



Zwitterionic surfactants in ion binding and catalysis



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ABSTRACT

Zwitterionic surfactants have unique properties for applications in separation methods and catalysis. Their properties and efficiencies depend on two main factors: surfactant structure and preferential interactions of zwitterionic surfactant interfaces with anions. Structural changes are related to hydrocarbon chain length, distance between charges, and type and order of functional groups in the polar head. Interactions of anions with zwitterionic micelles follow the Hofmeister series and change the surface charge. The interactions between surfactants and molecules/ions allow the rational control of separation by chromatography and micellar capillary electrophoresis; cloud point extraction; and stabilization and catalytic activity of biomolecules and nanoparticles.

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1. Introduction

Zwitterionic surfactants are amphiphiles with both negative and positive charges (Fig. 1 and Table 1) separated by an interchange or spacer segment, typically a short methylene segment $-(CH_2)_n-$ that results in a large dipole moment, which is not proportional to n because of the interchange spacer flexibility [1,2]. The properties of zwitterionic surfactants can be further tuned by changing their chemical structure. The primary structural changes are: i) the length of the hydrophobic hydrocarbon chain, m ; ii) the number, n , of $-(CH_2)_n-$ groups in the spacer; iii) the polar headgroup structure, which usually contains a positively charged ammonium or imidazolium group and a negatively charged carboxylate, sulfonate, sulfate or phosphate group; and iv) the relative position of the positive and negative charges of the zwitterion [3]. Table 1 lists the classes and structures of the main types of zwitterionic surfactants considered in this article.

An important additional factor that modulates the properties of zwitterionic surfactants in aqueous solution is their interactions with anions. Current studies show that there is preferential incorporation of anions into the interfacial region of zwitterionic micelles, regardless of the position of the positive or negative charges. Specific anion interactions with zwitterionic aggregates follows the Hofmeister series, in which large anions with low charge densities and hydration, such as PF_6^- and ClO_4^- , bind more strongly than small strongly hydrated hydrophilic anions such as OH^- and F^- [4].

Recent applications of zwitterionic surfactants in analytical separations such as ion chromatography and micellar capillary electrophoresis have employed these surfactants for stationary phase modification. The separation is a consequence of preferential hydrophobic or electrostatic interactions of molecules or ions with a surfactant coated stationary phase [5,6,7,8–10].

Similarly, cloud point extraction and structural stabilization of biomolecules, as well as catalytic activity, depend on specific interactions of substrates and/or ions with zwitterionic interfaces [11,12]. Zwitterionic surfactants have been used for the preparation of stable nanoparticles that exhibit high catalytic power [13–17]. Thus, changes in the surfactant structure and the presence of electrolytes make it possible to control the separation, extraction, stabilization and catalytic activities of biomolecules and nanoparticles.

2. Zwitterionic surfactant-based separations

2.1. Zwitterionic ion chromatography

The use of zwitterionic surfactant-modified reverse phase silica HPLC (High Performance Liquid Chromatography) columns allowed the development of a chromatographic method for ion separation based on the preferential incorporation of anions and/or cations on the surfactant-modified layer. Initially, this method was called “electrostatic ion chromatography” (EIC), and later “Zwitterionic Ion Chromatography” (ZIC) [5,6,7,8,18]. Among the advantages of ZIC in relation to conventional ion chromatography (IC) are: i) ideal conditions for conductimetric detection of ions using water as eluent;

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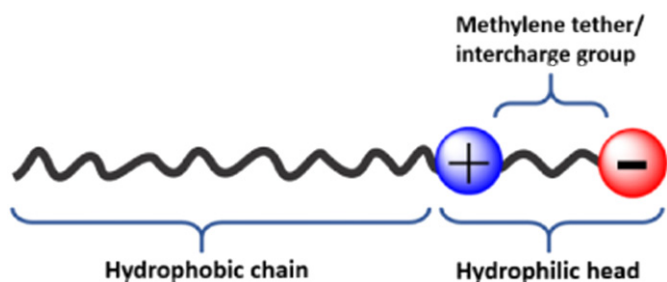


Fig. 1. Schematic representation of a zwitterionic surfactant molecule.

ii) tolerance for high ionic strength and; iii) simultaneous separation of cations and anions [19].

