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ARTICLES

Some Regularities of Interface Formation in Solid-Contact Potentiometric Surfactant-Selective Sensors

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Abstract—The regularities of interface formation in solid-contact potentiometric sensors for surfactants of different types were found. It was shown that the nature of electronic conductors and ionophores, the state of ionophores in aqueous and organic media, and the composition and ratios of membrane components had the decisive effect on the electroanalytical properties of these sensors.

Surfactants are the major components of highly toxic substances affecting the ecological state of the hydrosphere; concentrations of surfactants are regulated by MPCs. The ability of surfactants to adsorb on surfaces determines their biological activity, which consists in disturbing the function of biological membranes.

The control over the concentration of these toxicants in the presence of organic and inorganic substances is complicated by both the variety of surfactant types and wide ranges of their concentrations, namely, from traces in domestic sewage water to tens of per cent in industrial waste water.

At present, chromatographic and extraction–spectrophotometric methods are mainly used for determining surfactants. These methods involve the stage of preliminary separation, which makes the analysis longer and demands for toxic solvents [1–5].

Selective electrodes with liquid filling [6–8] were proposed for determining surfactants, but in virtue of their construction features, they were inapplicable to the determination of surfactants without preliminary sampling. The replacement of ISE internal solutions with a solid contact between the current lead and the membrane afforded some advantages to solid-contact electrodes (SCEs): they are convenient in service and can be used in any spatial orientation for monitoring technological processes and environmental samples.

Some publications were devoted to the application of solid-contact electrodes of the coated-wire type to the potentiometric titration of surfactants [9–11]. The main drawbacks of these electrodes are their instability and poor reproducibility of potentials in time.

The choice of electronic conductors and the elucidation of the factors responsible for the stability of the electrochemical and operational characteristics of such sensors are important for designing solid-contact, membrane, surfactant-selective electrodes.

In this work, some regularities of interface formation in solid-contact potentiometric surfactant-selective sensors with the given electroanalytical and operational characteristics are considered.

EXPERIMENTAL

The formulae and percentages of the major substances of the surfactant samples under study (anionic (ASs), cationic (CSs), and nonionic (NSs) surfactants) are summarized in Table 1.

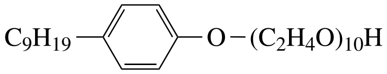
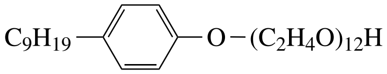
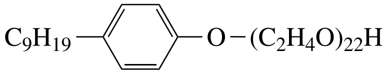
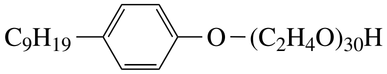
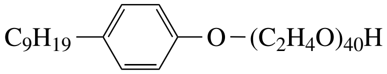
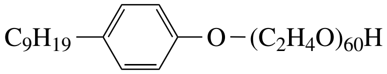
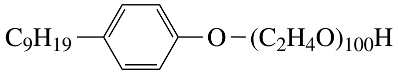
Solutions of surfactants (1×10^{-2}–5×10^{-4} M) were prepared by dissolving their weighed portions in water under slight heating; solutions with concentrations of 1×10^{-3} to 1×10^{-6} M were prepared by successive dilution. A 0.01 M solution of sodium tetraphenylborate (Chemapol Co.) with the concentration of the major substance 98.5% was used throughout.

Ion pairs of dodecylsulfate and alkylpyridinium cations (n = 10–18), those of cetylpyridinium with alkylsulfates (n = 10–16) and tetraphenylborate, as well as compounds of nonylphenol (NP-10, NP-12) or alcohol (Sintanol DS-10) polyethoxylates with ions of barium(II) and tetraphenylborate (NS-Ba-TPB) were used as ionophores. The synthesis of active components of membranes, the preparation of membranes, and the design of electrodes were described earlier in [12, 13].

