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Submicromolar determination of praepagen HY surfactant using new liquid inner contact electrodes

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ABSTRACT

New liquid membrane electrodes for submicromolar determination of praepagen HYCl surfactant have been prepared. These electrodes utilize HYCl with phosphotungstic acid (PTA) as ion-pair (HY–PT) dissolved in the plasticizers: dibutyl phthalate (DBP) encoded sensor S_1, dioctyl phthalate (DOP) encoded sensor S_2, dioctylsebacate (DOS) encoded sensor S_3 and tris(2-ethylhexyl) phosphate (TOPh) encoded sensor S_4. The proposed electrodes exhibit Nernstian slopes of 59.5 ± 0.6, 58.5 ± 0.6, 55.2 ± 0.6 and 57.3 ± 0.5 mV/decade in the concentration ranges 1.0×10^{-7}–1.0×10^{-2}, 2.5×10^{-8}–1.0×10^{-2}, 8.0×10^{-8}–1.0×10^{-2} and 1.0×10^{-7}–1.0×10^{-2} M and notably low limits of detection: 1.0×10^{-7}, 2.0×10^{-8}, 3.5×10^{-8} and 8.5×10^{-8} M for sensors S_1, S_2, S_3 and S_4 respectively. The sensors have considerably short response times (5–10 s) and good repeatability within the pH range 2.8–9.4. The electrodes exhibit excellent selectivity for HY^+ ions over many inorganic and organic cations. These electrodes are useful for determination of HYCl in shampoo and liquid detergent solutions as proved by standard addition and the calibration curve methods. Furthermore, the successful use as indicator electrode was culminated by the potentiometric titration of HY^+ ions in water samples.

1. Introduction

Over the last few years, the use of surfactants in home and industry has significantly increased. The uncontrolled use of surfactants results in their accumulation in natural, domestic, and industrial waste waters. Wide use of surfactants has become one of the major pollutants of soil and natural water. [1].

Praepagen HYCl, alkyl dimethyl hydroxyethylammonium chloride (HY) (Fig. 1), is a cationic surfactant and a common ingredient in laundry detergents [2–6] used worldwide for household cleaning [7]. HYCl has been used in several forms: granular detergent [8,9] granular enzymatic [10,11], gel [12], hard surface cleaning preparations [13], copolymer [14], liquid fabric [15], hair treatment preparations [16] and drying-spray detergent [17]. The toxicity testing of HYCl to the fresh water alga was studied [18].

Most of the reports on determination of HYCl are patents and it appears necessary to fabricate an alternative method with attractive characteristics. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as speed, selectivity, sensitivity, good precision, simplicity, low cost, reliability, reproducibility and nondestructive analysis [19]. The use of the ion-selective electrode to study the equilibrium properties of aqueous surfactant solutions has received much attention in recent years [20]. In addition, surfactant membrane selective electrodes have been quite successful to investigate the concentration of surfactants and their behavior in various media [20]. Moreover, they are useful for monitoring specific species in environmental samples such as soil and waste water [21].

The present work describes preparation, characterization, and analytical application of membrane electrodes for HYCl using the ion-pair HY-PT dissolved in plasticizers DOP, DBP, TEPh and DOS as plasticizer. The attractable characteristics of PVC membranes have been utilized to fabricate four novel electrodes for determination of praepagen HY surfactant. A few plasticizers with different characteristics are usefully incorporated in the membranes employed in building the electrodes. The designed electrodes have good characteristics and provided precise and accurate results. These electrodes detect submicromolar levels down to near nanomolar levels (about 2×10^{-8} M). They provide a response in a considerably short time 5–10 s. The proposed electrodes exhibit Nernstian slopes of 59.5 ± 0.6, 58.5 ± 0.6, 55.2 ± 0.6 and 57.3 ± 0.5 mV/decade with low limits of detection: 1.0×10^{-7}, 2.0×10^{-8}, 3.5×10^{-8} and 8.5 × 10–8 M for sensors S1, S2, S3 and S4 respectively. Wide concentration ranges are now

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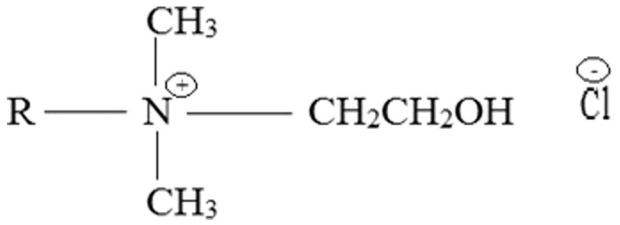

Fig. 1. The chemical structure of alkyl dimethyl hydroxyethylammonium chloride.

spanned by the present electrodes: 1.0×10^{-7}–1.0×10^{-2}, 2.5×10^{-8}–1.0×10^{-2}, 8.0×10^{-8}–1.0×10^{-2} and 1.0×10^{-7}–1.0×10^{-2} M. Moreover, determination of praepagen HY can be made in solutions of various acidities: in strongly acidic media (pH 2.8) up to moderately basic solutions (pH 9.4) These sensors were successfully applied in determination of HYCl in shampoo, liquid detergents solutions and aqueous solutions from various sources with many other components for their notably excellent selectivity for HY^+ ions over many inorganic and organic cations. These electrodes are adequate and useful for determination of HYCl in shampoo and liquid detergent solutions as proved by standard addition and the calibration curve methods. Furthermore, their successful use as indicator electrode was culminated by the potentiometric titration of HY^+ in water samples.

