



ISSN 2248-9649

International Journal of Research in Chemistry and Environment

Available online at: www.ijrce.org

Research Paper

Potentiometric Determination of Cationic Surfactant using 'Polymeric-Inorganic' Nanocomposite Sensor

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Abstract: A cationic surfactant-selective electrode for sensitive analysis of cationic surfactant has been developed by using a plasticized poly (vinyl chloride) membrane based on nanocomposite cation exchanger polypyrrole zirconium titanium phosphate. The electrode is excellently selective for the cetyl trimethyl ammonium bromide (CTAB) ion over inorganic ions and other cationic surfactants. The membrane electrode was mechanically stable, having wide dynamic range of $10^{-7}M$ to $10^{-3}M$ of CTA^+ ions, with quick response time and could be operated for at least 4 months without any considerable divergence in the potential response characteristics. The electrode was successfully applied for direct determination of cationic surfactant, CTAB, in commercial disinfectants. The electrode has been used as an end-point indicator for potentiometric titration of analytical and technical grade commercial surfactants.

Keywords: CTAB, cationic surfactant, nanocomposites, potentiometry, poly (vinyl Chloride) membrane, surfactant-selective electrode.

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Introduction

Synthetic surface-active substances (surfactants) (SAS) are produced worldwide in large amounts. The total world consumption was over 10 million tonnes in 2000^[1]. Surfactants as environmental pollutants are present in various materials, including natural and waste waters, process solutions of industrial enterprises, household consumer products, etc. Surfactants are widely used in industrial processes for their favourable physicochemical characteristics such as detergency, foaming, emulsification, dispersion and solubilization effects^[2-5]. Such extensive applications of surfactants have produced environmental pollution and have raised problems in wastewater treatment plants^[6,7]. The experimental data have shown that surfactants can kill microorganisms at very low concentrations (1-5mg/L) and harm them at even lower concentrations (0.5mg/L)^[8]. In addition, surfactants can produce foams, which are a significant problem in sewage treatment.

Therefore, the removal of the surfactants from wastewater is important in reducing their environmental impact.

Nowadays, SAS are determined by spectroscopic, chromatographic, and electrochemical methods, as well as by the methods based on measuring their colloidal and physical properties^[9-11]. The most widely used technique in surfactant analysis is the so-called two-phase titration method, but this technique suffers from large number of drawbacks^[12]. The main disadvantage of these methods are, the limitation of application to strongly coloured and turbid samples, the toxicity of organic chlorinated solvent used, the formation of emulsion during titration which can disturb visual end-point detection, the numerous matrix interferences, etc. Most of these limitations can be overcome by using of ion sensitive electrode. The potentiometry with selective electrodes (sensors) is a promising, simple,

rapid available and inexpensive method for determining surfactants [13-18]. The methods for the determination of cationic surfactants by direct potentiometry and potentiometric titration using surfactant selective electrodes have been reported [19-23]. The quest for techniques to determine cationic surfactants with high sensitivity, accuracy, and precision is important because owing to their positive charge, cationic surfactants adsorb more strongly to the negatively charged surfaces of sludge, soil, and sediments than do anionic surfactants.

The liquid membranes or the plasticized poly (vinyl chloride) (PVC) membranes which incorporate cation-exchanger are usually used as the sensing membranes for cationic surfactant-selective electrodes. However, relatively low hydrophobic cation-exchangers such as phosphotungstic acid and ferric thiocyanate are often used as sensing membrane, which has limited sensitivity and life time of the electrode. Furthermore, the working pH range of the electrodes is relatively narrow.

In this paper, the construction of a new potentiometric sensor having wide working range and high selectivity, for determination and analysis of cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), has been developed by using a plasticized poly (vinyl chloride) membrane based on nanocomposite cation exchanger polypyrrole zirconium titanium phosphate (*PPy-ZTP*).

Material and Methods

Reagents and Instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck and Qualigens (India Ltd., used as received). *N*-cetyl-*N,N,N*-trimethyl ammonium bromide ($C_{19}H_{42}NBr$) (CTAB) was obtained from CDH (India) All other reagents and chemicals were of analytical grade. Carlo-Erba, model 1108; a digital potentiometer (Equiptronics EQ 609, India; accuracy ± 0.1 mV with a saturated calomel electrode as reference electrode; an electronic balance (digital, Sartorius-210S, Japan).

