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Separate detection of homologous surfactants by means of solid-contact unmodified and modified with molecular sieves potentiometric sensors

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Abstract

To improve the selectivity of surfactant sensors, the surface of their membranes was modified with molecular sieves with predetermined pore sizes. Water-soluble anionic, cationic and non-ionic surfactants were used as pore generators in the molecular sieves and introduced into the source membrane at the stage of its formation. The modified sensors enable detection of alkylsulfates homologues and alkylpyridinium with different lengths of the hydrocarbon chain (C_{10}–C_{18}); homologous poly(oxyethylated nonylphenols) differing in the number of oxyethyl groups (m = 10–100).

A novel approach to separate detection of surfactant homologues implies the usage of inselective sensors as a multisensor system. The software-supported multisensor approach allows information of both mixture composition and concentrations of separate components in multicomponent systems to be obtained with a certain accuracy. Inselective non-modified sensors with the highest cross-sensitivity were used to design multisensor systems like an “electronic tongue”.

The cross-sensitivity parameters of both source and modified sensors were estimated and the possibility of their usage in multisensor systems like an “electronic tongue” for analysis of multicomponent solutions of homologous surfactant is shown. Analytical signals were processed by artificial neural networks.

Keywords: Surfactants; Potentiometric sensors; Electronic tongue; Artificial neural networks

1. Introduction

The wide usage of synthetic surfactants in various fields focuses much attention on the development and improvement of analytical techniques for both surfactant quality control and their detection in environmental objects. Synthetic surfactants not being, as a rule, individual compounds make their detection in various objects rather difficult. Quantitative surfactant determination means establishing the molecular-mass distribution of anionic and cationic surfactants by their hydrophobic chain and that of non-ionic ones by oxyethylation degree (the number of oxyethyl groups).

The variety of surfactant types causes a huge number of separation techniques with subsequent detection of homologous surfactants by means of various methods. To this end, chromatography [1–5], capillary zone electrophoresis [6–9], capillary isotachophoresis [10,11], reverse osmosis [12], ultrafiltration and microfiltration [13], chromato-mass spectrometry [14] are most often employed.

There has been an attempt to determine mixtures of surfactants employing a set of potentiometric sensors with different selectivities [15].

Selective-electrode potentiometry is a promising technique for detection of synthetic surfactants. Simultaneous de-

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tection of several components by means of direct potentiometry, however, is possible in some cases only, high-selective sensors are needed and some limitations are imposed on the composition of the solution under analysis.

Common potentiometric sensors enable either individual surfactants as well as the total content of those of certain types to be detected [16]. Modification of the electrode surface with some chemical compounds, polymeric films, covalently bound monolayers, clay and zeolite coatings is an important tool for raising the selectivity of electrochemical sensors. A number of ways of direct modification of the membrane surface of ion-selective electrodes, some aspects of making modified electrodes and their usage in analysis are reviewed in [17–23].

Membrane coatings and molecular sieves are most often used by means of their deposition from solution with subsequent removal of the solvent by drying in air [24,25]. On rinsing the resulting thin film with distilled water and drying, a porous polymeric material appears, the pore diameters corresponding to the sizes of the pore-generating molecules. In order to enhance the selectivity of such sensors, modification of the membrane surface with nylon, chitin, poly(methacrylate), poly(vinyl chloride) molecular sieves was proposed [26–28].

A multisensor approach is put forward in the literature for fast qualitative and quantitative examination of multicomponent solutions; it is based on the usage of inselective sensor arrays with subsequent mathematical treatment of analytical signals, mainly, by means of artificial neural networks [30–32,34–37,39,41,43]. Neural networks solve problems of image recognition and treatment: prediction, classification of data by a set of classes, function approximation with a set of points (regression), data clustering with searching for known classes-prototypes, information compression, restoring lost data, optimization and optimal control, etc. Neural networks are nonlinear in nature, being a tool of modeling which allows extremely complex dependencies to be reproduced. The neural network is used when no explicit dependence between input and output data is known, it is found in the course of training. The usage of multisensor systems like an "electronic tongue" is described for detection of lysin in food, for analysis of waters (natural, ground, drilling), quality control of wine, milk, various beverages (tea, coffee, beer, soft ones, juice, etc.) [29–43].

In the present work, we propose modification of ion-selective membranes with nanofiltering sieves with different pore diameters and the design of sensor matrices ("electronic tongue") on the basis of poor-selective electrodes sensitive to anionic, cationic and non-ionic surfactants for separate detection of homologous ionic (sodium alkylsulfates, alkylpyridinium chloride) and non-ionic (polyoxyethylated nonylphenols) surfactants.

2. Experimental

Homologous sodium alkylsulfates, alkylpyridinium chlorides and polyoxyethylated nonylphenols with a purity of 96–98% were used (Table 1). Source surfactant solutions (1.0×10^{-2}–1.0×10^{-3} mol L^{-1}) were prepared by weight; working solutions (1.0×10^{-3}–1.0×10^{-6} mol L^{-1}) were obtained by dilution.