Solid-contact surfactant-sensitive sensors with PVC membranes were studied. Silver, graphite, copper, steel, and silver coated with silver chloride were used as electronic conductors.

The composition of the membranes of surfactant-selective sensors was modeled using an inert matrix, S-70 PVC; plasticizing solvents, dibutyl phthalate (DBP), dioctyl phthalate (DOP), and *o*-nitrophenyl octyl ether (*o*-NPOE); the PVC-to-DBP ratio varied from 1 : 2 to 1 : 3 for NS-membranes and CS-, AS-membranes, respectively. An EI-21 electron-ion-exchange resin, a macroporous sulfocationite in the copper-hydrogen

Table 1. Types of surfactants under study

Name	Abbreviation	Formula	Concentration of the major substance, %
Anionic surfactants			
Sodium decylsulfate	DS	$C_{10}H_{23}–OSO_3Na$	96
Sodium dodecylsulfate	DDS	$C_{12}H_{25}–OSO_3Na$	96
Sodium tridecylsulfate	TriDS	$C_{13}H_{27}–OSO_3Na$	88
Sodium tetradecylsulfate	TDS	$C_{14}H_{29}–OSO_3Na$	89
Sodium hexadecylsulfate	HDS	$C_{16}H_{33}–OSO_3Na$	92
Sodium dodecylbenzenesulfonate (sulphonol)	DBS	$C_{12}H_{25}C_6H_4–SO_3Na$	98
Cationic surfactants			
Decylpyridinium chloride	DPC	$[CH_3–(CH_2)_9–C_5H_4N]Cl$	77
Undecylpyridinium chloride	UDPC	$[CH_3–(CH_2)_{10}–C_5H_4N]Cl$	86
Dodecylpyridinium chloride	DDPC	$[CH_3–(CH_2)_{11}–C_5H_4N]Cl$	98
Cetylylpyridinium chloride	CPC	$[CH_3–(CH_2)_{15}–C_5H_4N]Cl$	96
Octadecylpyridinium chloride	ODPC	$[CH_3–(CH_2)_{17}–C_5H_4N]Cl$	99
Cetyltrimethylammonium bromide	CTAB	$[C_{16}H_{33}N(CH_3)_3]Br$	97
Nonionic surfactants			
Nonylphenol polyethoxylates	NP-*n*		
Nonylphenol-10	NP-10		98
Nonylphenol-12	NP-12		99
Nonylphenol-22	NP-22		98
Nonylphenol-30	NP-30		97
Nonylphenol-40	NP-40		97
Nonylphenol-60	NP-60		96
Nonylphenol-100	NP-100		98
Sintanol DS-10 (alcohol polyethoxylate)	DS-10	$C_nH_{2n+1}–O–(C_2H_4O)_mH$ $n = 10–18, m = 8–10$	96
Triton X-100	TX-100	$C_8H_{17}C_6H_4–O–(C_2H_4O)_{9–10}H$	98
Emulsifier OP-10	OP-10	$C_nH_{2n+1}C_6H_4O–(C_2H_4O)_mH$ $n = 8–10, m = 10–21$	

form with additives of metallic copper and carbon black (redoxite), served as the redox system.

Potentiometric measurements were performed using an I-130.M multipurpose potentiometer with an error of ±1 mV. An EVL-1MZ silver–silver chloride electrode was used as the reference electrode. The transport properties of membranes were studied by the method of applied potential [12].

To determine the stoichiometric ratios of components in ion pairs and their solubility products K_s, solutions of sodium alkylsulfates and alkylpyridinium chlorides were titrated with standardized solutions of cetylpyridinium chloride and sodium dodecylsulfate or tetraphenylborate using ISEs based on the corresponding ionophores.