2. Experimental

2.1. Reagents and solutions

Alkyl dimethyl hydroxyethyl ammonium chloride was available commercially as Praepagen HY (Trade Mark) from Clariant GmbH, in the form of a 40 wt% aqueous solution. R group in this material corresponds to an alkyl group, C_nH_{2n+1} with n = 12–14 and used to make 0.01 M stock solution. Dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate TOPh, dioctylsebacate DOS, phosphotungstic acid (PTA) and sodium tetraphenyl borate (Na-TPB) were obtained from Sigma–Aldrich. Tetrahydrofuran THF, Poly(vinyl chloride) PVC, as well as metal salts were obtained from Sigma–Aldrich. The standard solutions of the cations were made in deionized water and diluted as required.

2.2. Equipment

Pocket pH/mV meters, pH315i from Wissenschaftlich-TechnischeWerkstatten GmbH (WTW) and saturated calomel electrode (SCE) from Sigma-Aldrich were used for potential measurements in cell assemblies: [22,23] Ag/AgCl||internal soln. KCl and HYCl||membrane||-analyte||Hg, Hg_2Cl_2(s), KCl(sat.).

2.3. Synthesis of ion-exchangers

These sensing materials containing HYCl were prepared from HY-phosphotungstate (HY-PT) according to a reported procedure [22]. HY-PT was made by mixing HYCl and PTA solutions in the ratio 3:1. A fast reaction occurred that produced essentially pure praepagen HY as it separated from the initially clear reaction mixture. The precipitate was copiously washed with water to ensure removal of any unreacted material. The precipitate was collected, washed and dried at room temperature.

The purity of the product was further confirmed by physical measurements. It decomposed sharply at 220 °C indicating a pure substance. Its IR spectrum comprises the major prominent peaks characteristic as well as their fingerprint parts of its component chromophores that appear in their individual spectra as clearly observed on matching against these spectra. These spectra comprise characteristic peaks for each compound. For the ion-pair: 3404, 2922, 2855, 1637, 1466, 1076, 974, 890, 790, 594, and 507 cm^{-1}; the surfactant: 3370, 2922, 2853, 1639, 1467, 967, 908 and 511 cm^{-1} and phosphotungstic acid: 3445, 1614 m 1074, 974, 888, 755, 593 and 499 cm^{-1}. The product is soluble in THF making it a useful PVC choice for electrode fabrication. The product was finely ground and used to fabricate the proposed electrodes.

2.4. Construction PVC membrane electrodes

PVC-membranes were fabricated as previously described elsewhere [24,25] where various amounts of 1.0 wt% ion-pair (HY-PT), 1.0 wt% lipophilic additive (NaTPB), 50.8 wt% PVC and 48.1 wt% a plasticizer from DOP, DBP, TEPh and DOS in 10 mL of tetrahydrofuran. The ingredients were properly mixed and the resultant solution was allowed to evaporate in a Petri dish leaving a transparent membrane. Small disks (10 mm) were punched from the cast films and mounted on home-made electrode bodies. The internal solution composition was introduced (0.01 mol L^{-1} KCl and 0.001 mol L^{-1} HYCl) to compose the electrode shown in. The electrode was soaked in 0.01 mol L^{-1} HYCl solution for 15 min. before use.

2.5. Selectivity coefficients

Potentiometric selectivity factors were determined using the separate solution method (SSM) and the matched potential method (MPM) [26].

In the SSM, the potential of a cell comprising a working electrode and a reference electrode is measured in two separate solutions, one containing HY^+ ions, E_1, and the other containing the interfering ions (J), E_2. and S is the slope of the calibration graph. These values were used to calculate the selectivity coefficient from the following equation:

$$\log K^{pot}_{HY,J^{z+}} = \frac{E_2 - E_1}{S} + \log[HY] - \log\left[J^{z+}\right]^{1/z}.$$

According to MPM the activity of HYCl was increased from $a_{HY} = 1.0 \times 10^{-5}$ M to $\breve{a}_{HY} = 5.0 \times 10^{-5}$ M and the resultant potentials were measured. Next, a solution of an interfering ion a_J in the range 1.0×10^{-1} M 1.0×10^{-2} M was added to a new 5.0×10^{-5} M until the same potential change (ΔE) was attained. The selectivity factor, for each interferent was calculated using the following equation:

$$K^{pot}_{HY,J} = \frac{\breve{a}_{HY} - a_{HY}}{a_J}.$$

Table 1
Response Characteristics of the HY-PVCEs. at 25.0 ± 0.1 °C.

No.	Sensor	Plasticizer	S	C.R.	LOD	L.S.	R(s)
1	S_1	DOP	57 ± 0.5	7.1×10^{-8}–1.0×10^{-2}	5.0×10^{-8}	30	6
2	S_2	DBP	59 ± 0.5	7.1×10^{-8}–1.0×10^{-2}	5.0×10^{-8}	32	5
3	S_3	TOPh	57 ± 0.6	2.0×10^{-8}–1.0×10^{-2}	3.0×10^{-8}	34	10
4	S_4	DOS	54 ± 0.8	7.1×10^{-8}–1.0×10^{-2}	5.0×10^{-8}	28	5

S: slope (mV/decade), C.R.: concentration range (M). LOD: limit of detection (M), L.S.: life span (days); R(s): response time(s).