Dibutylphthalate (DBP) and tetrahydrofuran (THF) were purified by fractionating distillation. The poly(vinyl chloride):dibutylphthalate wt. ratio was 1:3 and 1:2, the active component concentration $C_{EAC} = 0.001$ and 0.1 mol/kg of DBP for ionic and non-ionic surfactant sensors, respectively. Alkylpyridinium-alkylsulfates and alkylpyridinium-tetraphenylborates (e.g., cetylpyridinium-dodecylsulfate for CP-DDS, cetylpyridinium-tetraphenylborate for CP-TPB) were used as electrode-active compounds (EAC) of membranes sensitive to ionic surfactants, for non-ionic surfactant sensors – compounds of polyoxyethylated nonylphenols (NP-10, NP-12) or alcohol (syntanol DS-10) with barium and tetraphenylborate ions (e.g., nonylphenol-12-Ba-tetraphenylborate for NP-12-Ba-TPB).

Solid-contact potentiometric sensors with plasticized membranes (graphite as an electronic conductor) were examined. The membrane surface of these sensors was modified with poly(vinyl chloride) molecular sieves. Water-soluble alkylsulfates, alkylpyridinium cations, polyoxyethylated nonylphenols were employed as pore generators [26–28].

The synthesized molecular sieves with predetermined pore sizes ($C_{surf} = 0.2$–2%) were based on an inert poly(vinyl chloride) matrix plasticized with dibutylphthalate. To prepare the sieve composition, weighted samples of the solvent–plasticizer and pore-generating surfactant (the molecule sizes to match the pore sizes of the molecular sieve) were placed into a beaux, then 2 mL of tetrahydrofuran was added under permanent stirring with a magnetic stirrer, and a weighted sample of poly(vinyl chloride) was gradually added. The sieve composition obtained was poured into a Petri bowl and left for 2–3 days. On complete evaporation of the solvent, an elastic transparent film was placed into a beaker with 500 mL of distilled water and left for 7 days, the water to be freshened every 24 h. The completeness of surfactant removal from the molecular sieves was checked potentiometrically by means of solid-contact non-modified sensors.

To modify the membrane, the molecular sieves were stuck on the surface with a special glue (a blend of poly(vinyl chloride) and dibutylphthalate), then the sensors were kept in air during 24 h.

Prior to usage, both source and modified electrodes were conditioned for 24 h in a 1.0×10^{-3} mol L^{-1} solution of cetylpyridinium chloride (cationic surfactant sensors), sodium dodecylsulfate (anionic surfactant sensors) and distilled water (non-ionic surfactant sensors). Potentiometric measurements were made on an I-130 M universal ionomer with an accuracy of ±1 mV. A silver chloride electrode served as a reference one.

To design multisensor systems like an "electronic tongue", arrays of poor-selective sensors based on various electrode-active substances were used. The potentiometric selectivity coefficients K_{ij}^{pot} were estimated using the method of bi-ionic

Table 1
Types of surfactants

Name	Abbreviation	Formula	Purity (%)
Anionic surfactants			
Sodium decylsulfate	DS	$C_{10}H_{23}$—OSO_3Na	96
Sodium dodecylsulfate	DDS	$C_{12}H_{25}$—OSO_3Na	96
Sodium tridecylsulfate	TDS	$C_{13}H_{27}$—OSO_3Na	88
Sodium tetradecylsulfate	TTDS	$C_{14}H_{29}$—OSO_3Na	89
Sodium hexadecylsulfate	HDS	$C_{16}H_{33}$—OSO_3Na	92
Sodium decylsulfonate	DSN	$C_{10}H_{23}$—SO_3Na	96
Sodium hexadecylsulfonate	HDSN	$C_{16}H_{33}$—SO_3Na	95
Cationic surfactants			
Decylpyridinium chloride	DP	$[CH_3$—$(CH_2)_9$—$C_5H_4N]Cl$	77
Undecylpyridinium chloride	UDP	$[CH_3$—$(CH_2)_{10}$—$C_5H_4N]Cl$	86
Dodecylpyridinium chloride	DDP	$[CH_3$—$(CH_2)_{11}$—$C_5H_4N]Cl$	98
Pentadecylpyridinium chloride	PDP	$[CH_3$—$(CH_2)_{14}$—$C_5H_4N]Cl$	96
Cetylpyridinium chloride	CP	$[CH_3$—$(CH_2)_{15}$—$C_5H_4N]Cl$	99
Octadecylpyridinium chloride	ODP	$[CH_3$—$(CH_2)_{17}$—$C_5H_4N]Cl$	99
Nonionic surfactants			
Nonylphenol-10	NP-10	NP-10 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{10}H$	98
Nonylphenol-12	NP-12	NP-12 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{12}H$	99
Nonylphenol-22	NP-22	NP-22 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{22}H$	98
Nonylpheno-30	NP-30	NP-30 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{30}H$	97
Nonylphenol-40	NP-40	NP-40 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{40}H$	97
Nonylphenol-60	NP-60	NP-60 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{60}H$	96
Nonylphenol-100	NP-100	NP-100 C_9H_{19}—C_6H_4—O—$(C_2H_4O)_{100}H$	98
Syntanol DS-10	DS-10	C_nH_{2n+1}—O—$(C_2H_4O)_mH$, $n = 10$–18, $m = 8$–10	96

potentials and mixed solutions [44], the cross-sensitivity parameters were determined according to Ref. [45]. The sensing signals of the array were processed by three-layer artificial neural network with an error-back-propagation learning algorithm. The Neuro Pro 0.25 software (Institute of Computational Modelling, Russian Academy of Sciences) was employed.