The spectrophotometric determination of dibutyl phthalate was carried out using an SF-46 instrument ($\lambda = 295$ nm, $l = 1$ cm) according to the procedure described in [14]. The IR spectroscopic studies of interactions in the graphite–dibutyl phthalate system were performed using a Specord M-80 and IKS-29 instruments (the entire spectrum was recorded in Vaseline oil (1800–1500 and 1300–40 cm^{-1}) and in hexachlorobutadiene (4200–1800 and 1500–1300 cm^{-1}). Spectral slit width was 8 cm, spectra were recorded in 4 cm. The spectra of graphite and dibutyl phthalate were preliminary taken to interpret the spectra under study.

The values of K_s for ionophores were calculated from potentiometric titration curves [15], their extraction constants were found from the cationic and anionic selectivity of the test membranes [16], and dissociation constants were found from the steady-state values of conductivity by the Krauss–Bray method [17].

RESULTS AND DISCUSSION

Let us consider the regularities of interface formation between surfactant-selective sensors and a solid contact. Let us dwell on the effect of the electronic conductor nature.

The systematic study of the electrochemical and operational characteristics of surfactant-selective sensors with silver and graphite leads demonstrated the advantage of graphite as the of electronic conductor. Stainless steel and copper turned out to be unsuitable, because the potentials of SS-sensors in surfactant solutions were unstable and uncertain. Surfactant-selective electrodes with the graphite lead exhibited more stable operational characteristics: the drift of their potentials was 8–10 times lower than that of sensors with silver leads, while their service lives were 6–8 times longer (Fig. 1).

Sensors with the graphite lead are characterized by lower detection limits. For example, the detection limit for DDSNa was 0.29 mg/L, which is lower than its MPC level. The detection limit for the same surfactant estimated with electrodes on the silver support was no lower than 2.88 mg/L. The introduction of redox systems into membranes only slightly affected their characteristics.

It is necessary to create the conditions for the reversible transition from the ionic conduction in the membrane to the electronic conduction in the lead for developing stably operating solid-contact sensors with PVC membranes. Stable and reproducible potential differences should be attained between the membrane and the lead.

It should be noted that there is at present no unified approach to the explanation of the operation mechanism of solid-contact electrodes with PVC plasticized membranes [9, 11, 18]. Freiser has come to the conclusion that oxygen participated in the processes on the inner lead, because air and water penetrated through the membrane coating [9]. This is, probably the reason for the instability of characteristics of sensors with silver leads. In the opinion of Tarasevich [18], the presence of different defects and porosity is typical of real graphite structures. On the surface of carbon, water and oxygen are adsorbed. In the course of reduction of molecular oxygen, carbon is charged positively and gains the ability to attract anions. As this takes place, the formation of oxygen-containing surface groups, carbonyl, phenolic, and carboxylic, is possible. The authors of [19] quantitatively determined these groups. It should be noted that these processes are not typical of silver.

In our opinion, the long service life of electrodes with graphite leads is evidently due to the graphite structure and the possibility of membrane solvent penetration into it. The penetration of DBP into the structure of the graphite lattice either upon the direct contact with the plasticizer or upon the contact with membranes was proved by UV and IR spectroscopy [20]. DBP penetrates into graphite with time: the characteristic frequencies of DBP atomic groups appeared in the IR spectrum within a day, and the intensities of the corresponding lines enhanced after three weeks. DBP was quantitatively determined by UV spectroscopy; it was proved that the maximum concentration of DBP was observed already in the fifth day [20]. The plasticizer penetrated into graphite to a depth of 0.2–0.3 mm.

The penetration of a plasticizer into graphite pores can make the interface bulky, extend the contact area between the electronic and ionic conductors, and enhance the density of exchange currents.

The determination of the temperature coefficients of circuits involving solid-contact surfactant-selective sensors showed the reversibility of the inner membrane–graphite interface. This suggests that the graphite surface can gain redoxite properties. It is likely that these factors are responsible for the stable characteristics and long service lives of surfactant-sensitive sensors with graphite leads.

