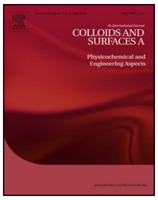
Colloids and Surfaces A: Physicochem. Eng. Aspects 454 (2014) 23–31

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Probing the alkyl chain length effects on molecular packing characteristics of mixed ion pair amphiphile/double-chained cationic surfactant vesicular bilayers with the Langmuir monolayer approach

An-Tsung Kuo, Wei-Ta Li, Chia-Yao Tseng, Fang-Wei Hsiao, Chien-Hsiang Chang*

Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan

HIGHLIGHTS

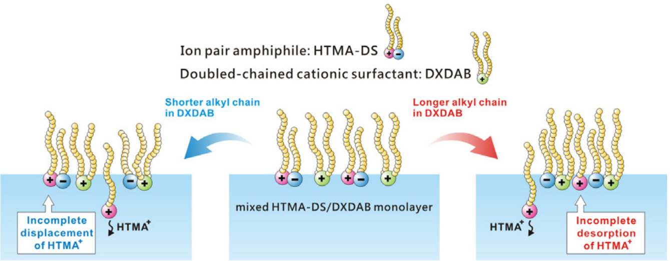
- Mixed layer behavior of ion pair amphiphile and double-chained cationic surfactant.
- Alkyl chain length effects on mixed layer behavior.
- Probing molecular packing characteristics in mixed layers.
- Investigating molecular desorption from mixed layers by infrared spectroscopy.

ARTICLE INFO

Article history:
Received 12 February 2014
Received in revised form 2 April 2014
Accepted 3 April 2014
Available online 13 April 2014

Keywords:
Air/water interface
Brewster angle microscopy
Infrared reflection–absorption spectroscopy
Ion pair amphiphile
Langmuir monolayer

GRAPHICAL ABSTRACT



ABSTRACT

Alkyl chain length effects of added double-chained cationic surfactants, dialkyldimethylammonium bromides (DXDABs), including ditetradecyldimethylammonium bromide (DTDAB), dihexadecyldimethylammonium bromide (DHDAB), and dioctadecyldimethylammonium bromide (DODAB), on the Langmuir monolayer behavior of a pseudodouble-chained ion pair amphiphile, hexadecyltrimethylammonium-dodecylsulfate (HTMA-DS), were analyzed with the Langmuir monolayer technique, infrared reflection–absorption spectroscopy, and Brewster angle microscopy. It was found that DXDA$^+$ of DXDAB could displace HTMA$^+$ from HTMA-DS and the displaced HTMA$^+$ might desorb into the aqueous subphase, with the extent depending on the alkyl chain length of DXDAB. In the mixed HTMA-DS/DODAB monolayer, DODAB possessing long alkyl chains was capable of restraining HTMA$^+$ from desorption with enhanced intermolecular interaction reflected by the favorable molecule aggregation. As for the mixed monolayers of HTMA-DS and DTDAB with short alkyl chains, incomplete displacement of HTMA$^+$ from HTMA-DS by DTDA$^+$ was detected and ascribed to weak intermolecular attraction exhibited by the fractal-like domain formation. Among the three DXDABs, DHDAB with the best molecular structure match to HTMA-DS in terms of alkyl chain length could form well-packed monolayer structures with HTMA-DS. The finding has the implication on the surface characteristic control of catanionic vesicles composed of ion pair amphiphile with double-chained cationic surfactant.

1. Introduction

Vesicles are hollow spheres with bilayered structures. The special structures of vesicles allow both hydrophilic and hydrophobic materials to be encapsulated [1,2]. Thus vesicles, especially the lipid-formed vesicles, or liposomes, have been received much attention as carriers for cosmetic and medical applications [1–5].

---

* Corresponding author. Tel.: +886 6 2757575x62671; fax: +886 6 2344496.
E-mail address: changch@mail.ncku.edu.tw (C.-H. Chang).

http://dx.doi.org/10.1016/j.colsurfa.2014.04.013
0927-7757/

Recently, ion pair amphiphile (IPA) prepared from mixed cationic/anionic surfactants has been developed as a novel material for forming vesicles. A pseudodouble-tailed IPA molecule is structurally similar to a lipid molecule, and it has been demonstrated that IPA molecules could form the so-called catanionic vesicles with proper approaches [6–8]. However, catanionic vesicles formed of IPAs with ultra-sonication and/or high pressure extrusion processes often suffered from poor physical stability. That is the catanionic vesicles prepared by a forced formation approach tended to fuse or aggregate and could not maintain their original sizes in long-term storage [9,10].

The physical stability of vesicles is dependent on physicochemical properties of the vesicles and there are two main strategies to stabilize vesicles. The intra-vesicle stabilization strategy is to modify the molecular packing in vesicular bilayer structures, such as adjusting the alkyl-chain symmetry of components [11–13] or adding additives [14–18]. The other is the inter-vesicle stabilization strategy. By adding ionic surfactants into vesicular bilayers, one can induce electrostatic repulsion between the vesicles and thus improve the vesicle physical stability [19–22].

For the inter-vesicle stabilization strategy, positively charged double-tailed surfactants, dialkyldimethylammonium bromides (DXDABs), have been chosen as the additives to fabricate charged catanionic vesicles composed of an IPA, hexadecyltrimethylammonium-dodecylsulfate (HTMA-DS), and to efficiently improve the vesicle physical stability [23]. However, the electrostatic repulsion between the vesicles induced by added DXDAB was not significantly varied with DXDAB molar fraction and was not the only factor to control the vesicle physical stability. It was found that DXDAB might displace cationic surfactant moiety ($HTMA^+$) to form DXDA-DS, leading to protrusion or dissolution of $HTMA^+$ and thus change of the molecular packing/interaction in the vesicular bilayers [23,24]. That is effects of added DXDAB on the intra-vesicle interaction might dominate the vesicle physical stability.