The structure of the surface of our poly(vinyl chloride) membranes and molecular sieves was studied by means of electron microscopy (a BS-50 translucent electronic microscope, $U = 60$ kV, $I = 20$ mcA; Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, Saratov). The electronic microscope (a 10,000 magnification) allows holes of 10 nm to be visualized.

3. Results and discussion

The potentiometric selectivity coefficients of our ion-selective membranes with respect to alkylsulfates, alkylpyridinium cations, polyoxyethylated nonylphenols, calculated by the mixed solution method are close to unity (0.6–1), i.e. the electrodes enable detection of either individual surfactants or the total content of those of certain types. Table 2 presents the potentiometric selectivity coefficients of the non-modified sensors sensitive to anionic surfactants, as an example.

The potentiometric selectivity coefficients of the modified electrodes reduce by 3–4 orders of magnitude, which provide

Table 2
Potentiometric selectivity coefficients of the sensors sensitive to anionic surfactants (alkylsulfate being the main ion in the membrane, $n = 3$, $P = 0.95$)

EAC (ions)	Hindering			
	DDC	TDC	TTDC	HDC
DDP-DDC	–	0.63 ± 0.03	0.68 ± 0.01	0.71 ± 0.02
DDP-TDC	0.67 ± 0.02	–	0.70 ± 0.04	0.79 ± 0.01
DDP-TTDC	0.73 ± 0.05	0.75 ± 0.02	–	0.78 ± 0.02
DDP-HDC	0.80 ± 0.02	0.82 ± 0.03	0.83 ± 0.04	–
CP-DDC	–	0.88 ± 0.01	0.94 ± 0.01	0.96 ± 0.04
CP-TDC	0.86 ± 0.01	–	0.93 ± 0.03	0.96 ± 0.03
CP-TTDC	0.94 ± 0.04	0.98 ± 0.06	–	0.98 ± 0.02
CP-HDC	1.00 ± 0.02	0.98 ± 0.02	1.00 ± 0.05	–

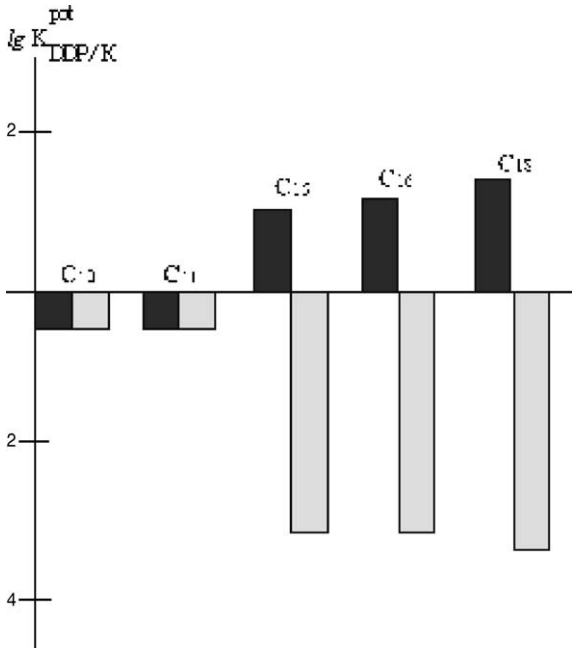

Fig. 1. Potentiometric selectivity coefficients log $K^{pot}_{DDP/K}$ of cationic surfactant sensors: EAC – CP-TPB, DDP as a pore generator: (■) non-modified; (■) modified.

the possibility of separate homologous surfactants detection. Fig. 1 presents, as an example, data on the selectivity coefficients of dodecylpyridinium with respect to alkylpyridinium cations (dodecylpyridinium chloride as a pore generator). One can see that K^{pot}_{ij} with respect to undecyl- and decyl pyridinium do not change since these anions are not retained by the molecular sieve. For pentadecyl-, cetyl- and octadecylpyridinium, the potentiometric selectivity coefficients decrease by several orders of magnitude.

Table 3 presents the electroanalytical characteristics of both source and modified sensors in solutions of anionic, cationic and non-ionic surfactants. The electromotive force of cetylpyridinium-dodecylsulfate electrode indicated a rectilinear behavior in the range from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} in sodium dodecylsulfate solutions. The slopes are close to the theoretical ones for univalent ions (58 ± 2 mV/pC). The ionic associate of cetylpyridinium-tetraphenylborate provides a cationic selectivity in 1.0×10^{-6}–1.0×10^{-3} mol L^{-1} cetylpyridinium chloride solutions, the slope being equal to 57 ± 2 mV/pC, which means transfer of univalent ions. The deviation of the electrode functions from linearity is due to solubility of the active components of the membranes in 1.0×10^{-5} (1.0×10^{-6}) mol L^{-1} solutions and micelle formation above 1.0×10^{-2} (1.0×10^{-3}) mol L^{-1} solutions.