The found regularities of interface formation were used in practice: surfactant-selective sensors with graphite leads possessing stable operational characteristics were applied to the detection of surfactants in

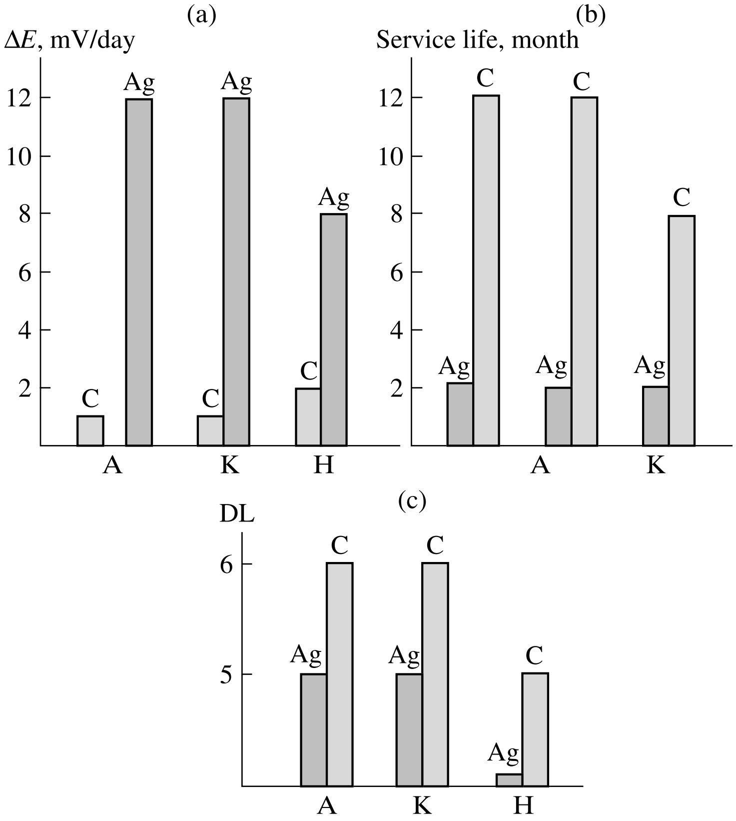


Fig. 1. Effect of the nature of electronic conductors on (a) potential drift, (b) the service life of surfactant-selective sensors with solid-contact, and (c) the detection limits (DL) for surfactants: A, anionic (DDS); C, cationic (CPC), and N, nonionic (sintanol DS-10).

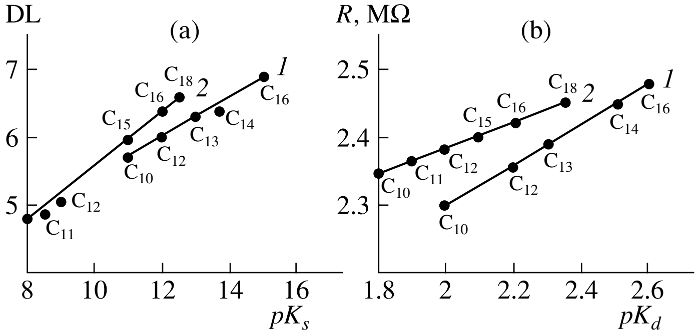


Fig. 2. (a) Detection limits (DL) for (*1*) sodium alkylsulfates and (*2*) alkylpyridinium chlorides as functions of the solubility products of ionophores and (b) membrane resistances as functions of their dissociation constants in the membrane phase.

flow systems [21]. Sensors with small-size silver leads were used for the test control over surfactant concentrations in samples of minor volumes on solid supports.

Let us consider the effect of the ionophore nature and state in aqueous and organic media on the surface and bulk properties of surfactant-selective membranes. It was shown that the detection limits for surfactants correlated with the K_s values of ionophores and the steady-state resistance of membranes correlated with the conventional dissociation constants of organic ion exchangers in the membrane (Fig. 2).