It is accepted that the Langmuir monolayer is a suitable model to study the molecular packing/interaction in bilayer structures of vesicles [25,26]. The mixed HTMA-DS/dihexadecyldimethylammonium bromide (DHDAB) monolayer behavior has been investigated with the Langmuir trough technique for exploring the intra-vesicle interaction of mixed HTMA-DS/DHDAB vesicles, and the displacement behavior of $HTMA^+$ from HTMA-DS by DHDAB has been demonstrated [27]. However, little was known about the relationship between the alkyl chain length of DXDAB and the displacement behavior of $HTMA^+$ from the IPA, HTMA-DS.

To fully understand the interactions between HTMA-DS and DXDAB with various alkyl chain lengths in a vesicular bilayer, the interfacial behavior of mixed HTMA-DS/DXDAB Langmuir monolayers was analyzed with the Langmuir trough technique. The analysis of surface pressure–area isotherms could provide information on molecular interaction within the monolayers. Infrared reflection–absorption spectroscopy (IRRAS) was adopted to further analyze the alkyl chain length effects of added DXDAB on the HTMA-DS monolayer characteristics. The intensity and wavenumber of antisymmetric methylene stretching vibration (ν_a-CH_2) at ~2920 cm^{-1} for mixed HTMA-DS/DXDAB monolayers were obtained upon monolayer compression. Quantitative reflectance absorbance (RA) analysis was then applied to estimate the loss of free molecules from the monolayers at the interface. In addition, the Brewster angle microscopy (BAM) was used to directly observe the morphology of the Langmuir monolayers at the interface. The influence of molecular structure match between DXDAB and HTMA-DS on the molecular arrangement and interactions within the mixed monolayers was revealed.

2. Experimental

2.1. Materials

Hexadecyltrimethylammonium bromide (HTMAB) (~99%) and sodium dodecylsulfate (SDS) (~99%) were purchased from Sigma, USA. Ditetradecyldimethylammonium bromide (DTDAB), dihexadecyldimethylammonium bromide (DHDAB), and dioctadecyldimethylammonium bromide (DODAB) were obtained from TCI, Japan with a purity of ~98%. Ethanol (99.9% min) and n-hexane (99% min) were spectroscopic grade and were purchased from Riedel-de Haën, Germany and J.T. Baker, USA, respectively. Chloroform of HPLC analytical grade was obtained from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). All the chemicals were used without further purification. Highly pure water obtained from a Milli-Q plus water purification system (Millipore, USA) was used in all experiments. The resistivity and surface tension of the purified water were 18.2 MΩ cm and 72 mN/m, respectively.

The IPA, hexadecyltrimethylammonium-dodecylsulfate (HTMA-DS), was prepared as precipitate by mixing 20 mM HTMAB and 20 mM SDS aqueous solutions with equal volume. The precipitate of IPA was washed with pure water to remove possible counter ions (Br^- and Na^+) and soluble residuals, such as HTMAB and SDS. The IPA has been proven composed of cationic and anionic surfactants in a molar ratio of 1:1 by elemental analysis (EA) [28]. All mixed IPA/DXDAB systems could be dissolved in the mixed solvent of ethanol/n-hexane (1/9, v/v) for surface pressure–area isotherm measurement and in situ Brewster angle microscopy (BAM) observation. For infrared reflection–absorption spectroscopy (IRRAS) measurement, the sample solution was prepared with pure chloroform.

2.2. Methods

A Langmuir trough (type 601BAM, Nima, England), equipped with the Wilhelmy plate accessory for surface pressure measurements, was used to probe the monolayer behavior at the air/water interface. The Wilhelmy plate is made of filter paper (10 mm × 24 mm × 0.15 mm) and was provided by the Langmuir trough manufacturer. Before each run, the Teflon trough (trough size 700 mm × 70 mm) was washed with ethanol and rinsed with purified water. For all the experiments, the trough was filled with purified water as the subphase, and the temperature was maintained at 20 ± 1 °C by an external circulator. A monolayer at the air/water interface of the trough subphase could be symmetrically compressed or expanded with two Teflon barriers at a desired rate. The cleanliness of the water subphase was ensured before each experiment by aspirating the water surface at minimum interfacial area, or trough area (160 mm × 70 mm).

To form a monolayer at the air/water interface, the mixed ethanol/n-hexane (1/9, v/v) solvent containing the monolayer-forming material was spread at the interface and was allowed to evaporate for 20 min. The monolayer at the interface was then compressed by Teflon barriers with a compression rate of 2–3 $Å^2$/molecule-min, and the surface pressure was recorded during the interface compression process. Repeated experiments were performed independently to confirm the reproducibility of the isotherm measurements.

IRRAS experiments were performed by using a PerkinElmer FTIR spectrometer (model Spectrum GX) with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector. IRRAS measurements were made by using a monolayer/grazing angle accessory (P/N 19650 series, Specac Inc.) with a set of removable Teflon Langmuir trough (size 94 mm × 22 mm × 10 mm) and embedded barrier [29]. Unpolarized light from the FTIR spectrometer with an incident angle of 40° from the surface normal [30,31]