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ARTICLES

Effect of Surfactant Hydrophobicity on the Physicochemical Properties of Alkylpyridinium Alkylsulfates and Electroanalytical Characteristics of Membranes Based on These Compounds

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Abstract—Reasoning from the regularities of the variation of electrochemical properties of sensors based on alkylpyridinium alkylsulfates ($n = 10–15$), we demonstrated that detection limits for surfactants are related to the solubility of ionophores. The slopes of electrode functions, selectivity, apparent extraction and dissociation constants of ionophores are governed by the hydrophobicity of the active components of membranes.

Synthetic ionic surfactants are the main components of cosmetic, hygienic, cleansing and cleaning agents, and different composite mixtures. Surfactants are also present in foodstuffs and pharmaceuticals.

The determination of total surfactants of one class, the separate determination of different surfactants present together, separate determination of surfactants in homologous series, etc., are the tasks of current concern for analytical services [1]. In the analysis of wastewater and multicomponent composite mixtures of synthetic surfactants, in the majority of cases, combinations of the known methods are used. These methods involve the stage of preliminary separation, which makes the analysis longer [2, 3].

To determine ionic surfactants, ISEs with liquid and polymeric membranes are used. As ionophores, the ion pairs of triphenylmethane dyes, quaternary ammonium bases, and tetraphenylborates with cationic or anionic surfactants are used. They are insoluble in water and possess the properties of a liquid ion exchangers [4–8]. Studies in the field of the potentiometry of the specified compounds are few in number and most of them are of applied character. The study of the physicochemical properties of ionophores in aqueous and organic media and the surface and bulk properties of the membranes based on organic ion exchangers is of high priority for the potentiometry of surfactants.

This work is dedicated to the investigation of the effect of surfactant hydrophobicity on the physicochemical properties of alkylpyridinium alkylsulfates and electroanalytical characteristics of membranes based on these compounds.

EXPERIMENTAL

Solid-contact potentiometric sensors selective for ionic surfactants were studied. These sensors are based on organic ion exchangers, dodecylsulfate with alkylpyridinium ($m = 10–18$) and cetylpyridinium with alkylsulfates ($n = 10–16$) $C_nH_{2n+1}OSO_3^- \cdot C_mH_{2m+1}C_6H_4N^+$, and use graphite as an electronic conductor. Commercial samples of anionic and cationic surfactants contained 96–98% of the major substance.

Solutions of sodium tridecylsulfate (TriDS) (5×10^{-3} M), sodium tetradecylsulfate (TDS) (1×10^{-3} M), sodium hexadecylsulfate (HDS) (5×10^{-4} M), dodecylpyridinium (DDP) chloride (1.25×10^{-2} M), undecylpyridinium (UDP) chloride (3.3×10^{-3} M), decylpyridinium (DP) chloride (1.5×10^{-4} M), octadecylpyridinium (ODP) chloride (1×10^{-4} M), and 1×10^{-2} M solutions of other surfactants were prepared by dissolving their weighed portions in water while slightly heating. Solutions with concentrations of 1×10^{-3}–1×10^{-6} M were prepared by subsequent dilution.

Dibutyl phthalate and tetrahydrofuran were rectified. The synthesis of ionophores and ion pairs of alkylpyridinium alkylsulfates, the preparations of membranes, and the design of electrodes were described in [9].

Potentiometric measurements were carried out using an I-130 multipurpose potentiometer with an error of ±1 mV. An EVL-1-MZ silver–silver chloride electrode was used as the reference electrode. The values of e.m.f. were measured using the following circuit with transference:

$$\text{Ag} \mid \text{AgCl, KCl}_{\text{sat}} \mathrel{\vdots} \text{Test solution} \mid \text{Membrane} \mid \text{C}.$$

The bulk properties of membranes were studied by the methods of electric conduction [10], e.m.f. [11], applied potential [12], and alternating-current impedance (in the frequency range from 15 to 100 kHz). The rates of anionic and cationic surfactant transport through the membranes with ionophores and background membranes (containing no ionophores) were found by the following equation:

$$v = \frac{\Delta c}{\Delta t} \text{ mol L}^{-1} \text{ s}^{-1},$$

where Δc is the change in the analyte ion concentration at the moment Δt; and Δt is the time of applying potential to the electrochemical cell.