The appearance of a membrane potential of non-ionic surfactant sensors is associated with dissociation of the complex cations [surfactant-BA]$^{2+}$ inside the membrane, transfer of metal ions through the membrane–solution interface with subsequent complex formation in the solution phase and extraction in dibutylphthalate [46,47]. This is confirmed by the value of the electrode function slope characteristic of bivalent ions. A significant response time of non-ionic surfactant sensors is also due to this factor. The significant response time of non-ionic surfactant sensors is due to the complex nature of potential formation (Table 3).

Membrane surface modification with proper poly(vinyl chloride) molecular sieves was found to exert no effect on their chief electrochemical characteristics; a shorter service life is apparently due to pores sticking. The filtrating ability of molecular sieves depends on the sizes of pore-generating molecules. The data in Table 3 tell that the molecular sieve lets pass only those surfactants whose molecules are smaller of comparable in size with the pore generator. Bigger ions are retained and exhibit no electrode functions.

Both source and modified non-ionic surfactant sensors possess the same linearity intervals and slopes of their electrode functions in solutions of nonylphenols with 10 and 12 oxyethyl groups. For nonylphenols with more oxyethyl

Table 3
Electrochemical characteristics of non-modified and modified solid-contact surfactant sensors in solutions of homologues of anionic, cationic and non-ionic surfactants ($n = 3$, $P = 0.95$)

EAC	Analyte(s)	Pore generator	Linear range (mol L^{-1})	Slope, α (mV/pC)	Detection limit (mol L^{-1})	$t_{0.95}$, min (C: $1 \times 10^{-4} \rightarrow 1 \times 10^{-3}$)	Potential shift (mV/day)	Service life (months)
CP-DDS	DDS	–	1×10^{-6}–1×10^{-2}	58 ± 4	8.9×10^{-7}	0.3–0.7	2–3	12
	DDS	DDS	1×10^{-6}–1×10^{-2}	59 ± 4	9.0×10^{-7}	1–2	2–3	4–5
	TTDS	DDS	1×10^{-6}–1×10^{-3}	20 ± 2	–	1–2	2–3	4–5
	DDS + TTDS (1:1)	DDS	1×10^{-6}–1×10^{-4}	57 ± 1	9.0×10^{-7}	1–2	3–5	4
CP-TPB	DDP	–	1×10^{-6}–1×10^{-3}	57 ± 2	9.0×10^{-7}	1–2	0.5–1	10
	DDP	DDP	1×10^{-6}–1×10^{-3}	56 ± 2	9.1×10^{-7}	2–3	0.5–1	4–5
	CP	DDP	1×10^{-6}–1×10^{-3}	17 ± 6	–	3–4	1–2	4–5
	DDP + CP (1:1)	DDP	1×10^{-6}–1×10^{-4}	56 ± 3	9.1×10^{-7}	3–4	1–2	4
NP-12-Ba-TPB	NP-12	–	1×10^{-5}–1×10^{-2}	28 ± 1	9.0×10^{-6}	3–4	3–4	6–7
	NP-12	NP-12	1×10^{-5}–1×10^{-2}	32 ± 1	9.2×10^{-6}	4–5	3–4	4
	NP-30	NP-12	1×10^{-5}–1×10^{-2}	11 ± 3	–	4–5	4–5	4
	NP-12 + NP-30 (1:1)	NP-12	1×10^{-5}–1×10^{-3}	32 ± 2	9.2×10^{-6}	4–5	4–5	3

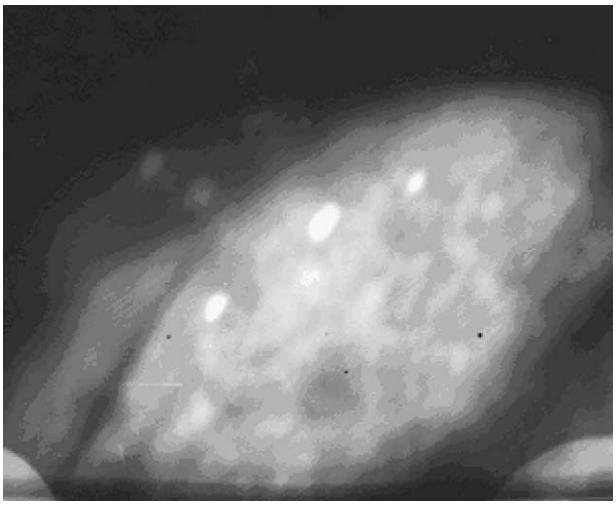

Fig. 2. A photo of the molecular sieve on NP-100 (a BS-500 electronic microscope, $U = 60$ kV, $I = 20$ μA).

groups, the slopes of the electrode function are significantly less than the theoretical value, i.e. poly(vinyl chloride) molecular sieves retain nonylphenols with more oxyethyl groups.

