

## Nanomolar Detection of Alkyl Dimethyl Hydroxyethyl Ammonium Surfactant by a Lipophile-doped Solid Contact Electrode

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### Abstract

Various methods for improving the lower detection limit of polymeric membrane ion-selective electrodes have been approached recently. The ion-selective electrode with solid-state membrane is described. Tetraphenyl borate as a lipophilic anion, is incorporated into the membrane of the electrode to improve its detection limit and selectivity. The detection limit was significantly lowered where nanomolar quantities were traced. Other favorable characteristics of the electrode are noticeably short response time of 5 seconds and good selectivity over the common interfering chemical species as well as its proven usefulness for determination of the surfactant in miscellaneous samples.

**Keywords:** Ion-selective electrode; Solid-contact ion-selective electrodes; Alkyl dimethyl ethanol ammonium chloride; Potentiometry

### Introduction

Ion-selective electrodes (ISEs) are typical examples of chemical sensors that use the principle of molecular recognition [1].

Solid-contact potentiometric ion-selective electrode (SC-ISE), a new generation of ISE, is a promising substitute for conventional liquid-contact ISE, drawing tremendous attention from both the experimental and theoretical scientific communities [2]. The solid-state electrodes in particular have great advantages of the mechanical flexibility, the possibility of miniaturization, and microfabrication. SC-ISE use a polymer-coated membrane that has direct contact with the metal substrate, which can be prepared by dipping the metal wire into a PVC cocktail membrane solution to form a bead. These membranes are easy to construct and are better suited for multi-ion sensors because they can be miniaturized and are not restricted to one side of the electrode. Therefore, these are gaining popularity in various medical, biotechnological, pharmaceutical, and environmental fields. Furthermore, this type of electrode allows for low detection limit which was attributed to the absence of trans membrane ion fluxes [2,3]. Lowering the detection limit of ion-selective electrodes has been a hot issue in electroanalysis since 1997 [4]. However, over the last decade the mainstream research was exclusively focused on application of plastic membranes, theory and practical aspects [5]. The mechanism of the potential formation of ion selective electrodes (ISEs) with a liquid or pseudo liquid (polymeric) membrane depends strongly on extraction and ion-exchange processes between the aqueous and organic phases [6]. The presence of salts consisting of a hydrophilic cation and a lipophilic anion [e.g., sodium tetraphenyl borate (NaTPB) or potassium tetrakis p-chlorophenyl borate (KTPClPB)] in cation-selective membranes based on neutral carriers has proved to be beneficial in many respects. It is known that the nature and amount of the lipophilic additive strongly affect the response of the membrane ion-selective sensors, for instance by reducing the membrane resistance [7], improving the response behavior and selectivity and in some cases [8], where the extraction capability is poor, increasing the sensitivity of the membrane sensor [9]. Consequently, it can be expected that increasing amounts of these salts will further decrease membrane resistance without changing the membrane selectivity. This can be important for electrokinetic studies (e.g., the evaluation of exchange current densities) on ion-selective macro electrodes where several difficulties can arise from high membrane resistance[8].

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. Because of their wide use, surfactants have become one of the major pollutants of soil and natural water [9]. This is why the increased interest of analysts in methods for determining these compounds in different samples is well understood. Gas chromatography, photometry and a number of other methods have been proposed for determining surfactants [9]. The reports on potentiometric methods, particularly on those dealing with ion-selective electrodes (ISEs) are of special interest [9]. Alkyl dimethyl ethanol ammonium chloride (HYCl) (Figure 1), is a typical cationic surfactant used throughout the world [10-12]. HYCl is used in granular enzymatic detergent, [8] gel surfactant and commonly used in household cleaning such as laundry detergent composition [13-15]. However, the toxicity testing of HYCl to the fresh water alga and selenastrum capicornutum was studied [16]. Therefore, there is an increasing need for rapid reliable method to measure HYCl concentrations in natural waters to minimize risks associated with its use.

The aim of this research was to devise graphite-coated electrode(GCE)sensitive to HY ions (ISEs) based on a PVC membrane phase containing sodium tetraphenyl borate (Na-TPB) as an ionic additive. The detection limit was lowered to  $8.0 \times 10^{-9}$  M with concentration range  $1.5 \times 10^{-8}$ - $1.0 \times 10^{-2}$ . This electrode was used successfully for determination of HY ion in real samples with notable characteristics of wide concentration range, low limit of detection, good Nernstain slope, high selectivity over a wide variety of other cations and short response time.

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Received January 15, 2014; Accepted February 08, 2014; Published February 10, 2014

Citation: Abu Shawish HM, Gaber M, Khedr AM, Abed-Almonem KI (2014) Nanomolar Detection of Alkyl Dimethyl Hydroxyethyl Ammonium Surfactant by a Lipophile-doped Solid Contact Electrode. J Environ Anal Chem 1: 101. doi:10.4172/2380-2391.1000101

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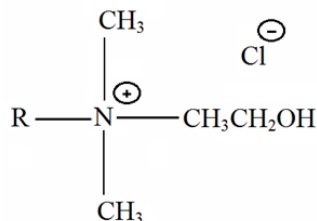


Figure 1: The chemical structure of HYCl.