The composition and solubility of ion pairs were found by the potentiometric titration of alkylpyridinium chlorides with solutions of sodium alkylsulfates. To determine the composition of ion pairs, 1–5 mL of 1×10^{-3} M solutions of alkylpyridinium chlorides were titrated with 1×10^{-3} M solutions of sodium alkylsulfate.

The solubility products (K_s) were calculated by the equation:

$$K_s = 10^{\frac{E_0 - E}{\alpha}} \frac{c_t(V_2 - V_{tep})}{V_1 + V_2},$$

where E is the potential value found from the titration curve after the titration end-point, mV; E_0 is the potential before the addition of the titrant, mV; α is the slope of the electrode function, mV/pc; c_t is the concentration of the titrant, M; V_1 is the volume of the solution consumed for titration, mL; and V_2 and V_{tep} are the titrant volumes after the titration end-point and at the titration end-point, respectively, mL.

The parameters of the electrode function E_0 and α were calculated from the titration curve before the equivalence point [13].

The constants of ionophore extraction with dibutyl phthalate and the dissociation constants of ionophores in the membrane phase were determined according to [14, 15].

Apparent dissociation constants (K_d) of the alkylpyridinium–alkylsulfate ion pairs were calculated on the assumption that the equilibrium between the ions and the ion pairs at low concentrations obeyed the Ostwald dilution law

$$K_d = \frac{\alpha^2 c}{1 - \alpha},$$

where c is the total molar concentration of the compound, and α is the degree of dissociation.

Expressing α via the relative equivalent conductivity λ/λ_0 (λ is the equivalent conductivity, and λ_0 is the limiting equivalent conductivity), we obtained the following expression for the dissociation constant:

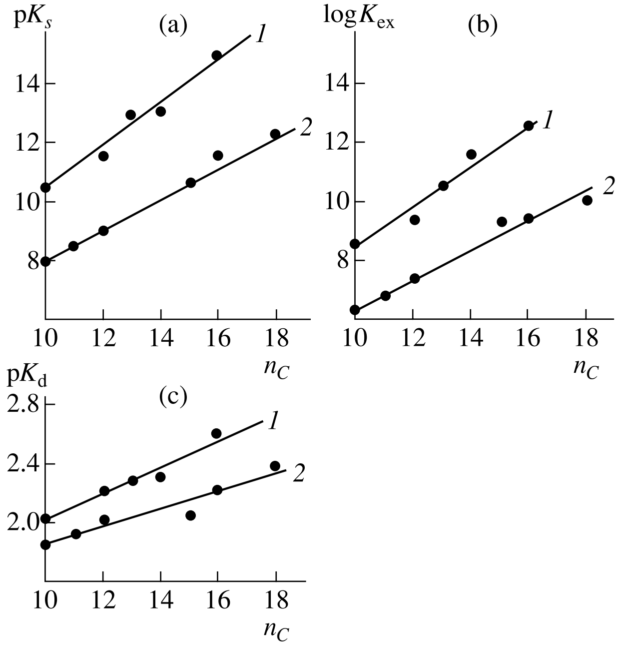

Fig. 1. (a) K_s, (b) constants of extraction with dibutyl phthalate, and (c) dissociation constants in the membrane ionophore as functions of the hydrophobicity of (*1*) sodium alkylsulfates and (*2*) alkylpyridinium chlorides.

$$K_d = \frac{c\lambda^2}{\lambda_0^2\left(1 - \frac{\lambda}{\lambda_0}\right)}.$$

The dissociation constants of the compounds under study were estimated by the Fuoss–Krauss iterative method by transforming the above expression as follows:

$$1/\lambda = 1/\lambda_0 + \lambda c/K_d\lambda_0^2.$$

The $1/\lambda$–λc dependence is the straight line with the slope $1/K_d\lambda_0^2$ and the Y-intercept $1/\lambda_0$. The values of dissociation constants were calculated from the obtained values of $1/\lambda_0$ and the slope.