Synthesis of 'polymeric-inorganic' nanocomposite polypyrrole zirconium titanium phosphate (*PPy-ZTP*)

The composite cation-exchanger was prepared by sol-gel mixing of an organic polymer, polypyrrole (PPy), into the inorganic precipitate of zirconium titanium phosphate (ZTP). The synthesis process was same as mentioned in our published work [24].

Preparation and Characterization of composite membrane

The method used by Coetzee et.al. [25] was employed in the preparation of ion exchange membranes of *PPy-ZTP*. A number of membranes were prepared using

varying amounts of different binding materials such as PVC. The preparation method was same as reported [26,27] earlier. Those membranes which exhibited good surface qualities, like porosity, thickness, swelling etc. as described in the published work [28] was selected for further investigations.

Preparation of cationic surfactant solution for potentiometric studies

The solution of cetyl trimethyl ammonium bromide (CTAB) was prepared in bidistilled water of varying concentration i.e. in the range of 10^{-10} M to 10^{-1} M for potentiometric studies.

EMF measurements

Membranes were fixed to one end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) using PVC as adhesive. The electrode was preconditioned with 0.1 M CTAB solution for 5 days. The tube was filled 3/4th with CTAB solution (0.1 M) and then immersed in a beaker containing the test solution of varying concentration of CTA^+ ion, keeping the level of inner filling solution higher than the level of the test solution to avoid any reverse diffusion of the electrolyte. The response behaviour of the PVC membrane electrode to a cationic surfactant was examined by measurement of the electromotive force (emf) of the following electrochemical cell assembly,

SCE | 0.1M CTA^+ || Membrane || 0.1M CTA^+ (test solution) | SCE

Potentiometric measurements were observed for a series of standard solutions of CTAB (10^{-10} – 10^{-1} M), prepared by gradual dilution of the stock solution, as described by IUPAC Commission for Analytical Nomenclature [29]. Potential measurements were made in unbuffered solutions to avoid interference from any foreign ion. In order to study the characteristics of the electrode, the following parameters were evaluated, lower detection limit, slope response curve, response time and working pH range. The calibration graphs were plotted three times to check the reproducibility of the system.

Storage of electrodes

The *PPy-ZTP* based nanocomposite electrode was stored in distilled water when not in use for more than one day. It was activated with (0.1 M) CTA^+ solution by keeping immersed in it for 2 h, before use, to compensate for any loss of metal ions in the membrane phase that might have taken place due to a long storage in distilled water. Electrode was then washed thoroughly with DMW before use.

Results and Discussion

Cetrimonium bromide [$(C_{16}H_{33})N(CH_3)_3Br$] or cetyltrimethylammonium bromide, (CTAB) is one of

the components of the topical antiseptic cetrimide. The severe or irreversible adverse effects of cetrimide, which give rise to further complications, include corneal irritation, erosion, ulceration. Cetrimide is an antiseptic agent with detergent properties, having molecular formula ,



Surfactant get adsorb onto solid substrate i.e. cation exchanger from aqueous solution by a number of different mechanism, ion exchange, ion pairing, hydrogen bonding or by physical adsorption. A number of factors strongly influence the adsorption of surfactants, i) the nature of the structural groups on the surface, ii) the molecular structure of the surfactant being adsorbed iii) the environment of aqueous phase, its pH, electrolyte content etc.

The adsorption mechanism of the surfactants metal ions on the ion exchange materials can be explained on the basis of micellar association which can be explained in terms of the electrostatic model, i.e., Gouy-Chapman electrical double layer approximations^[30, 31] and the counter ion binding approximation^[32]

Micelles are not rigid but highly mobile in spite of their aggregated structure. They exist in a dynamic equilibrium with the free monomers^[33]. The life time of a monomer in the micelle is about 10–5 s^[34]. The intramolecular motions of monomers within the micelle can be assumed to be rather unrestricted with an enhanced mobility of the terminal alkyl group predominantly oriented within the micellar core and of the ionic head groups situated at the surface of the micelle^[35]. Correlation limits of these motions are considerably shorter than residence times of individual monomers in the micelles. Thus, for a process, where a characteristic time range is slower than that of the ionic head group mobility, the micelles appear to be a sphere, uniform smeared-out surface charge. As a result, a constant surface potential can be assigned to the micellar surface.