## Experimental

### Reagents and solutions

Alkyl dimethyl hydroxyethyl ammonium chloride, (praepagen HY), 40% was obtained from Clariant LTD company (Pratteln-Switzerland). Stock solution was prepared to contain 0.01M. Dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate TOPh, dioctylsebacate DOS, Silicotungstic acid (STA), phosphotungstic acid (PTA) and phosphomolybdic acid (PMA) were purchased from Sigma-Aldrich (CH-9471 Buchs-Germany). Tetrahydrofuran THF, Poly(vinylchloride) PVC, as well as metal cations were purchased from was obtained from (Sigma-Aldrich, CH-9471 Buchs-Italy). All the standard solutions of cations were prepared from their analytical reagent grade chemicals in deionized water and then diluted as desired.

### Equipment

Potentiometric and pH measurements were made with a Pocket pH/mV Meters, pH315i (Wissenschaftlich-Technische Werkstätten GmbH (WTW), Weilheim, Germany). A saturated calomel electrode (SCE) was used as reference electrode for potential measurements and was obtained from Sigma-Aldrich Co. (St Louis, MO, USA). The emf measurements with the CGE were carried out with the following cell assemblies: Hg, Hg<sub>2</sub>Cl<sub>2</sub>(s), KCl (sat.) sample solution/membrane/graphite.

### Preparation of ion-exchangers

Ion-exchanger sensing materials containing HY were made according to a previously reported method, [17] from HY- silicotungstate, (HY-ST), phosphotungstate (HY-PT) and phosphomolybdate (HY-PM). Preparation of (HY- ST) was carried out by mixing the two solutions in the ratio of 4:1, i.e., 50 mL of 0.01M HY was mixed with 12.5 mL of 0.01M solution of silicotungstate (ST), phosphotungstate (PT) and phosphomolybdate (PM) were prepared by adding 50 mL of 0.01M solution of HY to the appropriate volume of 10<sup>-2</sup> M solution to 16.7 mL of 0.01 M of one of (HY-PT) or (HY-PM). The precipitates that formed were filtered off, washed thoroughly with distilled water, dried at room temperature and ground to fine powders. These ion-pair complexes were used as the active substances for preparing the proposed electrode of HY ion.

### Fabrication of electrode

Different membranes were fabricated by mixing various amounts of ion-exchanger (HY-ST), (HY-PT) or (HY-PM), lipophilic additive (NaTPB), plasticizers viz., (DOP, DBP, TOPh and DOS) and PVC using 10 mL of THF. All the components were mixed homogeneously with a glass rod until the solution became viscous. Graphite rod, about 1mm diameter and 50 mm long was first polished on a cloth pad, washed with water followed by acetone and sequentially air-dried. One end of the

wire (about 20 mm length) was coated by repeated dipping (about five times, a few minutes between dips) into the concentrated membrane solution. A membrane was formed on the rod wire surface was allowed to dry for 3-4 hours. The electrode was then sealed in syringe tube with parafilm, taking care that the electrode portion having membrane layer remains exposed. The prepared electrodes were conditioned for 1 h in 0.001M HYCl solution.

### Calibration of the sensors

The calibration of the HY sensor under investigation was established by immersing the HY working electrode in conjunction with the reference electrode in 50 mL beakers containing known aliquots of standard 2.0×10<sup>-9</sup> to 1.0×10<sup>-2</sup> M HY made by serial dilution. The potential was plotted against the negative logarithmic value of HY concentrations. Each solution was stirred and the potential was recorded when it became stable, and plotted as a logarithmic function of HY cation activities.

### Effect of foreign ions on the electrode selectivity

The potentiometric selectivity coefficients log K<sub>HY, jz<sup>+</sup></sub><sup>pot</sup> were determined according to IUPAC guidelines using the separate solutions (SSM) and matched potential (MPM) methods [18].

### Sample preparation

Samples of alkyl dimethyl Hydroxy Ethyl ammonium chloride (HY) ranging from 1.0×10<sup>-8</sup> to 1.0×10<sup>-2</sup> M HY were determined by the standard addition, potentiometric titration and the calibration curve methods. The required amount of the stock (40% solution) was transferred to a 50.0 mL volumetric flask and diluted to the mark with distilled water to make 0.01 M solutions of HY. Different volumes of these solutions equivalent to 1.5×10<sup>-8</sup> to 1.0×10<sup>-2</sup> M were taken and analysed by the above methods using the present electrode. Each analysis was repeated 5 times. Real samples include Nutra (liquid detergent) and Nutra (shampoo) contain 50.0 and 100.0 mg/mL of HYCl which correspond to 1.4×10<sup>-1</sup> and 2.8×10<sup>-1</sup> mol L<sup>-1</sup> of HY respectively. Dilute solutions that are 1×10<sup>-4</sup> M and 1×10<sup>-5</sup> M of each were made by transferring the required amounts to 25.0 mL volumetric flasks and properly diluted. These solutions were subjected to the standard addition method and the calibration curve method.