RESULTS AND DISCUSSION

For the intentional search for ionophores for the sensors selective for ionic surfactants, we studied the physicochemical properties of organic ion exchangers, dodecylsulfate with cations of alkylpyridinium (n = 10–18) and cetylpyridinium with alkylsulfates (n = 10–16) (Fig. 1).

The ratio of components in the ion pairs was 1 : 1, the solubility of ionophores decreased with an increase

Table 1. Analytical characteristics of CS-selective sensors

Ionophore	$pK_s \pm \Delta pK_s$	CS in a solution	Analytical range, M	$c_{\min}$, P, M
DP–DDS	8.03 ± 0.51	DP	5×10^{-5}–3×10^{-3}	4.3×10^{-5}
		DDP	1×10^{-6}–1×10^{-3}	
		DP	5×10^{-6}–5×10^{-3}	
		ODP	5×10^{-7}–1×10^{-4}	
DDP–DDS	9.12 ± 0.14	DP	3×10^{-6}–3×10^{-3}	
		DDP	1×10^{-5}–3×10^{-3}	9.1×10^{-6}
		DP	1×10^{-6}–1×10^{-2}	
		ODP	1×10^{-7}–1×10^{-4}	
CP–DDS	11.56 ± 0.21	DP	3×10^{-6}–3×10^{-3}	
		DDP	3×10^{-6}–3×10^{-3}	
		DP	5×10^{-7}–1×10^{-2}	3.9×10^{-7}
		ODP	5×10^{-7}–1×10^{-4}	
ODP–DDS	12.13 ± 0.37	DP	3×10^{-5}–1×10^{-3}	
		DDP	3×10^{-6}–1×10^{-3}	
		CP	5×10^{-7}–1×10^{-3}	
		ODP	5×10^{-7}–1×10^{-4}	3.7×10^{-7}

in the molar mass of alkylsulfate and alkylpyridinium cations in the ionophores (Fig. 1a).

The conventional constants of the extraction of alkylpyridinium alkylsulfate with dibutyl phthalate and the conventional constants of ionophore dissociation in the membrane also depend on the hydrophobicity of the incorporated surfactants (Figs. 1b, 1c).

The determination limit correlates with the K_s value of the ionophore (Table 1) and the steady-state resistance of membranes correlates with the conventional constants of the dissociation of organic ion exchangers in the membrane (Fig. 2a). Note that the slopes of electrode functions depend on the number of carbon atoms in the molecules of sodium alkylsulfates and alkylpyridinium chlorides ($\alpha = 50$–68 mV/pc for $n = 10$–18). Theoretical slopes (58 ± 2 mV/pc) were observed for the electrodes based on cetylpyridinium–dodecylsulfate ion pairs.

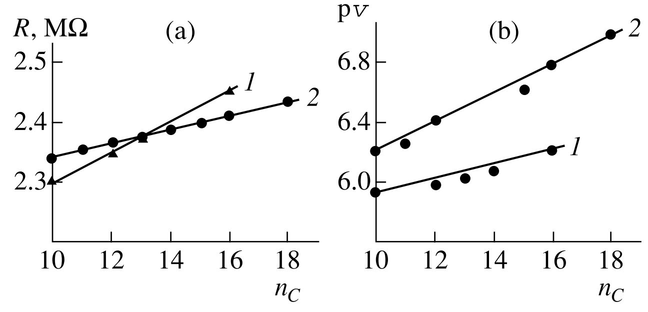

Fig. 2. (a) Steady-state resistance of membranes based on CP–DDS ion pairs and (b) the rates of ion transport through the membranes as functions of the number of carbon atoms entering into the composition of (*1*) alkylsulfates and (*2*) alkylpyridinium cations.

For the sensors based on cetylpyridinium–dodecylsulfate ion pairs, the electrode response was a linear function of their concentrations in the range from 10^{-6} to 10^{-2} M, the slopes were close to the theoretical ones and equaled 58 mV/pc, which points to the transfer of a singly charged ion. The deviation from linearity was due to the solubility of the active membrane component at DDS concentrations lower than 10^{-5}–10^{-6} M and due to micelle formation at concentrations higher than 10^{-2} M. Cetylpyridinium–dodecylsulfate ion pairs also impart cationic selectivity to sensors in 1×10^{-6}–1×10^{-3} M solutions of cetylpyridinium chloride, the slope was 56 mV/pc.

