A NEW POTENTIOMETRIC SENSOR FOR POLYETHOXYLATED NONIONIC SURFACTANTS

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ABSTRACT

In the present work, a new sensing material based on tetraphenylborate salt of barium polyethoxylate (C_{16}/C_{18}-Fatty alcohol polyglycol ether, 80 EO groups) has been synthesized. The new sensing material was incorporated in PVC membrane using bis(2-ethylhexyl) phthalate as plasticizer. Philips IS-561 electrode body was used as the carrier. The electrode exhibited non-Nernstian response toward different polyethoxylated nonionic surfactants. Non-Nernstian electrode behaviour can be attributed to complexed stoichiometry of ion-exchange reactions in the membrane phase. The influence of several cations investigated on the electrode response was expressed as selectivity factor and determined using matched potential method. The sensor has been employed as end-point detector at potentiometric titration of various polyethoxylated nonionic surfactants, using sodium tetraphenylborate as titrant.

INTRODUCTION

Nonionic surfactants hold second place in worldwide surfactants consumption, with a share of the total use of surfactants of about 35%. Nowadays, the increasing awareness of environmental problems impose the obligation of analytical determination and monitoring of themself.
Almost all the analytical methods for determination of ethoxylated nonionic surfactants are based on the formation of tetraphenylborate salts of pseudocationic complexes of nonionics surfactants with some metal cations (mainly barium) [1-7].

EXPERIMENTAL

Reagents

- Barium chloride solution (c = 2 x 10^{-1} mol dm^{-3}),
- Sodium tetraphenylborate (c = 5 x 10^{-3} mol dm^{-3}) standard solution, containing 10 g polyvinyl alcohol per liter, was used as titrant and buffered with borate buffer solution pH 10.0,
- Nonionic surfactants: various, containing variable EO groups number (7-80),
- Polyethylenglycols: PEG 200, (4 EO); PEG 1000, (22,3 EO).

Apparatus

- The 794 Basic Titrino (Metrohm, Switzerland), an all-purpose titrator was used for the performing of potentiometric titrations.
- Silver/silver (I) chloride reference electrode (Metrohm, Switzerland); reference electrolyte c (NaCl) = 3 mol dm^{-3}

Preparation of pseudocationic tetraphenylborate ion-exchange complex

The sensing ion-exchange complex was prepared by mixing of 0.1 M barium chloride solution with 0.01 M nonionic surfactant Genapol T 800 solution, and subsequent addition of 0.1 M sodium tetraphenylborate solution. The formed white precipitate was extracted with dichlormethane, washed with water, and dried with sodium sulfate. The purified extract was evaporated at the room temperature and the precipitate was dissolved in mixture of diethyleter-methanol (1:1).
The solvent was evaporated at -18 °C and the isolated precipitate was used as sensing material for membrane preparation.

Electrode preparation

The electrode membrane was composed from bis(2-ethylhexyl) phthalate as plasticizer, PVC, high molecular weight and isolated ion-exchange complex as sensing material (2.5 %). Before the first titration the electrode must be preconditioned by carrying out two to three titrations of a pure surfactant solution.
Between measurements, the electrode was kept in distilled water. The lifetime of the electrode was several months in pure surfactant solutions, but decreased in more complex solutions.

RESULTS AND DISCUSSION

3.1. Response characteristics

Response toward ethoxylated nonionic surfactants

Barium ion forms pseudocationic complexes with ethoxylated nonionic surfactants (EONS) according to the following schema:

$$\mathrm{Ba}^{2+} + \mathrm{x\ EONS} \rightleftharpoons \left[\mathrm{Ba}\left(\mathrm{EONS}\right)_{\mathrm{x}}\right]^{2+} \quad (1)$$

The “x” value varies depending on the number of ethoxy (EO) units in the surfactant molecul. For the sake of simplicity the above equation can be written as follows:

$$\mathrm{Ba}^{2+} + \mathrm{x\ L} \rightleftharpoons \mathrm{BaL}_{\mathrm{x}}^{2+} \quad (2)$$

where L=EONS.
The corresponding formation constant is

$$K_{\mathrm{f}} = \frac{\left[\mathrm{BaL}_{\mathrm{x}}^{2+}\right]}{\left[\mathrm{Ba}^{2+}\right]\left[\mathrm{L}\right]^{\mathrm{x}}} \quad (3)$$