### Sample analysis

In potentiometric titration, different volumes of HY solution containing 1.92-38.4 mg, were transferred to a 25.0 mL beaker, and titrated with a standard solution of Na-TPB using HY-PT as indicator electrode conjugated with Saturated Calomel Electrode (SCE). The potential was plotted against the volume added of the titrant and the end points were determined from the S-shaped curves using the first derivative plots.

The standard addition method in which known increments of (0.1 M) HY solution were added to 25.0 mL aliquot samples of two concentrations (1.0×10<sup>-7</sup> and 1.0×10<sup>-6</sup> M) HY was applied. The change in potential at (25 ± 0.1°C) was recorded after each increment and these data were used to calculate the concentration of HY in the sample solutions. In the calibration graph method, different amounts of HY were added to 50.0 mL of water comprising a concentration range from 1.5×10<sup>-8</sup> to 1.0×10<sup>-2</sup> M and the measured potential was recorded using the present electrode. Data were plotted as potential versus logarithm of the HY activity and the resulting graph was used for subsequent determination of the concentration of surfactant samples [19].

## Result and Discussion

The potentiometric response is dependent on the activity of the analyte as anticipated by Nernst equation:

$$EMF = E^{\circ} + \frac{RT}{Z_i F} \ln a_i = E^{\circ} + \frac{2.303RT}{Z_i F} \log a_i \quad (1)$$

This response is dependent on the potential difference across the phase boundary between the sample phase and the hydrophobic ion-selective membrane. The different affinities of the two ions in the aqueous and the organic phases result in charge separation across the interface between the two phases. This interfacial charge separation is the origin of the interfacial phase boundary potential. The sensitivity and selectivity of any membrane sensor are significantly related to the composition of the membrane, the nature and amount of the solvent mediators and additives used. The effects of these parameters on the behavior of the proposed sensor were studied and the results are provided in table 1.

### Ion-exchanger selection

Ion-exchangers used in ion-selective membrane sensors should have rapid exchange kinetics and adequate stability. In addition, they should have appreciable solubility in the membrane matrix and sufficient lipophilicity to prevent leaching from the membrane into the sample solution [20]. The ion-exchanger incorporated in each electrode was an ionassociation of the HY cation with a heteropoly anion: silicotungstate  $H_4(SiW_{12}O_{40})$ , phosphotungstate  $H_3(PW_{12}O_{40})$  or phosphomolybdate  $(H_3PMo_{12}O_{40})$ . These species with high molecular weights anions, 1823, 2880 and 1825 respectively, have different lipophilicities and stabilities. They were used as electroactive materials in plasticized poly(vinyl chloride) matrix membranes, and as candidates for the formation of highly lipophilic ion associates with many organic cations as well as active recognition elements in the proposed electrodes [21]. The electrodes containing some or no ion exchanger were made and their emf measured at various concentrations of the HY. The membrane with no ionpair showed no response (composition # 1). The electrode that contained HY-PT (composition # 4) gave the best results with a response that improved with optimization of the composition of the membrane according to Table 1. The lipophilicity of HY-PT is more than the others as it is more bulky and has the highest molecular weight. Therefore, the membrane containing 1.0% HY-PT

complex produced the best response (sensor # 4). Further addition of the ion-exchanger complexes (sensor# 5) resulted in a little decrease in the response of the electrode. This drop is most probably due to some inhomogenities and possible saturation of the membrane [22].

### Membranes with lipophilic anions as additives

It is known that the nature and amount of the lipophilic additive strongly affect the response of the membrane ion-selective sensors. That is likely due to reducing the membrane resistance [23], improving the response behavior and selectivity [24]. In addition, it causes increasing the sensitivity of the membrane sensors where the extraction capability is poor [9,25].

Therefore, tetraphenyl borate was used as a lipophilic additive to the designed electrode. The results are compiled in table 1 which indicates a clear improvement of the detection by about 100 fold. This improvement can be interpreted as described below. If no ionic sites are added in the membrane, coextraction of the analyte ion and its counter-ion into the organic phase occurs according to the following reaction [26]:



Thereby causing no charge separation at the interface. It is necessary to add a hydrophobic ion such as tetraphenyl borate ion (TPB) that has a charge sign opposite to the charge sign of the measured ion, to the organic phase in addition to the electrically neutral ionophore to keep the activity of the ion of interest in the bulk of the water-immiscible sensing phase sample-independent. The ionic sites in the membrane repel  $Cl^{-}$  ions from being coextracted into the organic phase, thus they are necessary for generation of analyte-ion activity (concentration)-dependent membrane potential changes. However, when the concentration of  $HY^{+}$  in the organic phase is very high because these ions balance the negative charge of the hydrophobic counter anions (TPB<sup>-</sup>), resulting in a very low  $Cl^{-}$  membrane as show in Figure 2. This can be understood from a Le Chatelier effect on the  $HYCl$  distribution between the two phases (eq. 2); a high concentration of  $HY^{+}$  in the organic phase favors chloride transfer into the aqueous phase [27].