The reactions of ion exchange at the membrane–solution interface are potential-determining reactions for sensors in the solutions of ionic surfactants:

$$C_{16}H_{33}C_5H_4N^+ \cdot C_{12}H_{25}OSO_3^-$$

$$\longleftrightarrow C_{16}H_{33}C_5H_4N^+ + C_{12}H_{25}OSO_3^-$$

(dissociation of the ion exchanger
in the membrane phase)

$$C_{12}H_{25}OSO^-_{3\mathrm{m}} \longleftrightarrow C_{12}H_{25}OSO^-_{3\mathrm{solution}}$$

$$E = E_0 \pm \frac{2.3RT}{F} \log c_{\mathrm{surfactant}}.$$

Considering the processes at the membrane–solution interface, one should take into account the adsorption of surfactants on the interface surface. It was found that the membrane potentials were different for the freshly prepared surfactant-selective electrodes and for those conditioned for 24 h. In the latter case, it is likely that surfactant ions migrated to the surface membrane layer, which significantly affected the E_0 potential during its measurement and E_{H_2O} in the preparation of the electrode for operation.

The bulk properties of surfactant-selective membranes based on alkylpyridinium alkylsulfates and exhibited cationic and anionic selectivity were studied by varying the compositions of membranes and concentrations of ionophores and contact solutions.

The transport numbers in the membrane phase were determined (Table 2). The closeness of the transport numbers to unity indicates that alkylsulfate anions and alkylpyridinium cations are the main charge carriers in the membrane phase of surfactant-selective sensors. This is confirmed by the closeness of the slopes of the electrode functions in the solutions of anionic and cationic surfactants to the Nernstian values for singly charged ions.

The steady-state specific conductivity of the membrane increases with an increase in the ionophore concentration. This is indicative of the dissociation of ion exchangers in the membrane phase, which makes the electrodes polyfunctional, because they exhibit both cationic and anionic selectivity.

The membranes under study are characterized by the stability of conduction currents over prolonged periods of time, even after a change in polarity. The resistance reached steady-state values 1–1.5 h after the beginning of passing the current through the cell in one or other direction (Fig. 3). This is indicative of the reversible ion exchange between the membrane DDS and the DDS of a contact solution. Similar relationships were obtained for cetylpyridinium solutions. The curves of the time dependence of membrane resistance were virtually identical for all membranes under study.

As the length of the hydrocarbon radical of alkylsulfates and alkylpyridinium in the ion pairs was increased, the steady-state electric conductivity of the membranes insignificantly decreased (Fig. 2a). The apparent dissociation constants of ionophores calculated from the steady-state values of membrane specific conductivity by the graphical Krauss-Bray method (Fig. 1c) suggest that the ionophores in the membrane phase dissociated:

$$[\mathrm{CH_3(CH_2)}_n\mathrm{C_5H_4N^+}][\mathrm{CH_3(CH_2)}_n\mathrm{OSO_3^-}]$$

$$\longleftrightarrow \mathrm{CH_3(CH_2)}_n\mathrm{C_5H_4N^+} + \mathrm{CH_3(CH_2)}_n\mathrm{OSO_3^-}.$$

Dissociation constant decreases with an increase in the number of carbon atoms in the hydrophobic radical of alkylsulfates or alkylpyridinium cations incorporated into the ionophores,; this is evidently due to an increase in the hydrophobicity of surfactants (Fig. 1c).