ZIC was initially based on the separation of monovalent inorganic anions using octadecylsilyl (ODS) columns modified with tetradecyldimethylammonium propanesulfonate, SB3-14, as the stationary phase (SP) and electrolyte solutions as the mobile phase. The separation mechanism is related to formation of an electrical double layer (EDL) on the stationary phase (Fig. 2) due to the retention of anions present in the mobile phase close to the positively charged groups of the zwitterionic surfactant and, therefore, forming a net negatively charged EDL. Thus, although anions in the analyte are electrostatically repelled by the anion-binding induced EDL layer [20,21], they also have differing degrees of affinity to the zwitterionic headgroups. As a result, relative anion retentions can be predicted from the binding constants to zwitterionic aggregates and follow the order of increasing ionic size, increasing polarizability and decreasing hydration energy of the anions in the analyte sample [20]. Cation separations follow similar principles and are promoted by interaction of the cations with the negatively charged EDL and depend on the factors discussed below.

Because sulfobetaine surfactants do not separate divalent and other multivalent anions efficiently in ZIC, Hu and co-workers used an ODS column coated with a mixture of a cationic surfactant,

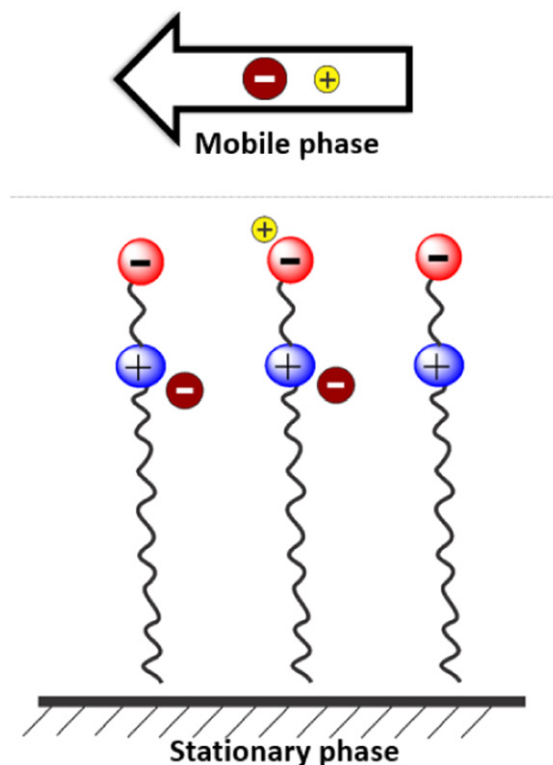


Fig. 2. Schematic model of ion binding in chromatography by zwitterionic surfactants.

e.g., tetradecyltrimethylammonium bromide (TTAB), with a zwitterionic surfactant (SB3-14) as the stationary phase [6]. In the presence of the TTAB/SB3-14 mixture, the interactions of the cations in the analyte are dominated by electrostatics, while the inorganic anions interact with the modified stationary phase by conventional anion exchange [8].

Table 1

Structures of selected zwitterionic surfactants.

Class	Structure	Symbol
Sulfobetaine		SBn-m
Hydroxypropyl Sulfobetaine		HSB3-m
Carboxybetaine		CBn-m
Phosphocoline		PCn-m
Sulfoimidazolium		ImSn-m
Rewoteric AM		CAS U
Amidosulfobetaine		ASB3-m
Amidosulfobetaine		ASHB3-m
Amidosulfobetaine		ASB4-m
Bile salt derivative		CHAPS

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