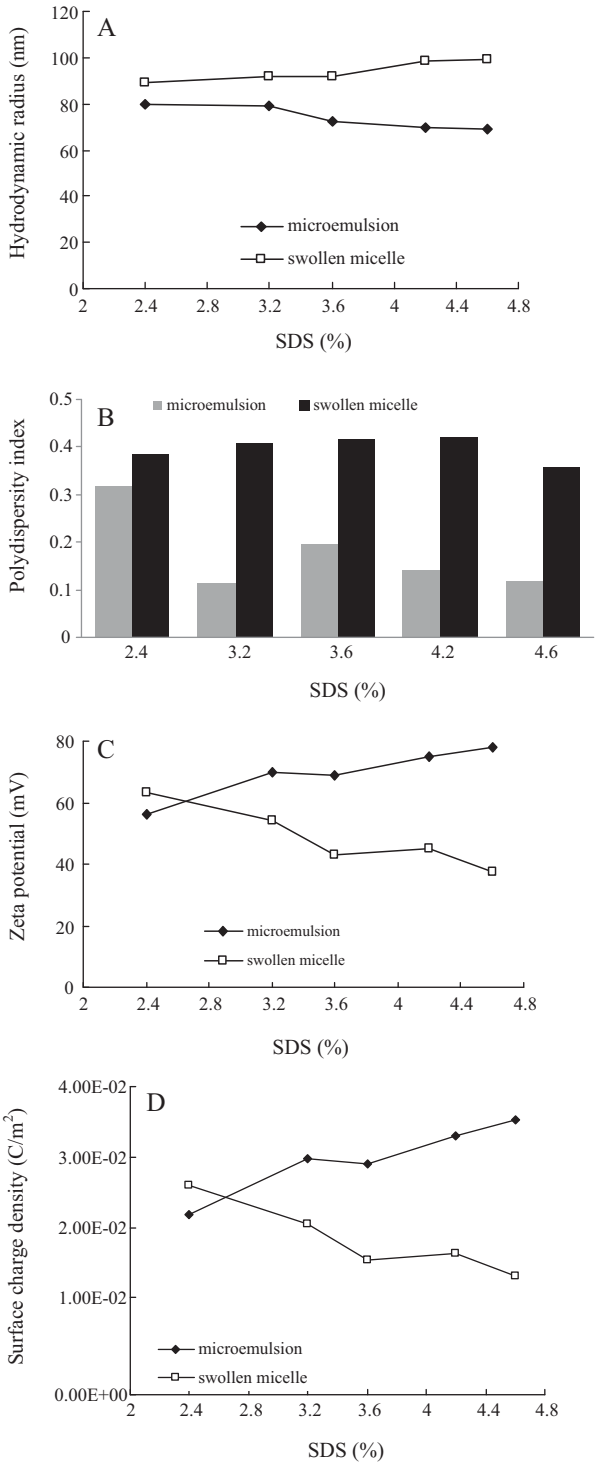

Fig. 2. Effect of SDS concentration on the microdroplet hydrodynamic radius (A), polydispersity index (B), ζ (C) and charge density at the surface of shear (D). The microemulsions comprised 6.6% 1-butanol, 0.8% n-octane and appropriate amount of SDS in 20 mM borax buffer pH 9.2, the swollen micelles were the same composition as the microemulsion but lack of n-octane.

On the contrary, ζ enlarged in micreoemulsion but lessened in swollen micelle with increasing SDS, shown in Fig. 2C. Charge density at the surface of shear had the same trends in Fig. 2D. In microemulsions, with increase of SDS, hydrodynamic radius of microdroplet reduced, the aggregation number of surfactant at the surface would correspondingly lessen due to electrostatic repulsion between SDS molecules. However, charge density at the surface of shear increased. Since negative charge was contributed from SDS, it indicated that density of surfactant molecules arranged at the microdroplets surface increased. The structure of droplets in microemulsion became more firm. On the other hand, in swollen micelle, the size of droplet enlarged with increase of SDS, more 1-butanol molecules enter the micelle, which inserted between SDS molecules, reduced shear surface charge density.

