



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Novel surfactant-selective membrane electrode based on polyelectrolyte–surfactant complex



Ivan Zorin*, Tatiana Scherbinina, Petr Fetin, Ivan Makarov, Alexander Bilibin

St.-Petersburg State University, Institute of Chemistry, 26 University Avenue, Peterhof, St.-Petersburg 198504, Russia

ARTICLE INFO

Article history:

Received 15 March 2014

Received in revised form

23 June 2014

Accepted 26 June 2014

Available online 5 July 2014

Keywords:

Ion-selective electrode

Surfactant

Polyelectrolyte–surfactant complex

ABSTRACT

Novel class of active ionophores for surfactant selective electrodes is proposed. PVC membrane doped with polyelectrolyte–surfactant stoichiometric complex is used for ion-selective electrode construction responsive to cetyltrimethyl ammonium bromide and related surfactants. New ionophore is quite stable and completely insoluble in aqueous media in wide range of pH. The electrode displays nearly Nernstian slope in CTAB concentration range 10^{-6} – 10^{-3} M. Polyelectrolyte platform allows to design wide range of different ionophores responsive to cationic organic substances.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Annual production of cationic surfactants reaches million tons in the world. They have found wide application in different areas. Analytical determination of surfactants is an important task in prevention of chemical pollution in both industrial and domestic waste waters. This task is very important in laboratory practice too.

Ion-selective electrodes responsive to amphiphilic part of the surfactant molecule are considered as convenient instruments for the expression of surfactant determination in water solutions. The problems of surfactant-selective electrodes are known: signal instability, necessity of frequent recalibration, and low lifetime. Several ways can exist to resolve these problems. The first one is improvement of an electrode construction and fine molecular design of sensor material. It may lead to excellent results and possibly to rather an expensive device. Another way is to produce cheap, easy-to-produce, and easy-to-use device, which should not contain expensive or chemically unstable components. In this way polymer membrane electrodes are the most preferable candidates.

Davidson [1] was the first, who introduced the use of plasticized PVC membranes doped with ionophores for making surfactant-selective electrodes.

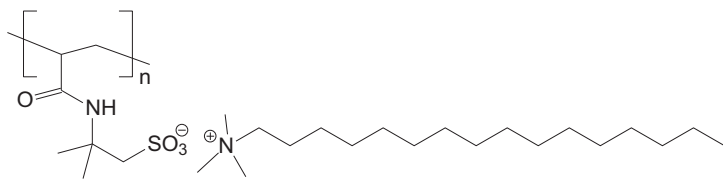
Known ionophores for PVC membranes are low-molecular weight organic compounds with low to moderate solubility in water. Consequently, possibility of leaching of the ionophore from the membrane may affect the life-time of membrane which can be dozens to hundred days [2]. Nevertheless, development of new organic ionophores is still actual [3–6]. PVC membrane electrode can be used not only in water but also in water–organic media [7]. An alternative approach is chemical linking of ionophore to membrane material such as copolymerization of vinyl chloride with 3-acrylamido-N,N-dimethylpropylamine [8] or direct modification of PVC by chemical (amine) treatment [9]. Recently modified carbon nanotubes (SWNT) were introduced as ionophore additive to PVC membranes for CTAB- and SDS-selective electrodes [10].

Polyelectrolyte–surfactant complexes (PESC) are novel perspective type of ionic polymeric materials which are stable and insoluble in water and soluble in organic media [11–13]. PESC in solid state possess highly ordered layer or channel structure and excellent elastic properties. Ionic nature of PESC allows considering them as ion-exchange material in selective membranes. The organic ion intended to be sensed by membrane should be the part of PESC composition, namely, the counterion. Thus, a set of ionophores could be easily obtained based on the given polyelectrolyte by using proper organic ion while preparing PESC. Strong polyelectrolytes, such as polystyrenesulfonic acid, poly-2-acrylamido-2-methylpropanesulfonic acid (PAMPS), and polydiallyldimethylammonium chloride, form stoichiometric complexes with

* Corresponding author. Tel.: +78124284075; fax: +78124286733.

E-mail address: i.zorin@spbu.ru (I. Zorin).

organic hydrophobic counterions by directly mixing in water or by polymerization of proper monomers [14–21]. In this paper we use PAMPS and set of ammonium surfactants to demonstrate the usability of PESC as ionophore to produce PVC membranes responsive to common surfactants. The structure of ionophore PAMPS–CTA is depicted below.



PAMPS-CTA

2. Experimental

CTAB, cetylamine, dodecylamine, dodecyltriethylammonium bromide (DTEAB), and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) were purchased from Merck. PVC and dioctylphthalate were of bulk industry technical grade. 18.2 M Ω deionized water was used for all preparations.

PESC synthesis was performed via original synthetic procedure [19,20] by polymerization of cetyltrimethylammonium (CTA), cetylammionium (CA) or dodecylammionium (DDA) salts of AMPS in water. Typical procedure was as follows: solution of 4.76 g of AMPS–CTA in 10 ml of water, containing 1 g/L ammonium persulfate, was bubbled with argon for 15 min and then placed in thermostat at 60 °C bath for 1 h. PESC precipitated during polymerization and was collected by filtration, washed with acetone and dried in vacuum. The stoichiometry of the PESC (1/1 by mole AMPS to CTA) is guaranteed by synthetic procedure used for its preparation (details are discussed in our previous papers [19,20]) and was proved by CHNS-analysis (calculated, % C 63.63, H 11.09, N 5.71, S 6.53; found, % C 63.06, H 11.12, N 5.75, S 6.50) and NMR-spectroscopy data.