The sensor membrane contains hardly soluble pseudocationic tetraphenylborate ion-exchange complex as the sensing material, which is obtained by reaction of tetraphenylborate (TPB) ion with pseudocationic complex:

$$\mathrm{BaL}_{\mathrm{x}}^{2+} + 2\mathrm{TPB}^{-} \rightleftharpoons \mathrm{BaL}_{\mathrm{x}}\left(\mathrm{TPB}\right)_{2} \quad (4)$$

Its solubility product can be defined as $K_{\mathrm{sp}} = \left[\mathrm{BaL}_{\mathrm{x}}^{2+}\right]\left[\mathrm{TPB}^{-}\right]^{2}$ (5)

The sensor responds obviously to the both, TPB^{-} and $\mathrm{BaL}_{\mathrm{x}}^{2+}$ ions according to the Nernst equation:

$$E_{\mathrm{TPB}^{-}} = E^{0}_{\mathrm{TPB}^{-}} - S_{\mathrm{TPB}^{-}} \log\left[\mathrm{TPB}^{-}\right] \quad (6)$$

And $$E_{\mathrm{BaL}_{\mathrm{x}}^{2+}} = E^{0}_{\mathrm{BaL}_{\mathrm{x}}^{2+}} + S_{\mathrm{BaL}_{\mathrm{x}}^{2+}} \log\left[\mathrm{BaL}_{\mathrm{x}}^{2+}\right] \quad (7)$$

By inserting $\left[\mathrm{BaL_x^{2+}}\right] = K_\mathrm{f} \cdot \left[\mathrm{Ba^{2+}}\right]\left[\mathrm{L}\right]^\mathrm{x}$, obtained from Eq. (3), into Eq. (7):

$$E_{\mathrm{BaL_x^{2+}}} = E^0_{\mathrm{BaL_x^{2+}}} + S_{\mathrm{BaL_x^{2+}}} \log\left(K_\mathrm{f} \cdot \left[\mathrm{Ba^{2+}}\right]\left[\mathrm{L}\right]^\mathrm{x}\right) \quad (8)$$

i.e. $E_{\mathrm{BaL_x^{2+}}} = E^0_{\mathrm{BaL_x^{2+}}} + S_{\mathrm{BaL_x^{2+}}} \log K_\mathrm{f} + S_{\mathrm{BaL_x^{2+}}} \log\left[\mathrm{Ba^{2+}}\right] + S_{\mathrm{BaL_x^{2+}}} \log\left[\mathrm{L}\right]^\mathrm{x}$ and after substituting:

$$E^0_\mathrm{L} = E^0_{\mathrm{BaL_x^{2+}}} + S_{\mathrm{BaL_x^{2+}}} \log K_\mathrm{f} + S_{\mathrm{BaL_x^{2+}}} \log\left[\mathrm{Ba^{2+}}\right] \quad (9)$$

and designating $E_{\mathrm{BaL_x^{2+}}} = E_\mathrm{L}$, the following forms are obtained:

$$E_\mathrm{L} = E^0_\mathrm{L} + S_{\mathrm{BaL_x^{2+}}} \log\left[\mathrm{L}\right]^\mathrm{x} \quad (10)$$

i.e.

$$E_L = E^0_L + S_{BaL_x^{2+}} \cdot x \log\left[L\right] \quad (11)$$

and the substitution of $S_{\mathrm{BaL_x^{2+}}} \cdot x = S_\mathrm{L}$ leads to the equation

$$E_\mathrm{L} = E^0_\mathrm{L} + S_\mathrm{L} \log\left[\mathrm{L}\right] \quad (12)$$

The barium ion originates from the dissociation of the formed pseudocationic complex:

$$\mathrm{BaL_x^{2+}} \rightleftharpoons \mathrm{Ba^{2+}} + \mathrm{x\,L} \quad (13)$$

which results from the dissociation of the sparingly soluble ion exchange complex:

$$\mathrm{BaL_x\left(TPB\right)_2} \rightleftharpoons \mathrm{BaL_x^{2+}} + 2\,\mathrm{TPB^-} \quad (14)$$