### Solvent mediators (plasticizer) effect

The plasticizer influences the mobility of the ion-pair through extraction of both ions into the organic phase [28,29]. Therefore, it is

No.	Kind of Wires	Composition (%)				Electrode characteristics				
		IE	PVC	P	A	S	C.R (M)	LOD (M)	R.S.D %	R <sub>(S)</sub>
1	Graphite	-	48.2	51.8 (DBP)		43 ± 0.2	1.4×10 <sup>-5</sup> -1.0×10 <sup>-2</sup>	3.4×10 <sup>-5</sup>	0.95	16
2		0.5 (HY-PT)	48.5	51.0 (DBP)		47 ± 0.3	9.1×10 <sup>-7</sup> -1.0×10 <sup>-2</sup>	3.2×10 <sup>-7</sup>	0.21	9
3		1.0 (HY-PT)	48.2	50.8 (DBP)		50 ± 0.6	6.3×10 <sup>-7</sup> -1.0×10 <sup>-2</sup>	1.0×10 <sup>-7</sup>	0.24	12
4		1.0 (HY-PT)*	48.1	50.8 (DBP)	0.1	57 ± 0.4	1.5×10 <sup>-8</sup> -1.0×10 <sup>-2</sup>	8.0×10 <sup>-9</sup>	0.24	4
5		1.5 (HY-PT)	48.3	50.2 (DBP)		47 ± 1.0	1.0×10 <sup>-7</sup> -1.0×10 <sup>-2</sup>	6.3×10 <sup>-6</sup>	0.17	14
6		1.0 (HY-PT)	48.2	50.8 (DOP)	0.1	46 ± 1.2	7.9×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	6.3×10 <sup>-6</sup>	1.25	11
7		1.0 (HY-PT)	48.1	50.8 (DOS)	0.1	43 ± 0.3	8.8×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	3.2×10 <sup>-7</sup>	1.01	8
8		1.0 (HY-PT)	48.1	50.8 (TOPh)	0.1	47 ± 0.3	1.6×10 <sup>-7</sup> -1.0×10 <sup>-2</sup>	1.0×10 <sup>-6</sup>	0.65	16
9		1.0 (HY-PM)	48.2	50.8 (DBP)		45 ± 0.6	5.1×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	3.0×10 <sup>-6</sup>	0.24	12
10		1.0 (HY-ST)	48.2	50.8 (DBP)		45 ± 0.6	6.3×10 <sup>-7</sup> -1.0×10 <sup>-2</sup>	1.0×10 <sup>-7</sup>	0.24	12
11	copper	1.0 (HY-PT)	48.2	50.8 (DBP)		46 ± 1.0	7.1×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	9.5×10 <sup>-7</sup>	1.21	8
12	Silver	1.0 (HY-PT)	48.2	50.8 (DBP)		46 ± 1.0	7.1×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	9.5×10 <sup>-7</sup>	1.21	4
13	Platinum	1.0 (HY-PT)	48.2	50.8 (DBP)		47 ± 1.0	1.6×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	1.2×10 <sup>-5</sup>	0.35	15

I.E: Ion-Exchanger, PVC: Poly Vinyl Chloride, P: Plasticizer, S: Slope (Mv/Decade), C.R.: Concentration Range, LOD: Limit Of Detection, R(S): Response Time(S)  
\*Selected composition, A: lipophilic additive (sodium tetraphenyl borate)

**Table1:** Composition and Slope of Calibration Curves for HY-Electrodes at 25.0 ± 0.1°C.

necessary to use other plasticizers with different physical parameters such as dielectric constant ( $\epsilon$ ), lipophilicity (log PTLC), viscosity ( $\eta$ ) and molecular weight (M.wt) [30]. Therefore, four different plasticizers, viz. DOP, DBP, DOS and ToPh were added in an attempt to improve the performance of the electrode and the results obtained are shown in figure 3. Generally, plasticizers improve certain characteristics of the electrodes, but in some cases, the response characteristics get affected adversely. In this study no relation between the physical parameters and the response characteristics was found. Nevertheless, better response characteristic values are obtained when the properties have intermediate values. Comparatively, DBP with relatively moderate viscosity, lipophilicity and low dielectric constant, produced the best result and was used in further characterization as shown in table 2. Out of the electrodes tested, the electrode containing ion-exchanger complex 1.0 wt% HY-PT, 48.1 wt% PVC, 50.8 wt% DBP and 0.1wt% Na-TPB exhibited the best response characteristics and the lowest detection limit. Therefore, this composition was used to study various operation parameters of the electrode. The electrochemical performance characteristics of this electrode were systematically evaluated according to the International Union of Pure and Applied Chemistry (IUPAC) recommendations [31].