Molecular weights of PESCs were in the range of 2×10^5 – 2×10^6 depending on details of the synthesis conditions.

Stock solution of PVC was prepared by dissolving 2 g of PVC and 3 g of dioctylphthalate in a mixture of 50 ml DMF and 10 ml cyclohexanol. For preparation of the membrane with 1% ionophore content, 5 mg of PESC was dissolved in 7 ml of PVC stock solution and spread on 4×6 cm² polypropylene plate. Membranes were first dried at room temperature for a week, until they became transparent and uniform and then at 60 °C for 24 h. This is necessary to remove high-boiling solvents and for membrane polymeric components to come to equilibrium. After drying the membranes were cut and glued to the end-face of 15 mm diameter PVC tube.

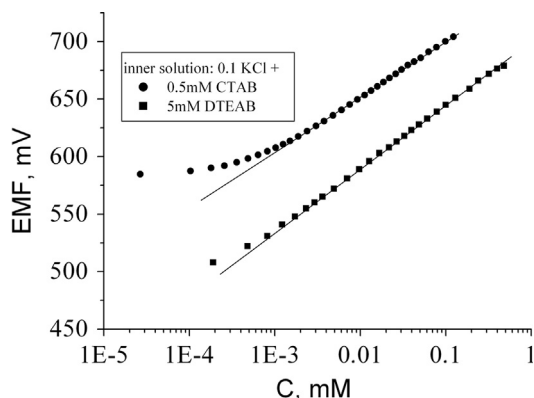


Fig. 1. Potential response to CTAB of two electrodes with CTA–DS ionophore and different electrode inner solutions.

Ag/AgCl electrode was used as inner reference and 5×10^{-4} M CTAB + 10^{-1} M KCl or 5×10^{-2} M DTEAB + 10^{-1} M KCl were used as the inner solution. Typically, working area of a membrane was 1.2 cm² and inner solution volume was 2 ml.

Prior to use electrodes were conditioned (24 h) and stored in solutions corresponding to the inner one. Potentiometric titrations

were performed at 20 ± 0.1 °C in a 250 ml glass beaker using Tl/TlCl electrode as reference. Each titration began from 150 ml of pure water or 10^{-1} M KCl solution; 10^{-3} to 10^{-1} M titrant solutions were used.

Table 1

Slopes, linear range, detection limits of different membranes with 1% ionophore content.

Ionophore	Analyte	Slope (mV/decade)	Linear range (mMol/L)	^a Detection limit $\times 10^7$ (Mol/L)	CTAB cmc (mMol/L)
DS–CTA ^b	CTAB	54.9 ± 0.5	0.0015–0.4	2	0.98 [23]
	CTAB/KCl	58.8 ± 0.7	0.002–cmc	3	0.053
	DTEAB/KCl	74.1 ± 1.5	0.14–5	3	
PAMPS–CTA ^b	CTAB/water	55.9 ± 1.2	0.002–0.5	1	0.98 [23]
	CTAB/water	57.7 ± 1.4^d	0.0004–0.5	1	
	CTAB/NaOH	60.7 ± 1.0	0.006–cmc	2	0.14
	CTAB/HCl	59.5 ± 0.5	0.002–cmc	1	0.056
	CTAB/KCl	58.6 ± 0.4	0.002–cmc	2	0.056
	DTEAB/KCl	76.5 ± 1.4	0.16–5	2	
PAMPS–DDA ^b	DDA*HCl	30.8 ± 1.0	0.005–3.8	2	15 [23]
	SDS	-47.6 ± 0.9	0.13–2	400	
PAMPS–DDA ^c	DDA*HCl	41.6 ± 1.6	0.045–2	80	
PAMPS–DDA ^c	DDA*HCl	45.3 ± 1.4	0.03–10	30	
	CTAB	57.8 ± 1.5	0.002–0.5	1	
	SDS	-43.1 ± 2.0	0.004–2	20	

^a Determined as a point at which two-fold increase of concentration causes not less than 5 mV change of EMF.

^b Inner solution 5×10^{-2} M DTEAB + 10^{-1} M KCl.

^c Inner solution 1×10^{-1} M DDA*HCl + 10^{-1} M KCl.

^d Ionophore content 3%.

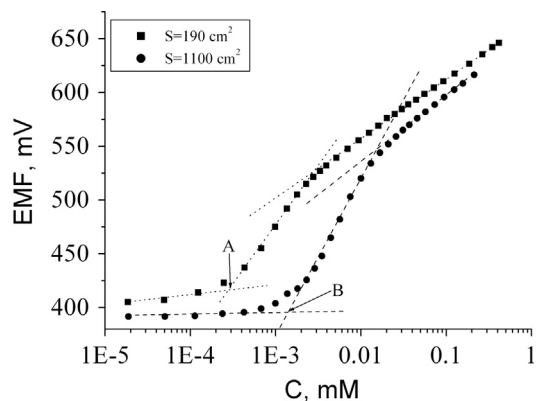


Fig. 2. Potentiometric study of CTAB adsorption on solid surfaces using PAMPS–CTA based electrode. (A, B – corresponds to CTAB amount required to cover all surface areas.)

Download English Version:

<https://daneshyari.com/en/article/1243577>

Download Persian Version:

<https://daneshyari.com/article/1243577>

[Daneshyari.com](https://daneshyari.com)