All ion pairs under study are poorly soluble in water and can be used as ionophores in membranes of AS- and CS-selective sensors; this is supported by the studies of the electrode properties of the membranes based on them. The ion pairs of cetylpyridinium with dodecyl sulfate and tetraphenylborate are easy to obtain and their states of aggregation are stable. Studies of the

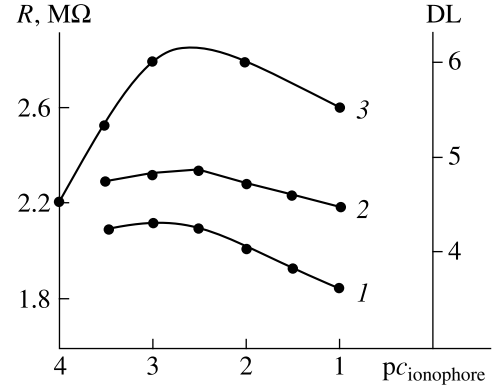


Fig. 3. Effect of cetylpyridinium dodecylsulfate concentration on the resistance of membranes in 1×10^{-3} M solutions of (*1*) DDS, (*2*) CPC and on (*3*) DL of sodium dodecylsulfate.

thermal stability of these ion pairs have demonstrated that the compounds were stable up to 60°C. In addition, sodium dodecyl sulfate and cetylpyridinium chloride are produced as reference substances of ionic surfactants. This allows the ion pairs of cetylpyridinium and dodecyl sulfate and tetraphenylborate to be recommended as the optimum membrane ionophores of sensors for detecting ionic surfactants.

The concentration of the ionophore affects the electrode properties of the membrane. As the concentration of ionophore increases, the number of ion-exchange centers and the number of charge carriers grow, which results in the enhancement of the membrane conductivity. However, the increase of the ionophore concentration in the membrane is limited by its solubility in the membrane solvent. At low concentrations of the ion exchanger, the electrode performance deteriorates (the resistance and the response time of the electrode grow, and the potential of the electrode becomes unstable) (Fig. 3).

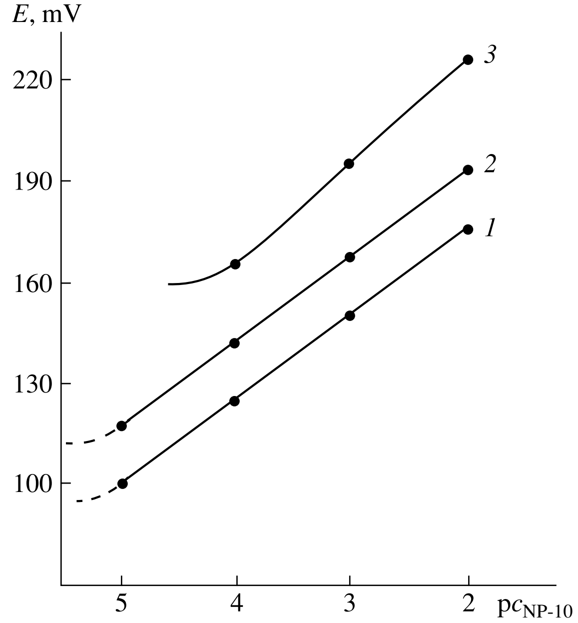


Fig. 4. Electrode functions of NS-sensors based on [NP-12-Ba] · 2TPB (electronic conductors: (*1*) graphite, (*2*) graphite + redoxite, and (*3*) silver).

The optimum compositions of sensor membranes selective for ionic and nonionic surfactants were determined from resistance values and detection limits for surfactants ($c_{\text{ionophore}}$ = 0.002–0.001 mol/kg DBP and 0.1 mol/kg DBP, respectively).

The main electrochemical and operational characteristics of surfactant-selective sensors (linearity ranges and slopes of the electrode response, response time (t_{95}), working ranges of pH and temperature, potential drift, and service life) were determined (Table 2).