As we could see, swollen micelle had much larger hydrodynamic radius and lower ζ than typical micelle. Compared with conventional micelle, swollen micelle had much looser structures. As pseudostationary phase in MEKC, the looser structures were beneficial to faster mass transfer of analytes between pseudostationary phase and surrounding phase, which was helpful to improve separation efficiency. The larger hydrodynamic radius of microdroplets would increase the phase ratio of pseudostationary phase volume to elution phase volume, therefore the mass distribution ratio accordingly was larger. Notably, 1-butanol remaining in aqueous buffer altered the polarity of elution phase, partition coefficients were also changed. Therefore, it was concluded that solvent modified MEKC would be of better selectivity and higher separation efficiency than conventional MEKC. In view of the similar microstructures between swollen micelle and microemulsions, solvent modified MEKC and MEEKC should have equivalent separation performances.

Remarkably, as SDS concentration was 3.3%, hydrodynamic radius and ζ in both swollen micelle and microemulsions were extremely alike. The facts interpreted why the separation performances in 1-butanol modified MEKC and in MEEKC were extremely similar in Hansen [23] and Luo [22] reports.

3.2. Effect of 1-butanol concentration

In this experiment, the SDS concentration fixed at 3.3%, the 1-butanol concentration varied from 2% to 10%. Beyond this range, the microemulsions and micelle might be unstable. Fig. 3A shows that with increase of 1-butanol concentration, hydrodynamic radius of the droplets increased in microemulsions, while decreased slightly in swollen micelle. In microemulsions, 1-butanol as cosurfactant mainly existed in the palisade layer to adjust the spontaneous curvature of the film to a negative value. But with an increase of co-surfactant, part of them might penetrate into the oil core to swell the droplet. Whereas in swollen micelle, only part of 1-butanol could penetrate to micelle, most of them remained in the surrounding aqueous phase. Since the content of 1-butanol was already saturated, added 1-butanol would not enlarge the micelle since SDS concentration fixed. PDI varied with increasing 1-butanol content in both systems were shown in 3B. PDI in microemulsion were also smaller than their corresponding swollen micelle. It was noticed that PDI became lessen with increase of butanol content. Enhanced butanol content seemed to be helpful to micelle stability. However as the content of 1-butanol was larger than 10%, the droplet was too small to be detectable. It was assumed the swollen micelle would be broken because too much 1-butanol entered into micelle.

As shown in Fig. 3C and D, ζ and charge density at the surface of shear were almost the same as 1-butanol concentration between 4% and 6% in both systems. As 1-butanol concentration larger than 6%, ζ and charge density increased in swollen micelle. In microemulsion, ζ also increased and were the same as 1-butanol amount of 8% and 10% In brief, ζ and shear surface charge density was higher in microemulsion than in swollen micelle.

