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Physico-chemical studies on mixed oppositely charged surfactants: Their uses in the preparation of surfactant ion selective membrane and monolayer behavior at the air water interface

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Abstract

Surfactant ion selective membranes, prepared using different sets of catanionic species, have been found superior to the membranes prepared earlier in terms of sensitivity and durability. The aggregates (or coacervates) of cetyltrimethylammonium (CTA$^+$) ion with dodecylsulfate (DS$^-$), dodecylbenzenesulfonate (DBS$^-$), dioctylsulfosuccinate (AOT$^-$), deoxycholate (DC$^-$), and taurochenodeoxycholate (TCDC$^-$) ions in 1:1 molar ratio were used as the carrier complexes in the membrane for estimating anionic surfactants whereas carrier complexes of DBS$^-$ with CTA$^+$, tetradecyltrimethylammonium (TTA$^+$) and dodecyltrimethylammonium (DTA$^+$) cations (1:1 molar ratio) were employed for estimating the cationic surfactants. Electrochemical behavior of membrane electrodes was, although, not always Nernstian, the cell emf versus log[surfactant] plots were linear with sharp breaks corresponding to the critical micelle concentration (CMC). Film behavior of complex aggregates (coacervates) was studied at the air–water interface by surface pressure (π)–area (A) measurements. Limiting area per molecule, maximum attainable surface pressure, film compressibility, etc., were evaluated from the experimental data. Formation of probe-excluded regions of compressed monolayers, doped with a fluorescent probe (NBD-PC) was observed by epifluorescence microscopy.

Keywords: Surfactant ion-pair (coacervate); Ion-selective membranes; CMC; Monolayer; Epifluorescence microscopy

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1. Introduction

The estimation of surfactants in dilute solution is inconvenient for they do not have concentration dependent sharply changing properties except for surface tension, the measurement of which needs extra care and it is significantly influenced by the presence of additives [1–4]. The method of conductance (relevant to ionic surfactants) becomes insensitive in salt environment [5]. Thus, monitoring of the continued change in surfactant concentration (as in a kinetic process) or its estimation in a dilute solution under equilibrium condition is a matter of concern to chemists and analysts. To obviate this difficulty, surfactant ion-selective membranes were developed and electrochemical method was used to determine the concentration of the constituent ionic surfactants. In this method, a complex of cationic and anionic surfactants (kind of a coacervate) was prepared which was incorporated in the polymer membrane of polyvinyl chloride (PVC) to prepare a membrane electrode reversible with respect to either of the constituent surfactant ions of the complexed ion-pair in terms of electrode potential essentially governed by Nernst equation. Such electrodes have been shown to be potentially useful in physico-chemical works involving ionic surfactants both under stable and dynamic conditions [1–5]. Although the principle described above looks simple, the membranes

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normally prepared using tetrahydrofuran (THF) as the solvent to dissolve PVC required to be always freshly distilled. The functioning of the membrane was found to decline within a short period of time; frequently the prepared membrane did not show any activity at all. The above inconvenient features are needed to be removed, in the development of surfactant ion selective membranes.

The coacervates formed by the interaction of cationic and anionic surfactants are insoluble products and are expected to form insoluble monolayer on water surface. It is known that insoluble monolayers of lipids and surfactants can be considered as model membranes [6–9]. The phospholipids in the cell membrane possess hydrophobic tails [10]. The 1:1 molar complexes (coacervates) of oppositely charged surfactant ion-pairs can be modeled as amphiphiles with more than one hydrocarbon tail (excepting those with DC^-, and AOT^-). They are expected to show surface activity like phospholipids, the integral components of cell membranes. Thus, the monolayer behavior of oppositely charged surfactant ion-pairs would be interesting from the view points of surface morphology and phase transition. So far our knowledge goes monolayer behavior of complexes derived from oppositely charged surfactants has not been done in the past.

In this work, employing coacervates of different catanionics (combinations of cationic and anionic surfactant ion-pairs) we have investigated (1) the formation of active and durable surfactant ion-selective membrane, and (2) the monolayer behavior of the catanionics at the air–water interface. Electrochemical method was used to study the membrane activity by constructing a suitable electrochemical cell. The monolayer properties were studied in a Langmuir film balance. The phase transitions of the compressed surface film were studied by epifluorescence microscopy.

2. Experimental

2.1. Materials

The surfactants cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB), sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), sodium-bis [2-ethylhexylsulfosuccinate] (AOT), sodium deoxycholate (NaDC), sodium taurochenodeoxycholate (NaTCDC) were all products of Sigma, USA. The polymer polyvinyl chloride (PVC, low molecular weight) was a product of Biolab, USA. Cyclohexanone and dioctylphthalate (used as plasticizer) were purchased from E. Merck, Germany. The surfactants were 99% pure and were used as received. Purities were checked by measuring their CMCs and surface tension behavior [11], wherein no minimum was observed. The solvent cyclohexanone was distilled following standard procedure. The plasticizer, dioctylphthalate was used without further purification.

2.2. Methods

The surfactant ion selective electrode membranes were prepared following the procedure of Hayakawa and Kwak [12] and Maulik et al. [2,3,10] wherein surfactant ion-pairs (CTA^+–DS^-) was prepared by mixing equimolar aqueous solutions of CTAB and SDS to form a semi-solid mass (coacervate). It was then extracted by chloroform using a separating funnel. The solvent was evaporated and the residue containing CTA^+–DS^- ion-pair was dried under vacuum. Following this method, a number of other ion-pairs were prepared. For the preparation of cationic surfactant ion selective membrane, a solution of equimolar mixture of CTAB, TTAB and DTAB was prepared. SDS solution equimolar to this mixed cationic solution was then added to form the complex coacervate. Similarly, for anionic surfactant ion selective membrane, a solution of equimolar mixture of SDS, SDBS, AOT, NaDC, NaTCDC was prepared into which CTAB solution equimolar to the mixed anionic solution was added to form the complex coacervate. The isolation of these coacervates by chloroform extraction and its recovery were done as mentioned above.

An amount of 20 mg of the carrier complex (either cation or anion selective), 400 mg PVC, 1.1 g dioctylphthalate were dissolved in 10 ml distilled cyclohexanone with gentle heating whereby a clear and transparent solution was obtained. The transparent liquid mixture in cyclohexanone was then poured on a cleaned mercury surface (cleaning done by rubbing the Hg surface with NaCl) taken in a Petri dish of internal diameter of 10 cm. The solvent cyclohexanone was evaporated off in air resulting in the formation of a thin, fairly stout membrane. The membrane was then cut into pieces and attached to a Teflon tube of 1.0 cm internal diameter (both end open) by rubber bands. It was conditioned for overnight in 0.001 mol dm^{-3} CTAB and 0.01 mol dm^{-3} NaCl before use [13].

For electrochemical measurements, a cell of the following set up was used:

calomel//reference solution/CTA^+-selective membrane/
test solution//calomel

The liquid junction potentials between the calomel and reference solution or test solution was nullified by using salt bridges of saturated KCl in agar agar gel [3]. The cell emf was measured with a digital millivolt meter (HIL, India) with an accuracy of ±0.1 mV. The entire set up was thermostated in a water bath of ±0.2 K (uncertainty).

The performance of the membrane electrode system was tested by measuring the emf of the cell against increasing concentration of the surfactant solution in the test solution. The plots of emf versus log[surfactant] were found to vary linearly with breaks at concentrations corresponding to the CMCs of the surfactants. The initial slopes were both Nernstian as well as non-Nernstian. The results were reproducible so that the linear curves could be used as