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

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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.

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 polydiallyldimethyammonium chloride, form stoichiometric complexes with

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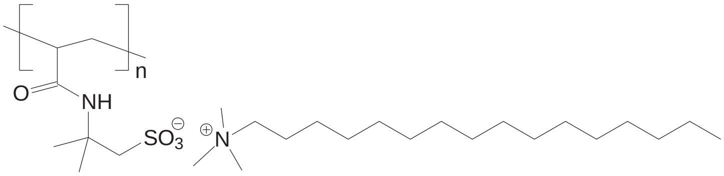
organic hydrophobic counterions by directly mixing in water or by polymerization of proper monomers [14–21]. In this paper we use PAMPS and set of ammonium surfactants to demonstrate the usability of PESC as ionophore to produce PVC membranes responsive to common surfactants. The structure of ionophore 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), cetylammonium (CA) or dodecylammonium (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 cm^2 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.

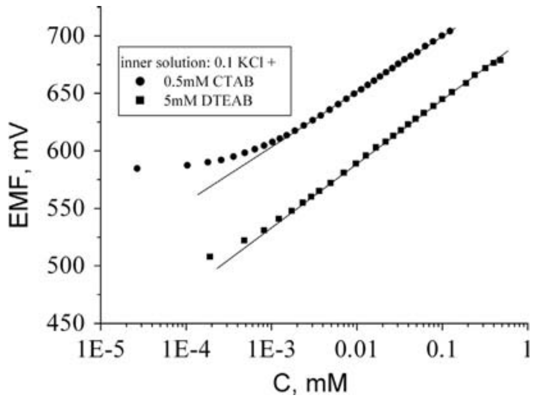


Fig. 1. Potential response to CTAB of two electrodes with CTA–DS ionophore and different electrode inner solutions.

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 cm^2 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 × 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/	55.9 ± 1.2	0.002–0.5	1	0.98 [23]
	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	
	DDA*HCl	30.8 ± 1.0	0.005–3.8	2	15 [23]
	SDS	− 47.6 ± 0.9	0.13–2	400	
PAMPS–DDA[b]	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%.

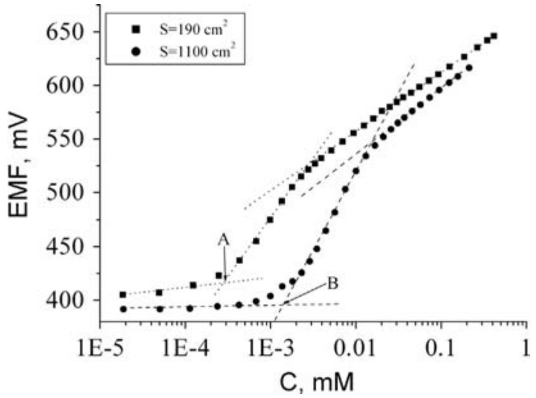


Fig. 2. Potentiometric study of CTAB adsorption on solid surfaces using PAMPS–CTA based electrode. (A, B – corresponds to CTAB amount required to cover all surface areas.)

3. Results

In this preliminary research, we used constant membrane composition reported to be workable with CTA–DS ionophore [22] which is the nearest analog to CTA–PAMPS PESC, although it was used in [22] for SDS-selective electrode. The only parameter varied was PESC constitution counterion, which regulates solubility and stability of PESC. Response times and low detection limits of the membranes might be dependent on membrane thickness and ionophore concentration and this could be the objective for further investigations. As it can be seen from Table 1, membrane with 3% ionophore shows better results, but for comparison with published data [22] we used 1% ionophore content for most experiments. In the present work we intended to explore some new polymeric derivatives, which may have some advantage in ion-selective membrane preparation.

In the first experiment, two inner solutions for the electrode were compared: 5×10^{-4} M CTAB+10^{-1} M KCl or 5×10^{-2} M DTEAB+10^{-1} M KCl (Fig. 1). Better results were obtained with DTEAB based solution. Worse results with CTAB may be due to CTAB micelle formation – in 10^{-1} M KCl its cmc is about 5×10^{-5} M. (Reproducibility of this cmc value for CTAB was used in further experiments as one of the reference points to compare different electrodes.)

CTAB is rather a complicated object for investigation. In addition to the ability of micelle formation which strongly depends on ionic strength of the solution, it is able to adsorb on different surfaces such as beaker walls, water–air interface, electrodes and membrane. At solution concentrations of about 10^{-7} M the quantity of adsorbed CTAB molecules is comparable with total quantity of CTAB in the system. (For 250 ml beaker containing 150 ml of the solution total area of the surfaces would be 190 cm^2.) The area of the polar head of the CTAB molecule is 0.75 nm^2 [23]; so to fill all surfaces 2.5×10^{16} CTAB molecules are required to form monolayer, which correspond to 150 ml of 2.8×10^{-4} mM solution (2.7×10^{-4} mM observed, point A in Fig. 2). As shown in Fig. 2 EMF response of electrode to CTAB addition below this concentration is weak. Just above this concentration strong non-linear EMF response is observed and above $c=2.5 \times 10^{-3}$ mM the electrode displays Nernstian EMF response. Similar behavior was observed in pure water or KCl, HCl or NaOH solutions. When polystyrene spheres ($d=2$ mm) with total surface area of 900 cm^2 were added to the solution, the amount of CTAB required to cover all surfaces was raised to 1.4×10^{17} molecules, which corresponds to a concentration of 1.6×10^{-3} mM and 1.4×10^{-3} mM was observed (point B in Fig. 2). Thus, the adsorption of CTAB should be taken in consideration; this is the reason why all CTAB concentrations (except Fig. 2) were corrected with a value of 2.8×10^{-4} mM.