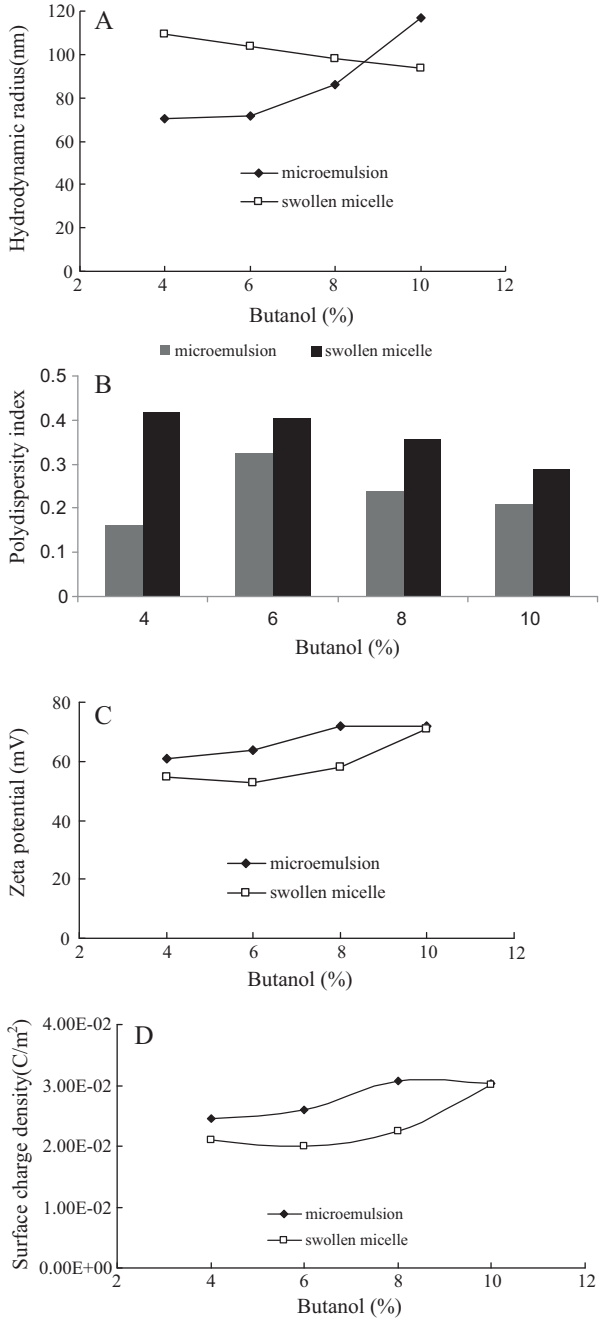

Fig. 3. Effect of 1-butanol concentration on the microdroplet hydrodynamic radius (A) polydispersity index (B), ζ (C) and charge density at the surface of shear (D). The microemulsion comprised 3.3% SDS, 0.8% n-octane and appropriate amount of 1-butanol in 20 mM borax buffer pH 9.2.

3.3. Comparison environment polarity between microemulsions and swollen micelle

A key difference between MEEKC and MEKC is that there is an oil core in a microemulsion droplet. As 1-butanol molecules are solubilized into the micelle, whether could they enter to the inner core or insert between SDS molecules in palisade layer? To make clear where 1-butanol is located in micelle, the environment polarity of swollen micelle, as well as typical microemulsions was investigated by determining pyrene fluorescence spectrum shown in Fig. 4. Further, fluorescence spectrums of pyrene in various media were also measured and the values of I_1/I_3 were calculated. As shown in Table 1, I_1/I_3 was the lowest in lipophilic solvent of n-octane, and it

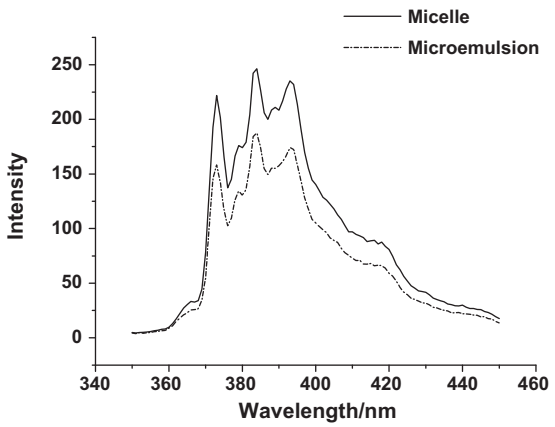

Fig. 4. Fluorescence spectrums of pyrene in microemulsion and swollen micelle. The composition of microemulsion and swollen micelle were the same as in Fig. 3, but 1-butanol was 6.6%. Fluorescence determination conditions: excitation wavelength of 335 nm; both excitation and emission slit width of 3.0 nm.

was the highest in water. In microemulsions, I_1/I_3 was 0.840, larger than in n-octane, which indicated that the environment polarity in the inner core was higher than in n-octane medium. Whether did it imply that part of 1-butanol molecules could pass through the barrier, formed by SDS and 1-butanol molecules to lower interfacial tension between the inner oil phase and outside aqueous phase, and penetrate into the inner core? If it was true, the inner phase consisted of n-octane and 1-butanol in microemulsions. Since I_1/I_3 was 0.897 in swollen micelle, larger than in microemulsion, it was assumed that in swollen micelle, 1-butanol not only located in the palisade layer, but also permeated the inner section. In other words, there was an inner core formed by 1-butanol molecules in swollen micelle, where polar head (hydroxyl group) was inward and hydrophobic alkyl chain was outward.

At relative high concentration of 1-butanol, a part of 1-butanol molecules might penetrate into the inner core. Compared with a small quantity of n-octane in microemulsions, 1-butanol might be the dominating component in the inner core. It was easily understood why the lipophilic solvent has insignificant effect on separation performance in MEEKC and microemulsion microstructure, and why MEEKC and 1-butanol modified MEKC had similar separation efficiency whether lipophilic solvent was present in the running buffer. However, slight differences of environment polarity between microemulsion and swollen micelle might result in subtle distinction in selectivity.

3.4. Comparison of separation performances between MEEKC and 1-butanol modified MEKC

Prednisone, prednisolone and hydrocortisone are molecular structurally similar corticosteroids. They could not separated by conventional MEKC with pure aqueous mobile phase. In the present work, they were analyzed with MEEKC with typical microemulsions and corresponding 1-butanol modified MEKC to testify separation performances. The two electropherograms of three analytes were shown in Fig. 5. The elution order, migration time and the resolution between prednisolone and hydrocortisone were simi-

Table 1
The results of fluorescence determination for pyrene in the different media.