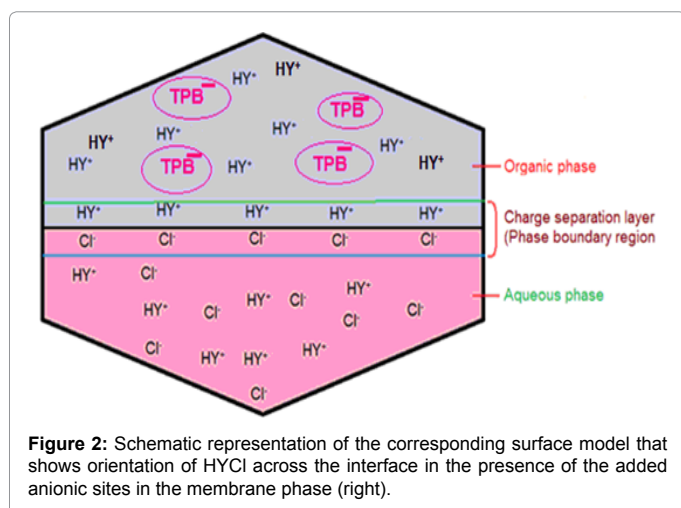


Figure 2: Schematic representation of the corresponding surface model that shows orientation of HYCl across the interface in the presence of the added anionic sites in the membrane phase (right).

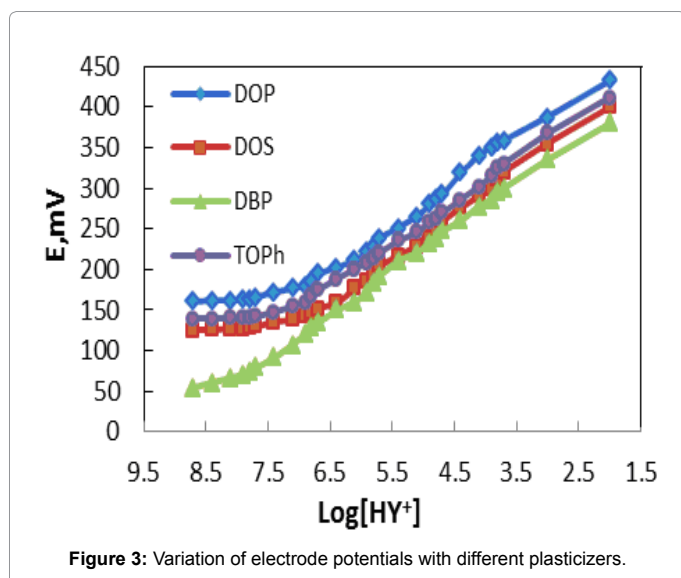


Figure 3: Variation of electrode potentials with different plasticizers.

Interfering ions	SSM	MPM
NH+	$4.48 \times 10^{-4}$	$6.48 \times 10^{-4}$
Na+	$1.59 \times 10^{-4}$	$3.33 \times 10^{-5}$
K+	$4.12 \times 10^{-4}$	$5.88 \times 10^{-5}$
Ag+	$1.06 \times 10^{-4}$	$8.96 \times 10^{-4}$
Li+	$5.54 \times 10^{-4}$	$1.18 \times 10^{-5}$
Pb+2	$4.11 \times 10^{-4}$	$2.53 \times 10^{-4}$
Mg2+	$5.15 \times 10^{-4}$	$1.29 \times 10^{-5}$
Ca2+	$5.47 \times 10^{-4}$	$4.44 \times 10^{-5}$
Ba2+	$4.09 \times 10^{-4}$	$3.97 \times 10^{-5}$
Zn2+	$3.56 \times 10^{-4}$	$6.50 \times 10^{-5}$
Ni2+	$6.61 \times 10^{-4}$	$3.47 \times 10^{-5}$
Cd2+	$4.77 \times 10^{-4}$	$5.17 \times 10^{-5}$
Co2+	$2.52 \times 10^{-4}$	$9.27 \times 10^{-5}$
Cu2+	$1.22 \times 10^{-4}$	$8.22 \times 10^{-5}$
Al3+	$2.13 \times 10^{-4}$	$2.45 \times 10^{-5}$
Cr3+	$1.02 \times 10^{-4}$	$2.88 \times 10^{-5}$
Hg+2	$7.10 \times 10^{-4}$	$3.78 \times 10^{-5}$
CTAB	$1.77 \times 10^{-2}$	$6.28 \times 10^{-2}$
Benzlkonium chloride	$1.90 \times 10^{-2}$	$2.38 \times 10^{-2}$
Na- dodocyl Sulphate	$9.02 \times 10^{-5}$	$2.43 \times 10^{-6}$
Na-EDTA	$3.33 \times 10^{-6}$	$4.21 \times 10^{-6}$
TEA	-	$5.44 \times 10^{-6}$
Glycerin	-	$3.00 \times 10^{-5}$
Propylene glycol	-	$5.52 \times 10^{-6}$
Luramide	-	$4.04 \times 10^{-7}$

Table 2: Selectivity coefficient of various interfering ions.

### The dynamic response time behavior and reproducibility of the proposed electrode

Dynamic response time is an important factor for any ion-selective electrode. The response time of the electrode was obtained by measuring the time required to achieve a steady state potential (within  $\pm 1$  mV) after successive immersion of the electrode in a series of HY solutions [31], each having a 10-fold increase in concentration from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M. As shown in figure 4, the electrode yielded steady potentials within 5-8 s. The potential reading stays constant, to within  $\pm 1$  mV, for at least 5 min. The reproducibility of the electrode was examined by determining  $1.0 \times 10^{-6}$  and  $1.0 \times 10^{-5}$  M HY ion solution. The standard deviation in emf measurements for five replicate solutions was found to be 1.12 for  $1.0 \times 10^{-6}$  M solution and 0.54 for  $1.0 \times 10^{-4}$  M solution. Considering the low value of the standard deviation for these replicate measurements it is clear that the repeatability of the present electrode is satisfactory.