The concentration of the ion-exchange complex, dissolved in the plasticizer, in the membrane phase is constant for the membrane defined. Therefore is the concentration of the pseudocationic complex $\mathrm{BaL_x^{2+}}$ constant too, and defined by the solubility product, Eq. (5). Consequently the barium ion concentration can also be considered as constant. The nonionic surfactant electrode (NSE) responses toward several selected polyethoxylated nonionic surfactants and polyethylenglycols are shown in Fig. 1. The response characteristics followed by the corresponding statistics are given in Table 1.

PARAMETERS	SURFACTANT INVESTIGATED		
	Triton X-100 $n_{EO} = 10$	Brij 35 $n_{EO} = 23$	Genapol T 800 $n_{EO} = 80$
Slope (mV/decade)	37.3 ± 1.1	46.0 ± 2.5	34.5 ± 0.3
Correlation coefficient (r)	0.9988	0.9970	0.9997
Detection limit (mol/dm^3)	5.8×10^{-6}	3.3×10^{-5}	4.5×10^{-6}
Useful conc. range (mol/dm^3)	6.0×10^{-6} - 4.0×10^{-4}	5.0×10^{-5} - 4.7×10^{-4}	5.7×10^{-6} - 2.2×10^{-3}

Table 1 Response characteristics of the NSE toward several selected nonionic surfactants given together with ± confidence limits.

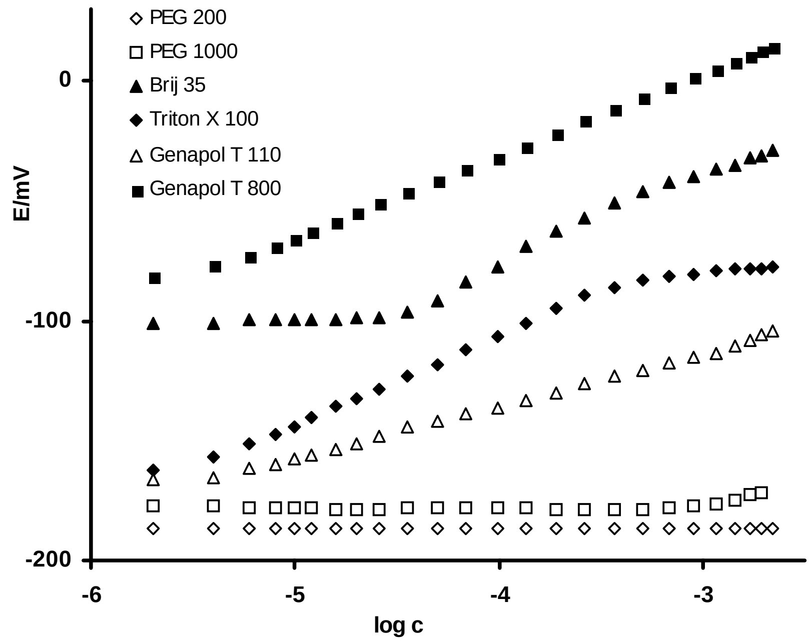

Figure 1. The NSE responses toward several polyethoxylated nonionic surfactants and polyethylenglycols.

3.2 Interferences

The EONS response of the sensor investigated is given by Eq. (12): $E_{\mathrm{L}} = E^0_{\mathrm{L}} + S_{\mathrm{L}} \log c_{\mathrm{L}}$.

The electrode (sensor) response toward the interfering ion Int is given by:

$$E_{\mathrm{Int}} = E^0_{\mathrm{Int}} + S_{\mathrm{Int}} \log c_{\mathrm{Int}} \qquad (15)$$

The both responses refer to the linear part of the function $E = \mathrm{f}\left(\log c_{\mathrm{L}}\right)$ and $E = \mathrm{f}\left(\log c_{\mathrm{Int}}\right)$.

