

Micellar and analytical implications of a new potentiometric PVC sensor based on neutral ion-pair complexes of dodecylmethylimidazolium bromide–sodium dodecylsulfate

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ARTICLE INFO

Article history:

Received 17 September 2012

Accepted 21 December 2012

Available online 4 January 2013

Keywords:

Potentiometric sensor

dodecylmethylimidazolium bromide

Super-Nernstian slope

Ionic liquid

Micellization

End point indicator

Triblock copolymers

Drugs

ABSTRACT

With an aim to characterize the micellar aggregates of imidazolium based ionic liquids, a new potentiometric PVC sensor based on neutral ion-pair complexes of dodecylmethylimidazolium bromide–sodium dodecylsulfate (C12Melm⁺DS⁻) has been developed. The electrode exhibited a linear response for the concentration range of 7.9×10^{-5} – 9.8×10^{-3} M with a super-Nernstian slope of 92.94 mV/decade, a response time of 5 s and critical micellar concentration (*cmc*) of 10.09 mM for C12MelmBr. The performance of the electrode in investigating the *cmc* of C12MelmBr in the presence of two drugs [promazine hydrochloride (PMZ) and promethazine hydrochloride (PMT)] and three triblock copolymers (P123, L64 and F68) has been found to be satisfactory on comparison with conductivity measurements. Various micellar parameters have been evaluated for the binary mixtures of C12MelmBr with drugs and triblock copolymers using Clint's, Rubingh's, and Motomura's approach. Thus the electrode offers a simple, straightforward and relatively fast technique for the characterization of micellar aggregates of C12MelmBr, complementing existing conventional techniques. Further, the analytical importance of proposed C12Melm⁺-ISE as end point indicator in potentiometric titrations and for direct determination of cationic surfactants [cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB), benzalkonium chloride (BC)] in some commercial products was judged by comparing statistically with classical two-phase titration methods.

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1. Introduction

Interesting physical and chemical behavior of room temperature ionic liquids in terms of negligible vapor pressure, unique permittivity, high thermal stability, high electrical conductivity and favorable solubility for a broad range of organic, inorganic and polymeric materials makes them extremely desirable for numerous novel applications, a reason to be the subject of recent investigations. Thus ionic liquids are no longer being employed merely as 'Green Solvents' in organic chemistry rather exhibiting a great potential in diverse fields namely nanomaterial technologies [1–3], electrochemical applications [4,5], biocatalytic transformations [6,7], colloid and interface science [8–10] and separation processes [11,12] in concert with other environment friendly systems. Moreover, all these promising applications involve the presence of one or the other substance in conjunction with ionic liquids. Thus monitoring the change in the concentration of the ionic liquid (as in a kinetic process) or its estimation in a dilute solution under equilibrium condition is a matter of great concern for both chemists and

analysts. Ion selective membranes provide a good substitute for this problem being inexpensive, allowing simple and straight forward operation, providing rapid responses and capable of being incorporated into a multisensor array [13].

A look in the recent breakthroughs in surfactant chemistry exploring the aggregation behavior of room temperature ionic liquids reveals imidazolium based ionic liquids to be most studied because of the fine tuning of hydrophobicity of these ionic liquids by changing the alkyl chain length, polarisability of the head group and the nature of the anions [14]. The effectiveness of imidazolium based ionic liquids as self assembly media [15–17], as antimicrobial agents [18] and in altering the key physicochemical properties of different surfactant systems has been earlier exemplified [19]. The micellar aggregates of imidazolium based ionic liquids have been well characterized by surface tension [20,21], conductivity [16,22] and spectroscopic techniques [23,24,16]. However, reports on potentiometric methods to depict the micellar behavior of these ionic liquids in the literature are very rare. This prompted us to develop a potentiometric PVC sensor for sensing long chain alkyl imidazolium ion. Such surfactant ion selective electrodes have been successfully exploited not only for the determination of ionic surfactants [25,26] but also to study their binding with other

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materials [27,28]. Electrodes sensitive for various ammonium based cationic surfactants [29], anionic surfactants like SDS, SDBS [30] and nonionic surfactants [31] have been reported by numerous research groups including ours [32,33].

In the present study, we designed and characterized a dodecylmethylimidazolium-ion selective electrode (C12Melm⁺-ISE) based on neutral ion-pair complexes of dodecylmethylimidazolium bromide–sodium dodecylsulfate (C12Melm⁺DS⁻) as ionophore and bis(2-ethyl-hexyl) phthalate (DOP) as plasticizer. Its performance was then adjudged to investigate the aggregational behavior of C12MelmBr in the presence of various other amphiphiles i.e. drugs (PMZ and PMT) and triblock copolymers (P123, L64 and F68). This was evaluated in terms of micellar parameters such as critical micellar concentration (*cmc*), micellar mole fraction in the mixed state (X_1), interaction parameter (β^m), excess free energy of micellization (ΔG_{ex}^0), etc. The critical micellar concentration values of C12MelmBr with and without these additives determined potentiometrically using this sensor were compared with those determined from conductometric studies.

In addition to the evaluation of aggregational behavior of C12MelmBr, the analytical applications including, end point indication in potentiometric titrations and direct determination of some cationic surfactants [cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB), benzalkonium chloride (BC)] in commercial products of the proposed C12Melm⁺-ISE were also explored. The results have been compared with the classical two phase titration method using statistical analysis.