The stability of the electrode was tested by making successive calibrations with the same electrode in  $1.0 \times 10^{-5}$  M of HY<sup>+</sup> over a period of 8 h. The relative standard deviation (RSD) of the electrode potential readings was 0.84 mV (n=5). This result indicates that the proposed electrode shows a good reproducibility and stability.

### Electrode selectivity

The separate solution method (SSM) is recommended by IUPAC to determine the selectivity coefficient of the ISE [18]. SSM is based on Nickolsky-Eisenman equation. However, it has been shown that this method suffers some limitations in terms of the values for ions of unequal charges, a non-Nernstian behavior of interfering ions [32]. Therefore another method named the 'matched potential method (MPM)' was recommended especially when the primary ion and/or the interfering ion dissatisfy with the Nernst response or when the involved

ions have unequal charges [33]. The resulting values, presented in table 2, show that the electrode displays significantly high selectivity for HY over many common organic and inorganic compounds and surfactants, except benzalkonium chloride and Cetyl Trimethyl Ammonium Bromide (CTAB) which showed moderate interference that is likely due to having similar structure. Fortunately, two cationic surfactants benzalkonium chloride and (CTAB) have moderate effect on the response of the electrode but these are not present in the same formulations. For this reason, they do not prejudice the quality of the determinations.

### Effect of pH

The influence of the pH of the solution on the response of the proposed electrodes was studied for  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  M  $\text{HY}^+$  ions in the pH range of 2.0-11.0. The pH was adjusted with 0.1 M solutions of hydrochloric acid or sodium hydroxide. It can be seen from Figure 5 that the variation in potential is acceptable in the pH range 3.0-9.4. Nevertheless, at pH values  $< 3.0$ , a decrease was observed that is probably caused by the  $\text{H}_3\text{O}^+$  effects on the electrodes and may also be due to leaching of the ion exchangers in acidic media. On the other hand, the potentials decreased gradually in solutions as the pH was raised above 9.4, a drop that can be attributed to the penetration of the  $\text{OH}^-$  ions into the membrane and reaction with  $\text{PT}^-$  ions which decreased the ion-pair and the amount of the electroactive material of the electrode.

### Analytical applications

In order to test the analytical applicability of the proposed sensor, it has been applied for determination of HY ions in some liquid detergent and shampoo.

### Determination of HY in liquid detergent and shampoo

The proposed electrode was used in the standard addition and calibration methods for determination of HY content (Nutra) liquid detergent and (Nutra) shampoo. It is clear that the amount of HY ion can be accurately determined with these electrodes as shown in table 3.

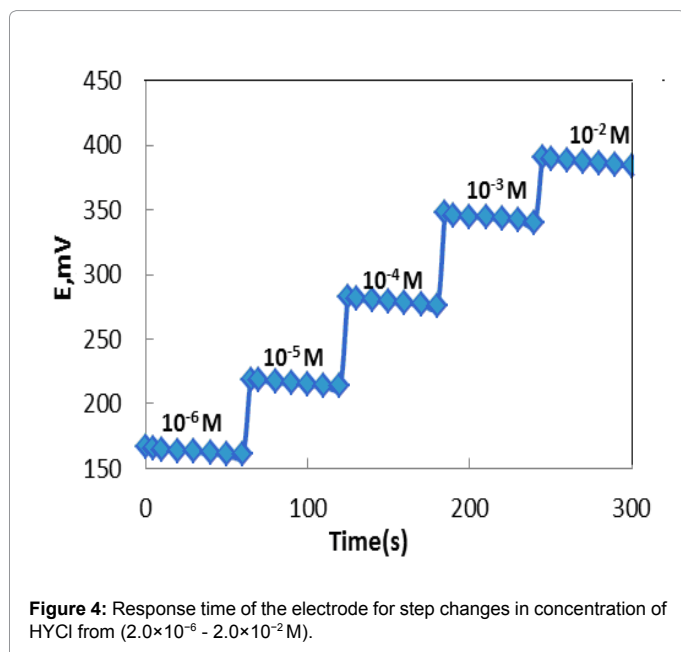


Figure 4: Response time of the electrode for step changes in concentration of HYCl from ( $2.0 \times 10^{-6}$  -  $2.0 \times 10^{-2}$  M).