PPy-ZTP has been used as an electro-active component in the preparation of the heterogeneous solid-state electrode sensitive to surfactant CTAB. Ion-selective electrodes work on the principle of measurements at zero current. The membranes were fixed in the electrode assembly and all measurements are made in a concentration cell. The concentration of the electrolyte on the inner side of the membrane was fixed at 0.1M of CTAB while outer solution varied from 10⁻¹⁰M to 10⁻¹M. When ions penetrated the boundary between the two phases leading to the attainment of electrochemical equilibrium, the potentials developed.

Electrochemical Characteristics of the Surfactant-Selective Electrode

The electrochemical performance of *PPy-ZTP* electrode was systematically evaluated according to IUPAC guidelines^[36]. Table 1 shows the response characteristics of the plasticized PVC composite cation exchange membrane electrode to CTAB. The electrode investigated showed Nernstian response with a slope of 57.7 mV/decade in the concentration range of 10⁻⁷M to 10⁻³M of CTA⁺ ion as shown in Figure 1. Furthermore, experiments were conducted three times to check the reproducibility of the results and emf values were reproducible within ±0.04mV.

Table 1: Response characteristics of the CTAB sensitive nanocomposite *PPy-ZTP* membrane electrode

Parameter	Response
Slope (mv/decade)	57.7± 0.04
Correlation coefficient (Y)	0.9992
Linear range	10 ⁻³ -10 ⁻⁷
Detection limit (M)	6× 10 ⁻⁸
C.M.C.(M)	1×10 ⁻³

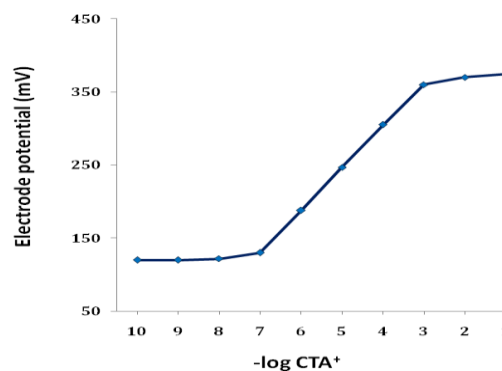


Figure 1: Calibration curve for surfactant sensitive PPy--ZTP membrane electrode in aqueous solution of CTAB

The effect of pH on the potential of the surfactant-selective electrode was investigated based on changes in pH over the range of 1-10. The pH was changed by adding very small volumes of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. At all concentrations, the electrode potential was stable and practically unaffected by the pH change over the working pH range 2.5-8.0, above which the potential reading decreased sharply as shown in Figure 2. This behaviour might be attributed to OH⁻ ion interference with the response of the electrode. It is clear from Figure 3 that the electrode showed stable emf reading within 40s for 10⁻⁷ -10⁻³ M CTAB solution after which it started deviating.

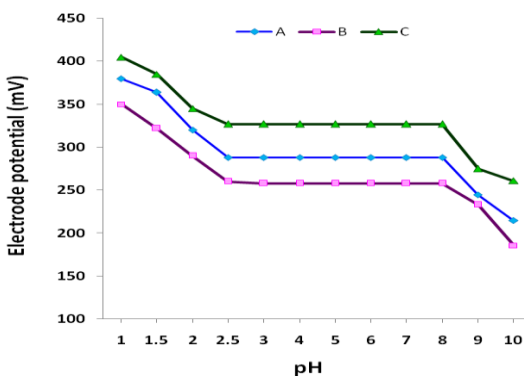


Figure 2: The influence of pH on the potential response of surfactant sensitive membrane electrode at A) 1×10^{-4} B) 1×10^{-5} and C) 1×10^{-6} M CTA^+ ion