The surface structure of poly(vinyl chloride) membranes and molecular sieves was examined by electron microscopy. Photographs of the molecular sieves (polyoxyethylated nonylphenol NP-100 as a pore generator) were obtained, a non-uniformity of the surface of the poly(vinyl chloride) films under study was established, the pore sizes ranging within 55–100 nm. Such differences are apparently due to possible aggregation of nonylphenol molecules (Fig. 2).

The separability of poly(vinyl chloride) molecular sieves in analysis of 2–3 component model mixtures of polyoxyethylated nonylphenols, alkylpyridinium chlorides, sodium alkylsulfates is illustrated by the diagrams shown in Fig. 3. The detection was carried out at different component ratios

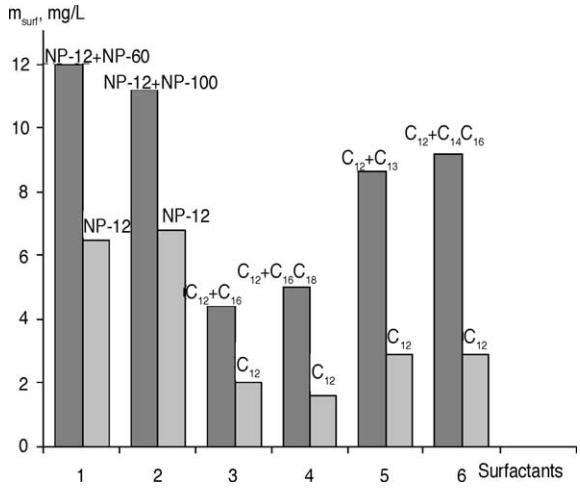

Fig. 3. Separate detection of homologous surfactants in binary and ternary model systems by means of modified sensors: poly(oxyethylated nonylphenols) (1 and 2), alkylpyridinium chlorides (3 and 4), sodium alkylsulfates (5 and 6); (■) added; (▩) found.

(10:1–1:10) and at varying concentrations (1.0×10^{-5}–1.0×10^{-3} mol L^{-1}). The surfactants were quantitatively determined by means of the modified solid-contact electrodes.

The results presented in Fig. 3 are direct evidence of the filtering ability of poly(vinyl chloride) molecular sieves (the relative standard deviation $S_r \leq 0.06$ at the number of repetitions $n = 3$ and the confidence level $P = 0.95$). It should be noted that the sensors modified with molecular sieves can be used for detection of only one homologue in a mixture.

The identity of the electrochemical characteristics of the sensors based on various electrode-active compounds and their inselectivity form the basis for multisensor systems like an "electronic tongue". Vlasov et al. [45] propose the following parameters of cross-sensitivity for evaluation of electrode eligibility for a multisensor systems: the average electrode slope (S, mV/pC), the inselectivity factor (F), the reproducibility factor (K): $S_{cp.} = (1/n)\sum S_i$, $F = S_{cp.}/s^2$, $K_{cp.} = (1/n)\sum(S_{cp.}/s_i^2)$, where S_i is the slope of the electrode function in an ith ion solution, n the number of ions, s the mean-square deviation of the average slope (which represents value scattering in this case) and s_i the mean-square deviation of S_i.

The higher the values of the named parameters, the higher the cross-sensitivity of the sensor. The inselectivity factor characterizes the "uniformity" of the sensor's sensitivity to given ions. The higher the value of F, the more uniformly sensitive the given sensor to all the ions. The reproducibility factor characterizes the integral reproducibility of the sensor's electrode function; the higher its value, the more reproducible the sensor's electrode behavior. It should be mentioned that all the three parameters are important at selecting a sensor with a high cross-sensitivity for multisensor analysis [48].

In the present work, a quantitative estimation of the said parameters of both source and modified sensors was carried out. To estimate the cross-sensitivity parameters, the electromotive force was recorded as a function of the concentration of the individual homologues in solution. Using the electrode function slopes, the average slope, the factors of reproducibility and selectivity were calculated.

Table 4 provides an example of the cross-sensitivity parameters of sensors selective to univalent homologues of sodium alkyl sulfates. For the anionic surfactant sensors under study, the value of the average electrode slope varies within 24–68 mV/pC, the inselectivity factor takes on values from 0.07 to 7.17, the reproducibility factor varies within 15.23–133.94. These sensors can be divided into four groups by their response to the concentration of alkylsulfate ions (Fig. 4). The first group includes sensors (No. 1–8) with low values of both the average electrode slope (24–28) and inselectivity factor (0.05–0.08). Such values speak for a high selectivity of the sensors to the potential-determining ion. The sensors of the second (No. 9–16) and third (No. 17–24) groups possess high values of the average slope of the electrode functions (39–45 and 47–55, respectively), and higher values of the inselectivity factor, which means their lower selectivity. The reproducibility factors of the sensors from these

Table 4
Slopes of the electrode functions and the cross-sensitivity parameters of surfactant sensors in solutions of sodium alkylsulfate and alkylpyridinium chlorides ($n = 3$, $P = 0.95$)