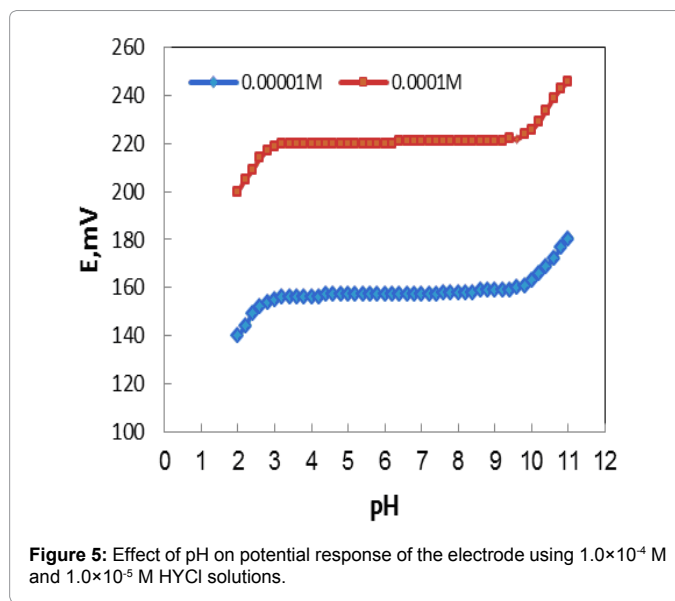


Figure 5: Effect of pH on potential response of the electrode using  $1.0 \times 10^{-4}$  M and  $1.0 \times 10^{-5}$  M HYCl solutions.

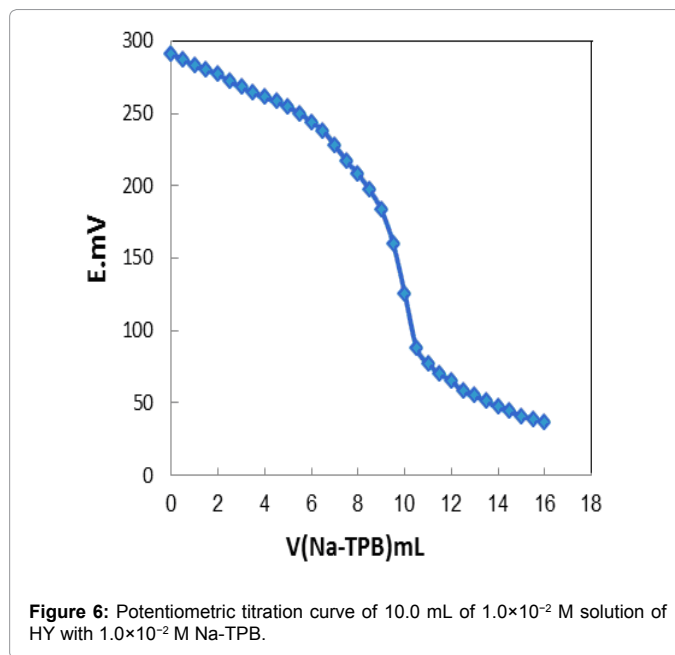


Figure 6: Potentiometric titration curve of 10.0 mL of  $1.0 \times 10^{-2}$  M solution of HY with  $1.0 \times 10^{-2}$  M Na-TPB.

Sample	Taken(M)	Found(M)	R.SD.%
Nutra(Liquid detergent)	s( $1.0 \times 10^{-5}$ )	s( $9.50 \times 10^{-6}$ )	0.58
	c( $1.0 \times 10^{-4}$ )	c( $9.45 \times 10^{-5}$ )	1.23
Nutra (Shampoo)	s( $1.0 \times 10^{-5}$ )	s( $9.30 \times 10^{-6}$ )	0.89
	c( $1.0 \times 10^{-4}$ )	c( $9.50 \times 10^{-5}$ )	1.46

Table 3: Analysis of Hy in various samples using calibration curve and standard addition method.

### Titration of benzalkonium chloride solution with Na-TPB solution

The present sensor was used as an indicator electrode in potentiometric titration of HY with Na-TPB. The resulting titration curve is shown in figure 6. It is clear that the amount of HY ion can be accurately determined with this electrode.

## Conclusions

A new graphite coated electrode based on HY-PT as ionophore was used for HY determination. The electrode shows high sensitivity ( $8.0 \times 10^{-9}$ ), reasonable selectivity, fast static response, long term stability and applicability over a wide concentration range ( $1.5 \times 10^{-8}$  to  $1.0 \times 10^{-2}$ ). The proposed potentiometric electrodes offer the advantages of simplicity, accuracy, automation feasibility and applicability to turbid and colored sample solutions.

