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Vesicles formed by mixed catanionic surfactants as novel pseudostationary phase in electrokinetic chromatography

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ABSTRACT

In this paper, a novel pseudostationary phase (PSP), the vesicle formed from octyltriethylammonium bromide (C_8NE_3Br) and sodium dodecyl benzene sulfonate (SDBS), has been developed in electrokinetic chromatography (EKC). Physicochemical parameters of the mixture of catanionic surfactants such as ζ potential and size of the aggregates were characterized as the molar ratio of C_8NE_3Br to SDBS varied from 2:8 to 8:2 and total concentration of surfactants fixed at 20 mM. At any ratio mentioned above, ζ potential of mixture of catanionic surfactants remained negative. The absolute values of ζ potential were even larger than in only SDBS system as the molar ratio of C_8NE_3Br to SDBS less than 4:6, and they decreased as increasing the ratio of cationic surfactants. The size of the aggregates became smaller as the ratio was close to 1. Unexpectedly, the size was smallest at ratio of 3:7 and 6:4, instead of at 5:5. Notably, coagulation did not occur in the catanionic system at any proportion of each other. TEM testified the formation of vesicles. The performance of the vesicle as PSP was evaluated by separating eight kinds of corticosteroids with EKC, these analytes were separated completely without any additives. Compared with SDS microemulsion modified with ionic liquid (IL) and polymeric micelle, the novel vesicle PSP had better separation performances.

1. Introduction

Vesicle is one of the amphiphilic molecule aggregates which has a spherical structure, with an internal cavity surrounded by one or more bilayers, like cell membrane. Vesicles have a variety of application in biological modeling [1], pharmaceutical packaging, targeted release [2–4], nanoparticle synthesis [5,6], as well as micro reactor [7]. A typical kind of vesicle, composed of natural lecithin, is referred to as liposome. Normally, liposome is always prepared with the help of external force such as sonication [8,9]. Vesicles could also be self-assembled spontaneously by surfactants with appropriate structures [10,11]. Packing parameter model introduced by Israelachvili [12] indicated that the morphology of surfactant aggregates in aqueous solutions could be predicted by the geometries of the surfactants and characterized by packing parameter P. $P = V/l_c a_o$, where V is the volume of the surfactant hydrophobic chain, l_c is the chain length of the surfactant, and a_o is the average cross sectional area of hydrophilic head group in closely packed monolayer. It is easy to form spherical micelle as P less than 1/3, and rod-like micelle as P between 1/3 and 1/2. If P is between 1/2 and 1, it tends to form the vesicle. The double layer structure is formed as P close to 1. If P is larger than 1, it is prone to form the reverse phase structure. According to the model, surfactants with two-tails hydrophobic chains, such as bis (2-ethylhexyl) sodium sulfosuccinate (AOT) [13], could formed vesicle spontaneously, since two-tails hydrophobic chain makes V enlarge and P lies between 1/2 and 1. Therefore, the formation of vesicles from surfactants attracted the wide attentions of the researchers because of spontaneity and vesicle stability.

The so-called "catanionic surfactants" is the mixtures of anionic and cationic surfactants in aqueous phase. This term was first used by Jokela in 1987 [14], and since then the number of articles published on catanionic mixtures has increased [15–18]. Vesicle formed from oppositely charged surfactants was reported by Kaler in 1989 [19]. He developed phase diagrams of *n*-dodecyltrimethylammonium (DTAB)/sodium dodecyl sulfate (SDS) [20] and cetyltrimethylammonium bromide (CTAB)/sodium *n*-octyl sulfate (SOS) [21] systems. Later, vesicles formed from oppositely charged surfactants as pseudostationary phase (PSP) in vesicle electrokinetic chromatography (VEKC) was first introduced

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by Hong et al. [22]. Chromatographic characteristics of DTAB/SDS vesicles, DTAB/SDS mixed micelle, and SDS micelle as PSPs were examined and compared. It was found that the spontaneous vesicles could provide better efficiency and selectivity, as well as a longer elution window in particular. CTAB/SOS vesicle was also selected as PSP by Razak to assess the hydrophobicity of 29 kinds of neutral and charged substances with EKC [23]. Klotz et al. [24] also used CTAB/SOS vesicle and AOT as PSPs for indirect measurement of octanol-water partition coefficients by separating a series of small organic molecules with varying functional groups. Similarly, with the advantage of the CTAB/SOS system possession of much larger stable vesicle region, CTAB/SOS vesicle at the molar ratio of CTAB to SOS of 3:7, an excess of the anionic surfactant SOS, was selected as PSP in EKC by Pascoe [25]. He also chose another three kinds of vesicles including the octyltrimethylammonium (OTAB)/SDS vesicles with an excess of the cationic surfactant OTAB, the double-tailed surfactant AOT vesicle and the phospholipid vesicle made by 1-palmitoyl-2-oleyl-*sn*-glycero-3-phosphocholine/phosphatidyl serine (POPC/PS) as PSPs in capillary electrophoresis. The differences among these four vesicular systems, and comparison between vesicular systems and typical SDS micellar system were investigated through evaluation of electrophoretic and chromatographic parameters, as well as linear solvation energy relationship (LSER) analysis. Recently, VEKC tends to be applied in chiral separation [26–28], pharmaceutical analysis [29–31], *etc*. Many experts are devoted to developing a novel surfactant mixing system possessing a larger vesicleregion. Catanionic surfactants system possesses much larger surface activity than individual component on account of the strong synergistic effect. The strong interaction comes from the hydrophobic effects between hydrocarbon tails and the electrostatic attractions among oppositely charged head groups, which results in extremely compact structure and huge aggregation number. Nevertheless, precipitates appear inevitably at certain range of mixing ratio between two surfactants, which is an obstacle to limit their application in capillary electrophoresis. In order to figure out this problem, we have developed a novel catanionic surfactant vesicle system—octyltriethylammonium bromide/dodecyl benzene sulfonate (C_8NE_3Br/SDBS). None of agglomeration phenomena appear while mixing cationic and anionic surfactants at any molar ratio. Furthermore, we have tried to use this vesicle system as PSP to separate 8 kinds of corticosteroids.