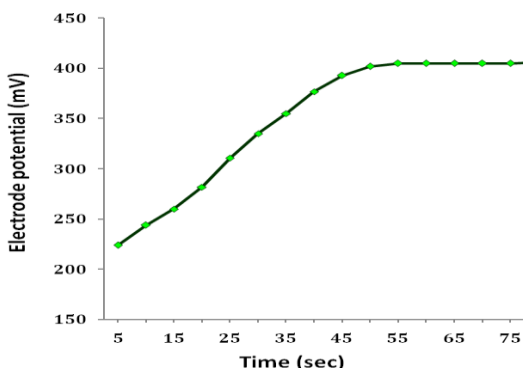


Figure 3: Response time of CTA^+ sensitive PPy-ZTP membrane electrode

The long-term stability was worked out by performing calibrations periodically with standard solutions and calculating the slopes over the concentration ranges of 10^{-10} M to 10^{-1} M of surfactant solutions over a period of 150 days. During this period, the electrodes were in daily use over an extended period of time (1 h per day), and the results are provided in Table 2 after that a very slight gradual decrease in the slopes and working range was observed. Subsequently, the electrochemical behavior of the sensor gradually deteriorated which may be due to ageing of the adhesive (PVC), the plasticizers, and the electroactive material [37]. A decrease in slope was a symptom of loss of the normal characteristics of the electrodes.

The surfactant electrode is capable to determine the critical micelle concentration (C.M.C.) of CTAB, since the electrode is highly selective for it. The observed calibration curve for the CTA^+ ion (Figure 1) has a

break point, which corresponds to the C.M.C. of the CTA^+ ion. These results agree well with reported C.M.C. value [38].

Table 2: The stability of the CTAB selective PPy-ZTP membrane electrode

Interferents	Selectivity coefficient (K_{MSM})
K^+	5.6×10^{-5}
Na^+	5×10^{-5}
Mg^{2+}	3.2×10^{-5}
Cu^{2+}	6×10^{-6}
Zn^{2+}	6×10^{-6}
Cd^{2+}	4.7×10^{-6}
Al^{3+}	7×10^{-5}
Cetylpyridinium chloride (CPC)	5×10^{-3}
Triton X-100	9×10^{-6}
Dodecyl pyridinium chloride (DPC)	2×10^{-5}

Potentiometric Selectivity

The selectivity of the surfactant-selective electrode for the CTAB ion was examined by the mixed solution method (MSM) [39]. The electrode potential was measured for various concentrations of the CTAB under constant concentrations of a potentially interfering ion. Inorganic cations, non ionic surfactant

and long-chain quaternary ammonium ions were examined as the potentially interfering ions. The results as shown in Table 3 reveal that the presence of different cations does not interfere with foreign basic compounds, and the electrode display reasonable selectivity for surfactant CTAB.

Analytical application

Application of the Electrode in the determination of other commercial Cationic Surfactants

The developed electrode has high selectivity for cationic surfactant ions over inorganic ions. Table 4 shows the results of the recovery test of CTAB added

to commercial surfactants by using the calibration curve with CTAB solutions. For all of the samples examined in this work, the recovery was satisfactory. This result shows that the present electrode can be applied to determine total cationic surfactants in commercial disinfectants/surfactants.

Table 3: The selectivity coefficient of CTAB selective PPy-ZTP membrane electrode for various interferents

Days	Slope (mV decade ⁻¹)	DL (M)	Working range (M)
1	57.7 ± 0.04	6 × 10 ⁻⁸	1 × 10 ⁻⁷ -1 × 10 ⁻³
10	57.7 ± 0.04	6 × 10 ⁻⁸	1 × 10 ⁻⁷ -1 × 10 ⁻³
20	57.7 ± 0.05	6 × 10 ⁻⁸	1 × 10 ⁻⁷ -1 × 10 ⁻³
30	57.6 ± 0.02	6 × 10 ⁻⁸	1 × 10 ⁻⁷ -1 × 10 ⁻³
40	57.6 ± 0.02	6 × 10 ⁻⁸	1 × 10 ⁻⁷ -1 × 10 ⁻³
60	57.5 ± 0.2	7 × 10 ⁻⁸	1 × 10 ⁻⁷ -1 × 10 ⁻³
90	57.2 ± 0.4	2 × 10 ⁻⁷	5 × 10 ⁻⁷ -1 × 10 ⁻³
120	57 ± 0.03	3 × 10 ⁻⁷	5 × 10 ⁻⁷ -1 × 10 ⁻³
150	56.5 ± 0.3	5 × 10 ⁻⁷	5 × 10 ⁻⁷ -1 × 10 ⁻³