Medium	I_1	I_3	I_1/I_3
Water	425.2	252.2	1.686
n-Octane	15.02	25.20	0.596
Microemulsion	161.8	192.4	0.840
Swollen micelle	201.2	224.1	0.897

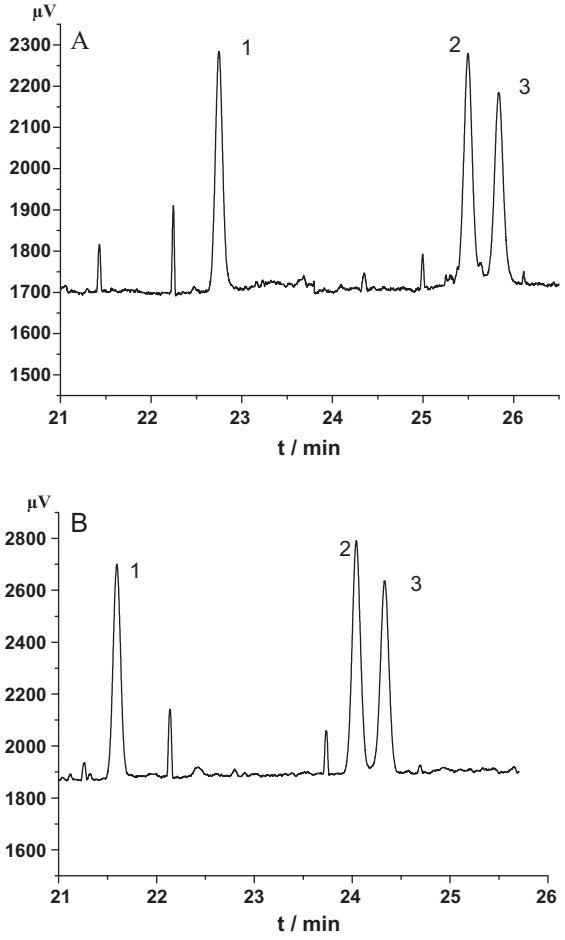

Fig. 5. Electropherograms of a mixed standard solution with MEEKC (A) and 1-butanol modified MEKC (B). The composition of microemulsion and swollen micelle were the same as in Fig. 4. The separation conditions were as follows: 75 cm(effective length 66 cm) × 50 μm i.d. un-coated fused silica capillary; separation voltage: 20 kV; electrokinetically injection: 3 s/20 kV; detection wavelength: 250 nm; capillary temperature: 20 °C; the concentration for three analytes: 10 μg ml^{-1}; the peak identification: 1, prednisone; 2, hydrocortisone; 3, prednisolone.

lar. From above experiment, it was known that pseudostationary phase had bigger hydrodynamic radius and lower charge density at the surface of shear in swollen micelle than in microemulsion, the carrier in swollen micelle should migrate more rapidly than in microemulsion. Thus, the migration time of the analytes was somewhat shorter in MEKC than MEEKC. The results were in agreement with the previous reported work, and also confirmed our experimental results that whether n-octane was present, the droplet microstructures were almost alike at 3.3% SDS and 6.6% 1-butanol.

4. Conclusions

Based on experimental results, four important viewpoints were pointed out in the present work. Firstly, the microemulsion and corresponding swollen micelle have extremely similar hydrodynamic radius, ζ and surface charge density of microdroplets at 3.3% SDS and 6.6% 1-butanol, the most commonly used microemulsions used in MEEKC. The same microstructures of pseudostationary phase would clearly account for the extremely similar separation performances between MEEKC and solvent modified MEKC, reported in previous work and confirmed in the present work. Secondly, though the influences of SDS and 1-butanol concentration on ζ were similar in two systems, the effects on the hydrodynamic radius had dramatically different trends. It revealed that even though n-octane as oil core was not a key factor, microemulsion and swollen micelle as pseudostationary phase in EKC should not be the exactly same. Thirdly, from the experimental results of PDI, swollen micelle would not be more stable than microemulsion. Lastly, the environment polarity in the inner of droplets in both systems was higher than in n-octane, it was speculated that 1-butanol molecules might penetrate into the inner core either in microemulsions or in swollen micelle. In conclusion, solvent-modified MEKC might have the same advantages in selectivity tuning and high separation efficiency as MEEKC.

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