Sensor	Membrane composition (EAC)	Molecular sieve	Slope α in solutions of homologues (mV/pC)				S (mV/pC)	F	K
			DDS	TDS	TTDS	HDS			
1	DDP-DDS	DDS	52 ± 3	23 ± 4	14 ± 2	8 ± 4	24	0.07	15.86
2	DDP-TDS	DDS	53 ± 2	26 ± 6	19 ± 2	11 ± 7	27	0.08	15.72
3	DDP-TTDS	DDS	58 ± 2	29 ± 5	21 ± 2	14 ± 5	30	0.08	18.86
4	DDP-HDS	DDS	58 ± 3	28 ± 4	19 ± 4	14 ± 4	30	0.08	15.23
5	CP-DDS	DDS	59 ± 4	28 ± 4	20 ± 2	11 ± 4	29	0.07	16.91
6	CP-TDS	DDS	59 ± 2	29 ± 4	21 ± 3	9 ± 5	29	0.07	17.82
7	CP-TTDS	DDS	61 ± 4	25 ± 2	18 ± 4	13 ± 4	29	0.06	16.67
8	CP-HDS	DDS	62 ± 3	25 ± 2	16 ± 7	10 ± 4	28	0.05	15.49
9	DDP-DDS	TDS	52 ± 3	54 ± 2	27 ± 5	23 ± 2	39	0.15	29.06
10	DDP-TDS	TDS	53 ± 3	55 ± 4	27 ± 3	19 ± 2	38	0.12	28.13
11	DDP-TTDS	TDS	57 ± 2	58 ± 2	26 ± 3	21 ± 10	41	0.10	28.46
12	DDP-HDS	TDS	58 ± 2	59 ± 4	27 ± 4	23 ± 4	42	0.11	23.81
13	CP-DDS	TDS	59 ± 4	59 ± 4	29 ± 3	22 ± 3	42	0.11	27.48
14	CP-TDS	TDS	59 ± 3	61 ± 3	28 ± 4	22 ± 4	43	0.11	25.14
15	CP-TTDS	TDS	60 ± 4	61 ± 2	29 ± 2	25 ± 5	44	0.12	29.20
16	CP-HDS	TDS	62 ± 2	63 ± 2	28 ± 4	26 ± 7	45	0.11	28.71
17	DDP-DDS	TTDS	52 ± 2	54 ± 2	57 ± 2	27 ± 4	47	0.24	40.64
18	DDP-TDS	TTDS	53 ± 3	55 ± 2	58 ± 2	27 ± 5	48	0.23	35.96
19	DDP-TTDS	TTDS	56 ± 2	58 ± 2	60 ± 2	27 ± 6	50	0.20	39.61
20	DDP-HDS	TTDS	58 ± 2	59 ± 2	62 ± 4	29 ± 2	52	0.22	44.50
21	CP-DDS	TTDS	59 ± 2	60 ± 2	62 ± 2	26 ± 5	52	0.18	47.93
22	CP-TDS	TTDS	59 ± 2	60 ± 4	63 ± 2	27 ± 4	52	0.19	37.44
23	CP-TTDS	TTDS	61 ± 4	62 ± 2	64 ± 2	26 ± 4	53	0.16	38.04
24	CP-HDS	TTDS	63 ± 3	63 ± 4	66 ± 3	29 ± 2	55	0.18	41.21
25	DDP-DDS	–	54 ± 2	55 ± 1	59 ± 1	61 ± 5	57	6.79	127.46
26	DDP-TDS	–	56 ± 1	57 ± 1	59 ± 3	63 ± 2	59	6.72	121.01
27	DDP-TTDS	–	57 ± 2	58 ± 1	62 ± 1	63 ± 3	60	7.17	133.94
28	DDP-HDS	–	57 ± 2	61 ± 1	62 ± 1	65 ± 4	61	5.84	128.80
29	CP-DDS	–	58 ± 4	61 ± 1	63 ± 2	66 ± 2	62	5.33	120.47
30	CP-TDS	–	63 ± 1	65 ± 1	67 ± 2	71 ± 2	65	4.78	129.17
31	CP-TTDS	–	60 ± 2	64 ± 0	66 ± 2	69 ± 1	66	5.18	132.67
32	CP-HDS	–	64 ± 1	67 ± 3	70 ± 2	73 ± 2	68	4.13	125.42

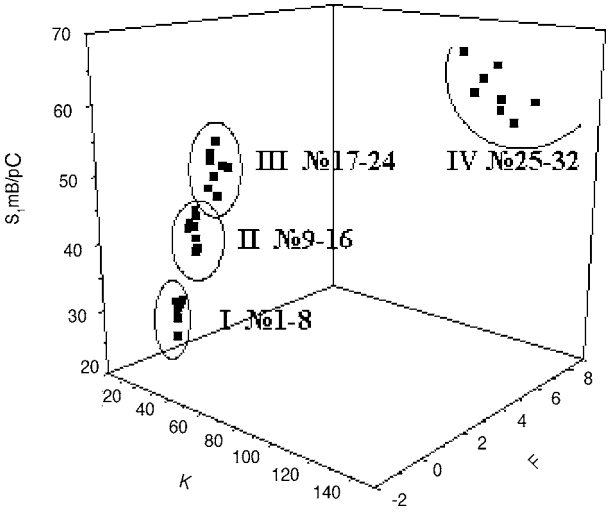

Fig. 4. Cross-sensitivity parameters of anionic surfactant sensors.

groups confirm the stability and reproducibility of their electrochemical characteristics. The fourth group includes the sensors (No. 25–32) with high values of the average slope of the electrode functions (57–68), the inselectivity factor (4.13–7.17) and the reproducibility factor (120.40–133.94). They are most suitable for the usage in multisensor analysis as inselective ones.