Change in pH or ionic strength causes small change in slope (Fig. 3, Table 1).Variation of EMF while changing pH at constant CTAB concentration does not exceed 2 mV in the range of 4–9 pH units and 7 mV in the range of 1–13 pH units. One can find some data on pH influence in Fig. 3 and Table 1, where EMF vs CTAB concentration plots, slopes and linear ranges are presented for 0.1 M HCl (pH 1), 0.1 M NaOH (pH 12), water and 0.1 M KCl solutions (pH 7). 24 h drift of electrode potential was about 5 mV (at pH 7), 2 mV (at pH 1) for PAMPS–CTA and 7 mV (at pH 7), 12 mV (at pH 1) for DS–CTA ionophore in a solution containing 0.1 M KCl and DTEAB. The characteristics of the drift and reproducibility depend not only on the ionophore and membrane quality, but mainly on the performance of the whole measuring system. The slope of the electrode function and the dynamic concentration range persist at least for 4–5 months provided the conditioning procedure application or storage in solutions corresponds to the inner one to avoid the memory effect, after each measurement series.

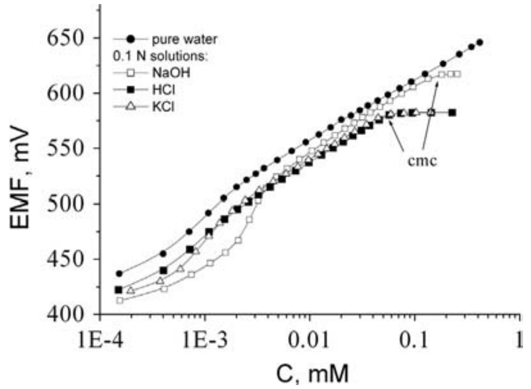


Fig. 3. PAMPS–CTA based electrode response to CTAB in different media (water, 0.1 N NaOH, 0.1 N HCl, and 0.1 N KCl).

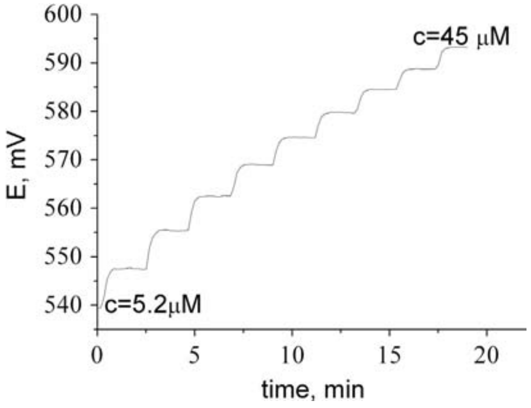


Fig. 4. Time response of CTA–PAMPS based electrode on step-wise CTAB addition.

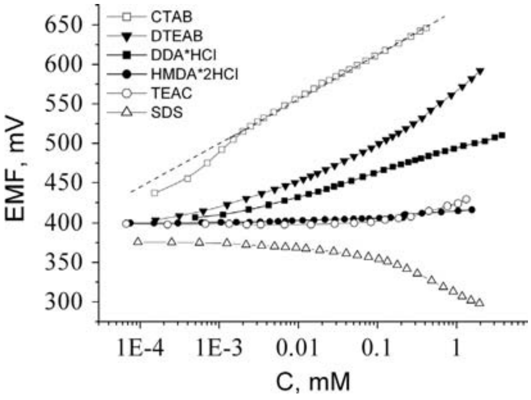


Fig. 5. CTA–PAMPS based electrode response to different analytes: CTAB, DTEAB (in 0.1 M KCl), DDA*HCl, hexanediamine dihydrochloride (HMDA*2HCl), tetraethylammoium chloride (TEAC), and SDS.

Detection limits and linear range for CTAB solutions in these cases are determined by cmc value (upper limit) and CTAB adsorption regime (lower limit). NaOH causes some anionic charge of glass surface which leads to enhanced CTAB adsorption and consequently increases detection limit in the used measuring cell.

Response time of CTA–PAMPS electrode to CTAB in the linear region was about 40 s. Fig. 4 shows electrode response to step-wise addition of CTAB every 130 s.