Table 4: Potentiometric determination and recovery of different cationic surfactant using CTA⁺ ion selective PPy-ZTP electrode

Sample	Added (mol/l)	Found (mol/l)	Recovered (%)
Tetradecyldimethylbenzylammonium chloride (TDBAC) (C ₂₃ H ₄₂ N ⁺ Cl ⁻)	8 × 10 ⁻⁵	7.96 × 10 ⁻⁵	99.5
Dodecyl pyridinium chloride (DPC) [C ₁₂ H ₂₅ N ⁺ (C ₂ H ₂) ₂ CHCl ⁻]	5 × 10 ⁻⁵	4.98 × 10 ⁻⁵	99.6
Cetylpyridinium chloride (CPC) [C ₁₆ H ₃₃ N ⁺ (C ₂ H ₂) ₂ CHCl ⁻]	10 ⁻⁶	9.97 × 10 ⁻⁵	99.7
Benzalkonium chloride (BAC) [C ₆ H ₆ CH ₂ N ⁺ (CH ₃) ₂ Cl ⁻]	4 × 10 ⁻⁶	3.92 × 10 ⁻⁵	98
Dodecyltrimethyl ammonium bromide (DDAB) [C ₁₂ H ₂₅ N ⁺ (CH ₃) ₃ Br ⁻]	10 ⁻⁵	9.88 × 10 ⁻⁴	98.8

Potentiometric titration

The proposed surfactant selective membrane sensor was found to work well under laboratory conditions.

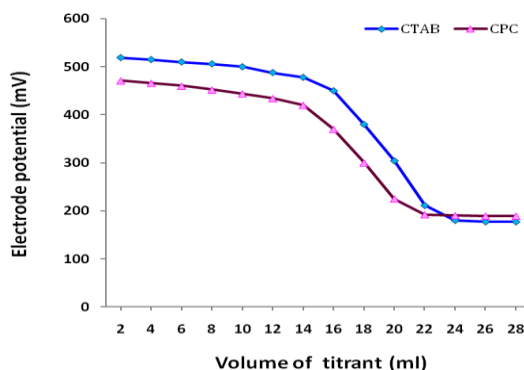


Figure 4: Potentiometric titration of cationic surfactant with 10⁻³ M sodium dodecyl sulphate solution using surfactant sensitive PPy-ZTP membrane electrode

The electrode was used successfully as an end-point detector in the potentiometric titration of ionic

surfactants, CTA⁺ and CP⁺ (cetyl pyridinium ion), with sodium dodecyl sulphate solution. The titration curves showed good inflection point at the equivalence point, showing perfect stoichiometry as shown in Figure 4. Surfactants with the same hydrocarbon chain length gave potential breaks to equivalence increasing in an order that parallels the selectivity coefficient behaviour. The accuracy of the method was checked by carrying out a series of titrations. The estimated relative error was lower than 1%.

Conclusion

This research work evaluated the performance of 'polymeric-inorganic' nanocomposite cation exchanger PPy-ZTP as cationic surfactant selective electrode. It shows high selectivity for the cationic surfactant CTAB over other inorganic cations having dynamic working range of 1 × 10⁻⁷-1 × 10⁻³ M of CTA⁺ ion. The electrode is also capable to determine the C.M.C. value of CTAB. Furthermore, the electrode can be used in a wide pH range over 2.5–8.0. The present electrode can be applied to the determination of total cationic surfactants in commercial surfactant.

Acknowledgment

The authors are thankful to University Grant Commission (India) for financial assistance. (Under the scheme of PDFW), Department of Applied Science and Humanities, Jamia Millia Islamia, (New Delhi), and Department of Applied Chemistry, Z.H. College of Engineering and Technology, A.M.U. (Aligarh) for providing research facilities.

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