Examples of separate detection of sodium alkylsulfates in binary and five-component model solutions by means of arrays of seven to eleven non-modified sensors with different membranes are collected in Table 5.

Analytical signals were processed by three-layer artificial neural networks. The number of neurons in the input and output layers corresponded to the number of the sensors in the array and the number of the analytes, respectively. The number of neurons in the hidden layer ranged from 3 to 20. To train the network, 12–200 standard solutions with different component ratios were used, the concentrations of the analytes in the mixtures varied from 1×10^{-6} to 2×10^{-3} mol L^{-1} and from 1×10^{-5} to 2×10^{-3} mol L^{-1} for ionic and non-ionic surfactants, respectively. The mean accuracy of ion detection was 0.1–7%.

Table 5
Results of detection of homologous sodium alkylsulfates in model mixtures with the aid of a matrix of solid-contact non-modified sensors made of alkylpyridinium-alkyl sulfates ($n = 3$, $P = 0.95$)

Sensor array (EAC)	Introduced (mg/L)	Found (mg/L)	S_r (%)
DDP: DDS, TTDS, HDS	C_{12}: 0.57	0.59 ± 0.04	3.51
	C_{16}: 3.51	2.05 ± 0.02	0.49
CP: DDS, TDS, TTDS, HDS	C_{12}: 2.88	3.14 ± 0.16	9.03
	C_{14}: 1.26	1.28 ± 0.17	1.60
	C_{16}: 6.88	6.08 ± 0.7	11.63
DDP: DSN, DDS, TDS, TTDS, HDS	C_{12}: 0.58	0.60 ± 0.08	3.45
	C_{13}: 1.51	1.49 ± 0.03	1.32
	C_{16}: 0.76	0.78 ± 0.05	2.63
	C_{12}: 5.18	5.08 ± 0.02	1.93
	C_{13}: 0.30	0.31 ± 0.02	3.33
	C_{14}: 0.32	0.30 ± 0.02	6.25
CP: DSN, DDS, TDS, TTDS, HDS, HDSN	C_{16}: 4.13	4.05 ± 0.02	1.79
	C_{10}: 0.49	0.51 ± 0.13	3.74
	C_{12}: 2.25	2.15 ± 0.04	4.26
	C_{13}: 2.42	2.43 ± 0.25	0.75
	C_{14}: 0.63	0.64 ± 0.06	1.11
	C_{16}: 1.38	1.43 ± 0.06	3.64

The possibility of separate detection of homologous anionic surfactants in various river waters with the aid of a 10 anionic-surfactant sensor array is shown. The neural network was trained on pure multicomponent mixtures. The solutions for calibration were samples of natural water artificially polluted with sodium do-, tri-, hexadecyl sulfates. The mean accuracy of ion detection was 0.2–12%.

4. Conclusions

Thus, modified surfactant sensors and multisensor analysis enable the problem of fast separate detection of homologous surfactants of various types in multicomponent model mixtures and natural water to be solved.