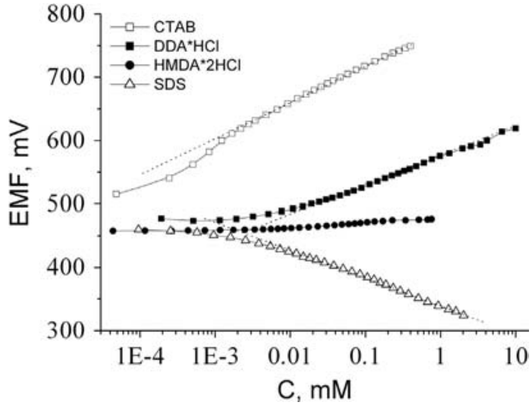


Fig. 6. DDA–PAMPS based electrode response to different analytes: CTAB, DDA*HCl, hexanediamine dihydrochloride (HMDA*2HCl), and SDS.

As shown in Fig. 5, CTA–PAMPS electrode demonstrates selective response to CTAB, much less response to other cationic surfactants, practically no response to non-surface-active organic cations, and displays some response to surface active anion SDS. The response of the electrode was Nernstian for CTAB only. Thus, selectivity of the membrane is determined mainly by ionophore component (CTA), but the membrane is responsive to substances with chemical structure similar to CTA. Surprisingly membrane doped with DDA–PAMPS ionophore shows better response to CTAB than to DDA*HCl (Fig. 6). This membrane displays good results (three decades of linear response) for SDS. The electrode response to SDS was expected because the ionophore consists of two counterparts – anionic polyelectrolyte and cationic surfactant – and can exchange both cations and anions. In [22] DS–CTA ionophore was used for SDS-responsive membrane. We assume that in the real system anionic and cationic surfactants do no present at the same time in the same solution at considerable concentrations, so there is no need to exclude SDS response. Moreover, the opportunity of using same electrode for cationic and anionic surfactants may be considered as an advantage.

Selectivity coefficients for dodecylammonium hydrochloride $\lg(K_{\mathrm{CTAB,\ DDA}}) = -4.2$, tetraethylammonium chloride $\lg(K_{\mathrm{CTAB,\ TEAC}}) = -5.0$, hexamethylene dihydrochloride $\lg(K_{\mathrm{CTAB,\ HMDA}}) = -5.4$ were determined using the fixed interference method considering CTAB as the principal cation and using 6×10^{-2} M for interfering cations [24].

For CTAB solution with fixed concentration of 0.022 mM measured value was 0.023 mM, SD in 12 repeats was 1.46%.

Titrimetric [25], spectrophotometric [26] and polarographic [27] techniques have been applied for determination of CTAB. Many approaches for the determination of the cationic surfactants involve an initial extraction process. However such methods usually need special sample pretreatment and are rather time-consuming. Simple PVC membrane electrodes provide chief express method for potentiometric determination of CTAB concentration. Detection limit by the potentiometric technique is less than for example the detection limit by the method indirect adsorptive stripping voltammetry on a hanging mercury-drop electrode [27], but the first one requires simple laboratory equipments.

The electrodes were used to determine cmc values of CTAB in acidic, alkaline and saline media (Fig. 3 and Table 1), to investigate CTAB adsorption on surfaces (example given in Fig. 2) and to investigate PESC formation for several systems, comprising of sodium poly(2-acrylamido-2-methylpropane sulfonate) PAMPS-Na, sodium poly(N-acryloyl-11-aminoundecanoate) and surfactants – CTAB, 11-acryloyloxyundecyltrimethylammonium bromide (AUTAB) (Fig. 7). In the latter case special ionophore PAMPS–AUTAB was prepared and used in membrane composition (1%).

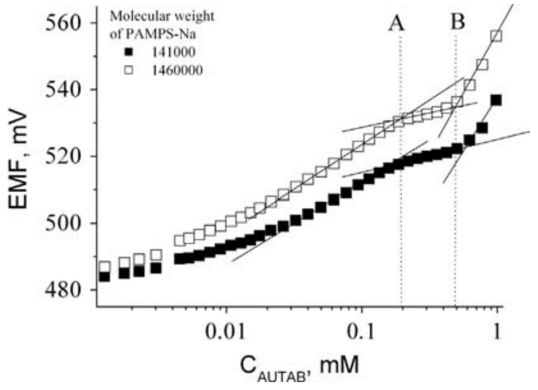


Fig. 7. Potentiometric investigation of PESC formation. Polyelectrolyte – PAMPS-Na, surfactant – AUTAB, ionophore PAMPS–AUTAB. For upper curve point A corresponds to the beginning of cooperative surfactant binding to polyelectrolyte (critical association concentration), point B corresponds to stoichiometric PAMPS to AUTAB amounts.

4. Conclusion

Organosoluble PESC appeared to be a versatile material to use as a surfactant-selective ionophore in ion-selective potentiometry. PVC membranes doped with PESC display nearly Nernstian slope for CTAB, DDAC and some other cationic surfactants, in the concentration range of 10^{-6}–10^{-3} M. The advantages of the proposed ionophore material are usability for cationic and anionic surfactants, ability of a simple and cheap preparation of ionophore for different surfactants, and up to six months stability of the membranes.

Acknowledgments

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