HPLC [32], HPLC-ESI-MS [33], GC-MS [34], and LC-MS/MS [35–37] had been used to detect corticosteroids. However, there exists some problem such as complicated pretreatment, high expense, time-consuming and trouble-operating. Recently, EKC was utilized to separate these corticosteroids. Wiedmer [38] used lipsome as PSP in EKC to separate 6 corticosteroids (1-dehydroaldosterone, cortisone, cortisol, 21-deocycortisol, 11-deoxycortisol and dexamethasone). Pomponio et al. [39] tried to alter the types and concentrations of surfactants, add non-ionic surfactant, and choose β-cyclodextrin (β-CD) as an additive to establish the optimum microemulsion system to obtain a baseline separation of six corticosteroids (prednisolone acetate, hydrocortisone acetate, cortisone acetate, prednisolone, hydrocortisone and cortisone). Wu et al. [40] also reported the successful separation of these six corticosteroids with the microemulsion. However, it took a longer analysis time. Our group also used microemulsion modified with ionic liquid (IL) [41] or amphiphilic polymer [42] as PSPs for the separation of seven or eight corticosteroids. In our present work, most common used eight structurally similar corticosteroids including prednisone, hydrocortisone, prednisolone, hydrocortisone acetate, prednisolone acetate, dexamethasone, cortisone acetate and triamcinolone acetonide (their molecular structures shown in Fig. 1) were separated using the novel vesicle as PSP. Furthermore, comparison among microemulsion modified with IL, amphiphilic polymer micelle, and the novel vesicle as PSP was conducted through separation of these eight corticosteroids with EKC.

2. Experimental

2.1. Materials

SDBS and sodium borate were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Prednisone, hydrocortisone, prednisolone, hydrocortisone acetate, prednisolone acetate, dexamethasone, cortisone acetate, and triamcinolone acetonide were purchased from Anpel Scientific Instrument Co, Ltd. (Shanghai, China). Decanophenone were purchased from J&K scientific (Shanghai, China). All above materials were of analytical grade. C_8NE_3Br was synthesized according to the reference [43].

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 65 cm × 50 μm i.d. un-coated fused silica capillary (Yongnian Photoconductive Fiber Factory, China) was utilized with an effective length of 50 cm. Samples were injected electrokinetically with a voltage of 20 kV for 3 s. The applied voltage was 10 kV. All experiments were performed at 25°C.The new capillary was flushed with 1 M HCl for 1 h, deionized water for 10 min, and 1 M NaOH overnight at extremely low rate of 50 μl/h with self-made device. Between two runs, the capillary was flushed, respectively with deionized water, 0.1 M NaOH, deionized water, and the running buffer for 5 min. The UV detection wavelength was set at 250 nm.

ζ potential was determined by NanoBrook ZetaPALS (Brookhaven Instruments Corporation) at ambient temperature. The data was processed by BIC PALS Zeta potential Analyzer software. ζ potentials of catanionic surfactants solutions were obtained according to Helmholtz-Smoluckowski equation. ζ potential of 20 mM SDBS was obtained according to Huckel equation.

The hydrodynamic diameter was measured by DLS with a NanoBrook-90 Plus instrument (Brookhaven Instruments Corporation) at room temperature and the data was processed by BIC Particle Sizing software to obtain the average values.

Transmission electron microscopy (TEM, JEOL JEM-2100) was employed to characterize morphology of the vesicles. A drop of solution was placed on a copper grid and stained with a drop of 2% phosphotungstic acid aqueous solution. The excess solution was removed by blotting with a filter paper.

2.3. Preparation of C8NE3Br/SDBS vesicle solutions

The C_8NE_3Br/SDBS vesicle solutions were prepared by weighing appropriate amounts of C_8NE_3Br and SDBS into a 100 ml volumetric flask, and then dissolved and diluted with 10 mM sodium borate buffer to obtain a total surfactant concentration of 20 mM and ionic strength of 30 mM (pH 9.2). The vesicle solutions were sonicated for 5 min. These solutions were stable for at least 4 weeks at ambient temperature after preparation.

2.4. Preparation of standard solutions

Standard stock solutions of prednisone, hydrocortisone, prednisolone, hydrocortisone acetate, prednisolone acetate, dexamethasone, cortisone acetate, and triamcinolone acetonide were prepared in methanol and all of them were 2 mg/ml. The standard solutions of a series of concentrations were prepared by appropriately diluting the stock solutions with the running buffer.