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References

[1] S.F. Maki, J. Wangsa, N.D. Danielson, Anal. Chem. 64 (1992) 583.
[2] N. Pan, D.I. Pietrzyk, J. Chromatogr. A 706 (1995) 327.
[3] S.D. Scullion, M.R. Clench, M. Cooke, A.E. Aschcroft, J. Chromatogr. A 773 (1996) 207.
[4] S. Efkemann, U. Pinkernell, U. Karst, Anal. Chim. Acta 363 (1998) 97.
[5] T. Austad, J. Fjelde, Anal. Lett. J. 25 (1992) 957.
[6] P. Jandera, J. Fisher, V. Stanek, M. Kucherova, P. Zvonicek, J. Chromatogr. A 738 (1996) 201.
[7] M.J. Cugat, F. Borrull, M. Calull, Chromatographia 46 (1997) 332.
[8] P.A. Gallagher, N.D. Danielson, J. Chromatogr. A 781 (1997) 153.
[9] E. Piera, P. Erra, M.R. Infante, J. Chromatogr. A 757 (1997) 275.
[10] H. Salimi-Moosavi, R.M. Cassidy, Anal. Chem. 68 (1996) 293.
[11] K. Heinig, C. Vogt, G. Werner, Frezenius' J. Anal. Chem. 358 (1997) 500.
[12] N.A. Bernovaksys, T.I. Opasmyae, A.I. Tomberg, Chem. Technol. Fuel Oil (1980) 56.
[13] V.M. Saenko, N.A. Veleshko, Problems of Chemical Cleaning and Dyeing of Cloth, Moscow, 1983, p. 130.
[14] R. Reiser, H.O. Tojander, W. Ciger, Anal. Chem. 69 (1997) 4923.
[15] H. Fukui, A. Kaminaga, T. Maeda, K. Hayakawa, Anal. Chim. Acta 481 (2003) 221.
[16] E.G. Kulapina, R.K. Chernova, A.I. Kulapin, S.A. Mitrokhina, Ind. Laboratory Mater. Testing 66 (2000) 3.
[17] J. Janata, M. Josowicz, Anal. Chem. 70 (1998) 179R.
[18] J. Schreurs, E. Barendrecht, Rec. Trav. Chim. Pays-Bas. 103 (1984) 205.
[19] A.R. Guadalupe, H.D. Abruna, Anal. Chem. 57 (1985) 142.
[20] R.W. Murray, A.G. Ewing, R.A. Durst, Anal. Chem. 59 (1987) 379.
[21] Ya. Labuda, Anal. Chem. 45 (1990) 629.
[22] D.R. Rolison, Chem. Rev. 90 (1990) 667.
[23] E. Barendrecht, J. Appl. Mectrochem. 20 (1990) 175.
[24] S. Matysik, F.-M. Matysik, J. Mattusch, W.-D. Einicke, Proceedings of the Abstracts of International Symposium on Electrochemistry and Biosensors, Matrafured'98, Budapest, 1998, p. 10.
[25] P. Abel, W. Kantek, T. Woedtke, J. Kruger, Membran und anordnung fur definierten analyt transfer, COIN 33/48, Patent 19547923 Germany (1999).
[26] A.I. Kulapin, R.K. Chernova, E.B. Nikol'skaya, E.G. Kulapina, J. Anal. Chem. 58 (2003) 318.
[27] E.G. Kulapina, V.A. Ovchinski, J. Anal. Chem. 55 (2000) 189.
[28] A.I. Kulapin, R.K. Chernova, E.G. Kulapina, J. Anal. Chem. 57 (2002) 760.
[29] M. Baret, D.L. Massart, P. Fabry, C. Menardo, F. Conesa, Talanta 50 (1999) 541.
[30] A. Rudnitskaya, A. Ehlert, A. Legin, Y. Vlasov, S. Buttgenbach, Talanta 55 (2001) 425.
[31] P. Ciosek, E. Augustyniak, W. Wryblewski, Analyst 129 (2004) 639.
[32] J. Gallardo, S. Alegret, M. del Valle, Sens. Actuators B 101 (2004) 72.
[33] A. Riul Jr., R.R. Malmegrim, F.J. Fonseca, L.H.C. Mattoso, Artificial Organs 27 (2003) 469.
[34] C. Di Natale, A. Macagnano, F. Davide, A. D'Amico, A. Legin, Y. Vlasov, A. Rudnitskaya, B. Selezenev, Sens. Actuators B 44 (1997) 423.
[35] L.S. Ferreira, M.B. De Souza Jr., Sens. Actuators B 75 (2001) 166.
[36] A. Riul, H.C. de Sousa, R.R. Malmegrim, D.S. dos Santos, A.C.P.L.F. Carvalho, F.J. Fonseca, O.N. Oliveira, L.H.C. Mattoso, Sens. Actuators B 98 (2004) 77.
[37] F. Despagne, D.L. Massart, Analyst 123 (1998) 157R.
[38] Y. Miyanaga, A. Tanigake, T. Nakamura, Y. Kobayashi, H. Ikezaki, A. Taniguchi, K. Matsuyama, T. Uchida, Int. J. Pharmaceutics 248 (2002) 207.
[39] J. Gallardo, S. Alegret, R. Munoz, M. De-Roman, L. Leija, P.R. Hernandez, M. del-Valle, Anal. Bioanal. Chem. 377 (2003) 248.
[40] N. Garsia-Villar, J. Saurina, S. Hernandez-Cassou, Frezenius' J. Anal. Chem. 371 (2001) 1001.

[41] A. Legin, A. Rudnitskaya, L. Lvova, Yu. Vlasov, C. Di Natale, A. D'Amico, Anal. Chim. Acta 484 (2003) P33.
[42] A. Legin, A. Ru dnitskaya, Y. Vlasov, C. Di Natale, F. Davide, A. D'Amico, Sens. Actuators B 44 (1997) 291.
[43] A. Legin, A. Smirnova, A. Rudnitskaya, L. Lvova, E. Suglobova, Y. Vlasov, Anal. Chim. Acta 385 (1999) 131.
[44] I. Koryta, K. Shtulik, Ion-selective Electrodes, Mir Press, Moscow, 1989, 272 pp.
[45] Y. Vlasov, A. Legin, A. Rudnitskaya, E. Bychkov, Sens. Actuators B 34 (1996) 456.
[46] B. Doyle, G.J. Moody, J.D.R. Tomas, Talanta 29 (1982) 257.
[47] E.G. Kulapina, R.K. Chernova, E.A. Materova, S.A. Mitrokhina, J. Anal. Chem. 55 (2000) 1154.
[48] A.B. Legin, A.M. Rudnitskaya, A.A. Smirnova, L.B. L'vova, Y.G. Vlasov, J. Appl. Chem. 72 (1999) 105.