## References

1. Shim JH, Jeong IS, Lee MH, Hong HP, On JH, et al. (2004) Ion-selective electrodes based on molecular tweezer-type neutral carriers. *Talanta* 63: 61-71.
2. Yuan X, Chai Y, Yuan R, Zhao Q (2013) Improved potentiometric response of solid-contact lanthanum (III) selective electrode. *Anal Chim Acta* 779: 35-40.
3. Lenik J, Wardak C, Grabarczyk M (2012) Application of Ionic Liquid to the Construction of Cu(II) ion-selective Electrode with Solid Contact. *Procedia Eng*, 47: 152-155.
4. Sokalski T, Ceresa A, Zwickl T, Pretsch E (1997) Large Improvement of the Lower Detection Limit of Ion-Selective Polymer Membrane Electrodes. *J Am Chem Soc* 119: 11347-11348.
5. Han WS, Lee YH, Jung KJ, Ly SY, Hong TK, et al. (2008) K<sup>+</sup> Ion Selective Polyaniline Solid Contact Electrode based on 4',4''(5'')-Di-tert-butylidibenzo-18-crown-6-ether Ionophore. *J Anal Chem* 63: 987-993.
6. Yoshida Y, Matsui M, Maeda K, Kihara S (1998) Physicochemical understanding of the selectivity at an ion selective electrode of the liquid membrane type and relation between the selectivity and distribution ratios in the ion-pair extraction. *Anal Chim Acta* 374: 269-281.
7. Nieman TA, Horvai G (1985) Neutral carrier potassium-selective electrodes with low resistances. *Anal. Chim. Acta* 170: 359-363.
8. Ammann D, Pretsch E, Simon W, Lindner E, Bezegh A, et al. (1985) Lipophilic salts as membrane additives and their influence on the properties of macro- and micro-electrodes based on neutral carriers. *Anal. Chim. Acta* 171: 119-129.
9. Lizunova GM, Orlova AO, Zorin AD (2004) Liquid Ion-Selective Electrodes for Determining Nonionic Surfactants. *J Anal Chem* 59: 775-779.
10. Abera OC, Beers I, Paassen M, Schadewijk, Marinus S (2006) US Patent 0111 266.
11. Banies FL, Finich TD, Peckham EJ, Roth SP (2006) Fabric Detergent Composition. US Patent 7 012 059.
12. Gallotti M, Nunes G (2001) Light duty liquid cleaners. *Eur Patent Appl* 1: 158 040.
13. Burrows J, Crawford JR, Norris JP, Thorley CD (2006) Laundry Detergent Compositions. US Patent 7 078,373.
14. Prabhat M, Swan BG (2012) Laundry Compositions. US Patent 8: 153 579.
15. Alhendawi HMH (2011) Intercalation of malachite green ([C<sub>6</sub>H<sub>5</sub>C(C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>]Cl) in layered  $\gamma$ -zirconium phosphate. Effect of cationic surfactants. *J Mater Chem* 21: 7748-7754.
16. Ward JT, Spognardi A, Boeri LR (2001) U.S. Environmental Protection Agency CMD-011028.
17. Gaber M, Abu Shawish HM, Khedr AM, Abed-Almonem KI (2012) *Mater. Sci. Eng C* 32: 2299.
18. Umezawa Y, Buhlmann P, Umezawa K, Tohda K, Amemiya S (2000) *Pure Appl Chem* 72: 1851.
19. Ibrahim H, Issa YM, Abu Shawish HM (2005) Potentiometric flow injection analysis of dicyclomine hydrochloride in serum, urine and milk. *Anal Chim Acta* 532: 79-88.
20. Abu-Shawish HM (2008) Potentiometric Response of Modified Carbon Paste Electrode Based on Mixed Ion-Exchangers. *Electroanal* 20: 491-497.
21. Kharitonov SV (2006) Electrochemical response characteristics and analytical application of papaverine ion-selective membrane electrodes. *Anal Lett* 39: 259-273.
22. Arvand M, Asadollahzadeh SA (2008) Ion-selective electrode for aluminum determination in pharmaceutical substances, tea leaves and water samples. *Talanta* 75: 1046-1054.
23. Abu-Shawish HM, Saadeh MS, Dalloul MH, Najri B, Al Athamna H (2013) Modified carbon paste electrode for potentiometric determination of silver(I) ions in burning cream and radiological films. *Sensors and Actuators B: Chemical* 182: 374-381.
24. Amemiya S, Buhlmann P, Pretsch E, Rusterholz B, Umezawa Y (2000) Cationic or anionic sites? Selectivity optimization of ion-selective electrodes based on charged ionophores *Anal Chem* 72: 1618-1631.
25. Bakker E, Bühlmann P, Pretsch E (1997) Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics. *Chem Rev* 97: 3083-3132.
26. Faozia H, Itadani N, Nomura M, Suzuki K, Yasui T, et al. (2013) *Electroanal. Chem* 696: 20.
27. Tani Y, Umezawa Y (2005) *Sensor Lett* 3: 99.
28. Abu Shawish HM, Abu Ghalwa N, Hamada M, Basheer A (2012) *Mater Sci Eng C* 32: 140.
29. Egorov VV, Bolotin AA (2006) Ion-selective electrodes for determination of organic ammonium ions: Ways for selectivity control. *Talanta* 70: 1107-1116.
30. Abu-Shawish HM (2009) A mercury(II) selective sensor based on N,N'-bis(salicylaldehyde)-phenylenediamine as neutral carrier for potentiometric analysis in water samples. *J Hazard Mater* 167: 602-608.
31. Buck, R. P., Lindner, E (1994) IUPAC recommendation for nomenclature of ionselective electrodes. *Pure and Applied Chemistry* 66: 2527-2536.
32. Chandra S, Agarwal H, Singh KC (2007) A highly selective and sensitive thorium(IV) PVC membrane electrode based on a dithio-tetraaza macrocyclic compound. *Anal Sci* 23: 469-473.
33. Wang HX, Pu M (2002) *Chinese Chem. Lett* 13: 355.