Table 2. Transport numbers of alkylsulfate and alkylpyridinium ions ($c_{\text{ionophore}} = 0.01$ mol/kg DBP)

Ionophore	Carrier	Numbers of transfer
DDS–DP	DP$^+$	0.89
DDS–UDP	UDP$^+$	0.85
DDS–DDP	DDP$^+$	0.83
DDS–PDP	PDP$^+$	0.54
DDS–CP	CP$^+$	0.80
DDS–ODP	ODP$^+$	0.81
CP–DS	DS$^+$	0.91
CP–DDS	DDS$^+$	0.86
CP–TriDS	TriDS$^+$	0.90
CP–TDS	TDS$^+$	0.88
CP–HDS	HDS$^+$	0.88

An increase in the concentrations of solutions of alkylpyridinium chlorides and sodium alkylsulfates that are in contact with membranes, resulted in an increase in the steady-state values of membrane conductivities, because the amount of ions absorbed by the membrane increases and, consequently, the concentration of mobile charge carriers in the membrane phase also increased.

The steady-state resistance of membranes based on organic ion exchangers, alkylpyridinium alkylsulfates, correlates with the dissociation constants of ionophores, the composition of membranes, and the concentration of ionophores in the membrane.

The rates of the transport of alkylpyridinium and alkylsulfate ions through membranes of different compositions under the action of the applied potential also

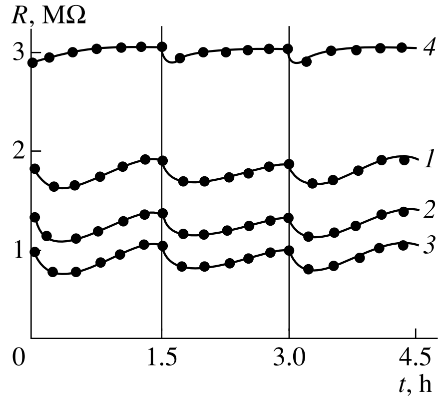

Fig. 3. Resistance of membranes based on CP–TriDS ion pairs at a constant potential ($V = 3.0$ V) as a function of a change in polarization (marked by vertical lines) in solutions of sodium dodecylsulfate (ionophore concentrations in membranes, mol/kg DBP: (*1*) 0; (*2*) 1×10^{-4}; (*3*) 1×10^{-3}; and (*4*) 1×10^{-2}.

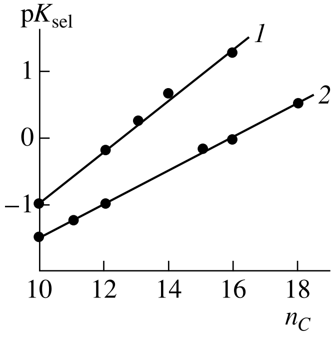

Fig. 4. Coefficients of the potentiometric selectivity of surfactant-selective sensors based on CP–DDS ion pairs as functions of the hydrophobicity of (*1*) sodium alkylsulfates and (*2*) alkylpyridinium chlorides.

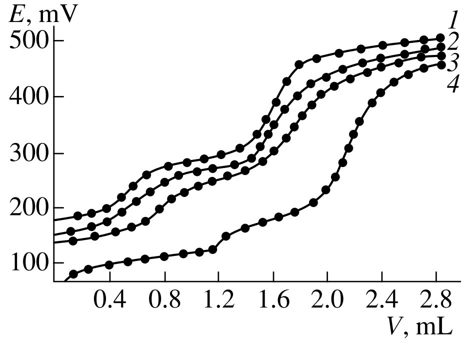

Fig. 5. Curves of the potentiometric titration of 1 : 1 mixtures of alkylsulfates: (*1*) C_{10}–C_{13}; (*2*) C_{10}–C_{14}; (*3*) C_{10}–C_{16}; (*4*) C_{12}–C_{16}; $c_{AS} = 1 \times 10^{-3}$ M; $V_{mixture} = 10$ mL; $c_{CP} = 5 \times 10^{-3}$ M; ionophore, CP–DDS.

correlate with the number of carbon atoms in the hydrophobic radical of the surfactant (Fig. 2b).

The electrode functions of the studied surfactant-selective sensors are linear in $n \times 10^{-6}(10^{-5})$–$n \times 10^{-3}(10^{-2})$ M solutions of alkylsulfates (C_{10}–C_{16}), alkylsulfonates, alkylbenzenesulfonates, alkylpyridinium chloride, and cetyltrimethylammonium (the upper boundary of the concentration range is related to the different values of the critical concentration of micelle formation for alkylsulfates and alkylpyridinium cations with different lengths of hydrocarbon radical) (Table 1).