The influence of several inorganic cations to the electrode response characteristics was investigated, expressed as selectivity factor and determined using matched potential method (MPM). This method is totally independent of the Nikolskii-Eisenman equation, but strongly dependent of the experimental conditions, primarily concentration.

Thereby the selectivity factor is defined as the activity (concentration) ratio of the primary ion (molecule) and the interfering ion which gives the same potential change in a reference solution:

$$k^{\mathrm{MPM}}_{\mathrm{IJ}} = \frac{\Delta a_{\mathrm{I}}}{\Delta a_{\mathrm{J}}} \qquad (16)$$

where a_{I} and a_{J} are the activities of the primary and interferent ion respectively.

To determine the selectivity factor, one would measure the change in potential upon changing the primary ion (molecule) activity (concentration). The interfering ion would then be added to an identical reference solution until the same potential change is obtained, *i.e.:* $E_{\mathrm{L}} = E_{\mathrm{Int}}$.

By all the measurements Triton X-100 was conventionally used as reference nonionic surfactant. The calculated selectivity factors are given in Table 2.

Interferent	k_{ij}^{MPM}
NH_4^+	0.0003
Li^+	0.0026
Na^+	0.14
K^+	0.10
Mg^{2+}	0.25
Ca^{2+}	0.35
Sr^{2+}	0.13
Ba^{2+}	0.77
Cu^{2+}	0.34
Zn^{2+}	0.10
Pb^{2+}	0.76

Table 2 Potentiometric selectivity factors (k_{ij}^{MPM} *) for different inorganic cations obtained by matched potential method (MPM) for the NSE electrode (the concentration of Triton X-100 was 1 x* 10^{-4} *mol* dm^{-3}*).*

For the sake of comparison the all selectivity factors are calculated at the definite concentration of Triton X-100 (10^{-4} mol dm^{-3}).
The small inorganic cations (NH_4^+, Li^+) practically do not interfere at the measured concentration level of Triton X-100. The alkaline earth metals interfere more strongly. Barium and lead interfere seriously according to the expectation (see Eq. (1).
The sensor can be used in a wide pH range (3 - 11). Anionic surfactants do not interfere at potentiometric titration of EONS. Cationic surfactants interfere strongly.

3.3. Potentiometric titration of pure and technical grade ethoxylated nonionic surfactants

The main application of the sensor investigated is the end-point detection at potentiometric titration of barium-ethoxylated nonionic surfactant pseudocationic complexes using sodium tetraphenylborate as titrant. A series of polyethoxylated nonionic surfactants containing 7 to 80 EO groups have been titrated potentiometrically using the sensor mentioned. The resulting potentiometric titration curves of some selected nonionic surfactants, covering the entire range of EO groups investigated, are shown in Fig. 2. The values of the stoichiometric factors calculated from the titrations performed are given in Table 3.

Surfactant Investigated	Mean M_r declared	Mean number of EO groups	Stoichiometric constant, $n(OEU)/n(BPh_4^-)$* (found ± std.dev)
Genapol OX 070	510	7	5.51 ± 0.07
Dehydol LT 7	515	7	4.94 ± 0.08
Slovasol 458	570	8	5.54 ± 0.07
Genapol O 080	615	8	5.20 ± 0.06
Arkopal N 090	620	9	5.33 ± 0.16
Triton X-100	647	10	5.42 ± 0.03
Genapol OX 100	645	10	5.50 ± 0.12
Slovasol 6811	738	11	5.73 ± 0.04
Genapol T 110	745	11	5.38 ± 0.02
Genapol T 150	920	15	5.60 ± 0.04
Empilan NP 20	1100	20	5.97 ± 0.06
Genapol O 200	1143	20	5.62 ± 0.08
Brij 35	1200	23	6.21 ± 0.03
Genapol T 800	3780	80	5.71 ± 0.03

* average of 5 determinations ± σ_{N-1}

Table 3. Results of potentiometric titrations of some selected ethoxylated nonionic surfactants using sodium tetraphenylborate (c = 5 x 10^{-3} mol dm^{-3}) as titrant and NSE as indicator.