2. Experimental

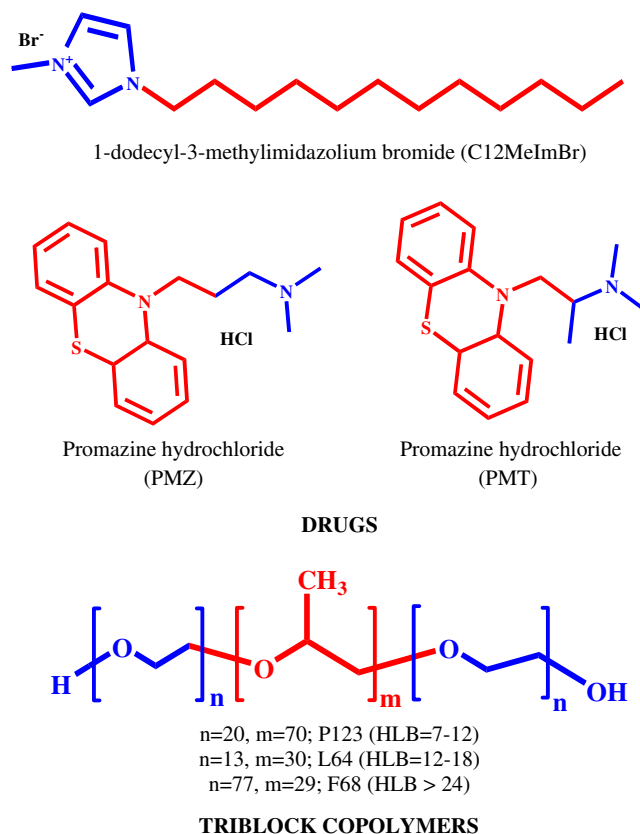
2.1. Materials

Dodecylmethylimidazolium bromide (C12MelmBr) was synthesized in the laboratory according to the procedure mentioned elsewhere [34], which involved alkylation of 1-methyl imidazole with 1-bromo dodecane. The product was then recrystallised from ethyl acetate and dried under vacuum. The purity of the product was ascertained by ¹H NMR spectrum in CDCl₃. The triblock copolymers; P123, L64 and F68 as well as the drugs; Promazine hydrochloride (PMZ) and Promethazine hydrochloride (PMT) were obtained from Sigma Aldrich. The compounds tetradecyltrimethyl ammonium bromide (TTAB), and sodium dodecylsulphate (SDS) from Spectrochem, India, cetylpyridinium chloride (CPC), benzalkonium Chloride (BC) and tetrahydrofuran (THF) from Lancaster Synthesis, UK, Sodium tetraphenylborate (TPB) from Sigma Aldrich were procured. The plasticizer, bis(2-ethyl-hexyl) phthalate (DOP) was a product of Qualigens, India. All chemicals were used as received and were of analytical grade. An analytical balance (Sartorius analytic) with a precision of ± 0.0001 g was used for weighing the amount of different substances. The solutions were prepared by dissolving accurately weighed quantities in requisite volumes of deionised double distilled water. The basic structure of C12MelmBr, drugs and triblock copolymers used in the present study are given in Scheme 1.

2.2. Methods

2.2.1. Preparation of ion-pair complex

The neutral ion-pair complexes of dodecylmethylimidazolium bromide–sodium dodecylsulfate (C12Melm⁺DS⁻) were prepared by the procedure earlier described by us [32,33]. Equimolar aqueous solutions of dodecylmethylimidazolium bromide (C12MelmBr) and sodium dodecylsulfate (SDS) were mixed and after continuous stirring for a considerable time, the white precipitates of



Scheme 1. Basic structure of ionic liquid, drugs and triblock copolymers used in the present study.

C12Melm⁺-DS⁻ were obtained, washed repeatedly with water and recrystallized thrice from acetone.

2.2.2. Electrode preparation

The PVC, ion-pair complex (C12Melm⁺DS⁻) and plasticizer, bis(2-ethyl-hexyl) phthalate (DOP) were mixed in appropriate proportions and dissolved in minimum quantity of THF. The resulting mixture was poured into 50-mm petri dish after removing the air bubbles. Solvent was allowed to evaporate at room temperature and the resulting membranes were cut to size, attached to PVC tubes with PVC glue and equilibrated in 1×10^{-3} M C12MelmBr solution. Several different compositions of the membrane in terms of ionophore content, plasticizer nature as well as plasticizer amount were tested against response for the C12Melm⁺ ion. However, PVC (176 mg), C12Melm⁺DS⁻ (12 mg) and DOP (546.4 mg) represented the best system in terms of the slope values, correlation coefficient, linear range, detection limit, etc.

2.2.3. Potentiometric measurements

All measurements were done using an Equiptronics digital potentiometer, Model EQ-602 employing the following electrochemical cell assembly;

Ag/AgCl | 3 M KCl | Test Solution | PVC Membrane | Internal Reference Solution | 3 M KCl | Ag/AgCl.

The internal reference solution used was 1×10^{-3} M C12MelmBr solution. The EMF measurements were carried out at a temperature of 298.15 ± 0.1 K in the presence of 10^{-3} M NaCl solution in the background.

2.2.4. Conductometric measurements

The specific conductivity (κ) measurements of C12MelmBr both in the absence and presence of different additives (drugs and

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