Table 2. Main electrochemical and operational characteristics of solid-contact potentiometric surfactant-selective sensors

Characteristic	Ionophores, electronic conductors					
	CP–DDS		CP–TPB		DS–10-Ba-TPB	
	C	Ag	C	Ag	C	Ag
$E = f(-\log c_{\text{DDS}})$, M	1×10^{-6}–1×10^{-2}	1×10^{-5}–1×10^{-2}	–	–	–	–
$E = f(-\log c_{\text{CPC}})$, M	1×10^{-6}–1×10^{-3}	1×10^{-5}–1×10^{-3}	1×10^{-6}–1×10^{3}	1×10^{-5}–1×10^{-3}	–	–
$E = f(-\log c_{\text{NP-10}})$, M	–	–	–	–	1×10^{-5}–1×10^{-2}	1×10^{-4}–1×10^{-2}
α, mV/pc	58 ± 1	60 ± 2	56 ± 1	58 ± 2	28 ± 1	30 ± 2
$t_{0.95}$, min	1–2	2–3	2–3	3–4	3–4	4–5
Potential drift ΔE, mV/day	1–2	10–15	1–2	10–15	3–4	7–8
Service life, month	18	1–2	12	2–3	6–7	1–2

Table 3. Determination of different types of surfactants ($n = 3$; $P = 0.95$)

Ionophore	Surfactants under study	Sample	Found	RSD, %
CP–DDS	Anionic surfactants	Wastewater, mg/L	2.25 ± 0.46	12
			2.62 ± 0.16	4
CP–TPB	Cationic surfactants	Hair rinser ω (%)		
		Balet	1.09 ± 0.06	5
		Linda	0.056 ± 0.004	5
DS–10-Ba-TPB	Nonionic surfactants	Industrial solutions (g/L)	4.85 ± 0.16	1
			3.94 + 0.12	1
		Wastewater (mg/L)	$(7.25 \pm 0.84) \times 10^{-2}$	5
			$(3.28 \pm 0.08) \times 10^{-4}$	2

It was found that solid-contact NS-selective electrodes with graphite leads also exhibited more stable operational characteristics. They are characterized by lower detection limits for nonionic surfactants (Figs. 1, 4). DS-10-Ba-TPB and NP-12-Ba-TPB are suitable for ionophores.

The electrode, dynamic, and transport properties of the membranes and the results of radiochemical studies demonstrated that the membrane potential of NS-selective electrodes was due to the transfer of alkaline-earth ions, the formation of $[Ba–NS]^{2+}$ complex cations, and their extraction into the membrane phase [22]. $[Ba–NS]^{2+}$ complex cations serve as charge carriers in the membrane. The slopes of the electrode functions correspond to the transfer of doubly charged cations. A long response time of solid-contact NS-selective sensors may be explained by the complex mechanism of potential formation (Table 2).

Based on the found regularities of interface formation and on the mechanism of membrane operation, we developed solid-contact potentiometric sensors for anionic, cationic, and nonionic surfactants. The sensors were metrologically certified by the Russian Federation State Committee for Standardization.

The electrodes were used for determining individual surfactants in model solutions, nonionic surfactants in waste and industrial waters, and cationic surfactants in hair rinsers. The electrodes were also used for estimating the ability of sulphonol to be washed out from dishes as a safety index and for determining total anionic surfactants in wastewater (Table 3).

The accuracy of determination was verified by extraction–spectrophotometric and added–found methods (RSD ≤ 6%). A comparison of the results of analysis using F and t tests showed the absence of a systematic error.

Thus, the role of the graphite lead in the stabilization of the potential of surfactant-selective sensors with solid contacts was elucidated. It was shown that the state of the ionophoric compounds in aqueous and organic media is the decisive factor in optimizing the electroanalytical properties of membranes selective for anionic, cationic, and nonionic surfactants.

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