It can be seen, that the stoichiometric constant values reveal increasing tendency with the increasing number of EO groups in the surfactant molecul indepedently of the chemical nature of the surfactant. The change of EMF value at the inflexion of the titration curves increases with the increasing number of EO groups in the surfactant molecul as well. By titration of surfactants with lower number of EO groups, the symmetric titration curves are obtained, while those of surfactants with higher EO groups number are more asymmetric (except nonylphenol polyglycol ethers). The degree of asymmetry increases with the increasing number of EO groups.

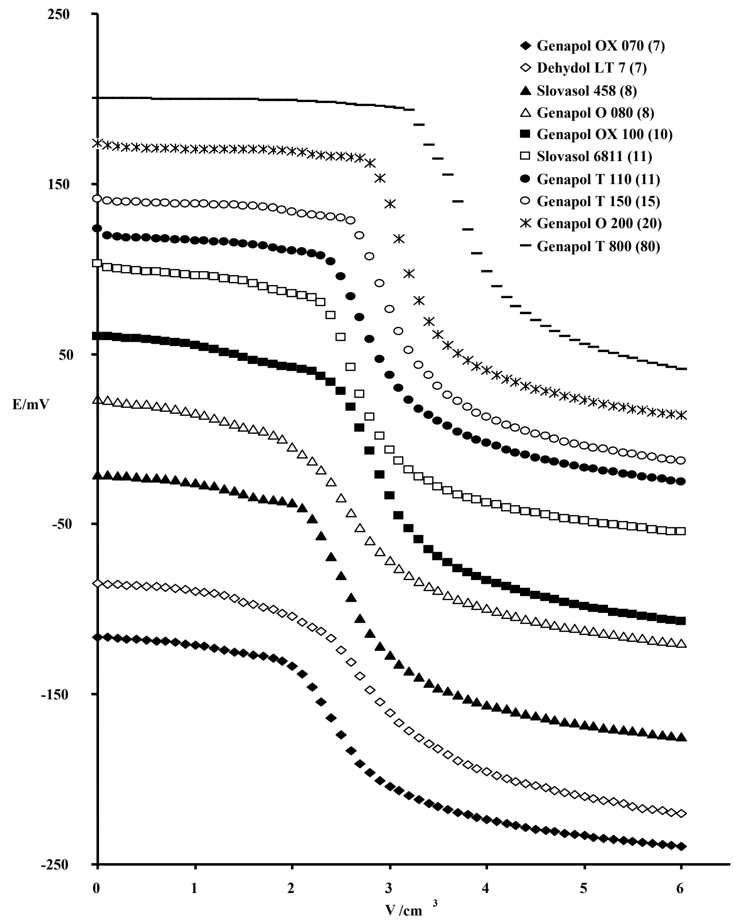

Figure 2. Titration curves of selected nonionic surfactants with NSE using 5 x 10^{-3} mol dm^{-3} sodium tetraphenylborate as titrant. Here and in further figures some curves are displaced laterally or vertically for clarity. The values in parenthesis in the figure legend refer to EO groups number of the particular surfactant.

CONCLUSION

A liquid membrane nonionic surfactant sensitive electrode has been prepared, based on a new pseudocationic tetraphenylborate ion-exchange complex as sensing material incorporated into the plasticized PVC-membrane. The non-Nernstian response of the electrode toward different nonionic surfactants can be explained by variable number of ethoxy groups of each particular surfactant investigated. The main application of the electrode described was indication of the end-point in potentiometric titration of EONS in form of their barium pseudocationic complexes using sodium tetraphenylborate as titrant. A series of polyethoxylated nonionic surfactants containing 7 to 80 EO groups have been succesfully titrated. The accuracy and precision of the determination has been evaluated by using standard addition method. The values of the stoichiometric factors for surfactants investigated were calculated from the titrations performed. The response mechanism of the sensor toward the neutral EONS molecule was proposed. The sensor can be used for titrations within pH range 3 - 11. Anionic surfactants and polyethylenglycols do not interfere at potentiometric titration of EONS. Cationic surfactants interfere strongly. The selectivity performances of the electrode toward some alkaline, alkaline earth and heavy metal cations, expressed as selectivity factor were determined using matched potential method.

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