The coefficients of the potentiometric selectivity of surfactant-selective membranes for alkylsulfates and alkylpyridinium cations estimated by the mixed-solution method are low (0.6–1); this means that the electrodes allow either individual surfactants or total surfactants of certain types to be detected. The coefficients of potentiometric selectivity also correlate with the hydrophobicity of surfactants (Fig. 4).

Based on the difference in the values of K_s of cetylpyridinium–alkylsulfate ion pairs, one can separately determine anionic surfactants by potentiometric titration (Fig. 5). We have found analytical ranges and ratios of components in binary mixtures of sodium alkylsulfate homologues for which their separate potentiometric determination is possible.

Table 3. Increments of methylene groups to the physicochemical properties of alkylpyridinium alkylsulfates and the electrochemical characteristics of membranes based on them

Characteristic	Sodium alkylsulfates	Alkylpyridinium chlorides
pK_s	0.65	0.51
$\log K_{ex}$	0.65	0.67
pK_g	0.10	0.07
pK_{sel}	0.13	0.17
$p\upsilon$	0.05	0.09
R, MΩ	0.025	0.011
p DL, M	0.21	0.26

Our investigations showed that the solubility of ionophores, constants of extraction with dibutyl phthalate, and dissociation constants in the membrane phase depend on the length of the hydrocarbon radical of alkylsulfate and alkylpyridinium cation entering into the composition of ionophores. The resistance of membranes, transport rates, coefficients of potentiometric selectivity, and detection limits for surfactants also depend on the hydrophobicity of surfactants. The contributions of increments, CH_2 groups, to chemical and electrochemical parameters of membranes are presented in Table 3.

Based on the found effect of surfactant hydrophobicity on the physicochemical parameters of alkylpyridinium alkylsulfates and electroanalytical properties of membranes based on these compounds, we could reasonably search for ionophores for potentiometric sensors for solving specific analytical problems.

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REFERENCES

1. Perov, P.A., *Tematicheskii obzor. Analiticheskii kontrol' za soderzhaniem poverkhnostno-aktivnykh veshchestv i soputstvuyushchikh komponentov v proizvodstvennykh i stochnykh vodakh* (Analytical Control of Surfactants and Attendant Components in Process and Waste Waters: A Review), Moscow: TsNIITENeftekhim, 1990.
2. Shoester, M. and Kloster, G., *Fresenius' J. Anal. Chem*, 1993, vol. 345, no. 12, p. 767.
3. Kulapin, A.I. and Arinushkina, T.V., *Zavod. Lab. Diagn. Mater.*, 2001, vol. 67, no. 11, p. 3.

4. Birch, B.J. and Cockeroff, R.N., *Ion-Sel. Electrode Rev.,* 1981, vol. 3, p. 1.
5. Vytras, K., *Ion-Sel. Electrode Rev.*, 1985, vol. 7, p. 77.
6. Chernova, R.K., Kulapina, E.G., Materova, E.A., and Chernova, M.A., *Zh. Anal. Khim.*, 1988, vol. 43, no. 12, p. 2179.
7. Thomas, J.D.R., *Anal. Lett.,* 1990, vol. 22, no. 5, p. 1057.
8. Kulapina, E.G., Chernova, R.K., Kulapin, A.I., and Mitrokhina, S.A., *Zavod. Lab.*, 2000, vol. 66, no. 11, p. 3.
9. Chernova, R.K., Kulapina, E.G., Materova, E.A., *et al.*, *Zh. Anal. Khim.*, 1995, vol. 50, no. 7, p. 705.
10. Bates, R.G., *Determination of pH: Theory and Practice*, New York: Wiley, 1964. Translated under the title *Opredelenie pH. Teoriya i praktika*, Leningrad, 1968.
11. Yurinskaya, V.E., Stefanova, O.K., and Materova, E.A., *Elektrokhimiya*, 1981, vol. 17, no. 11, p. 1618.
12. Kulapin, A.I. and Arinushkina, T.V., *Zh. Anal. Khim.*, 2000, vol. 55, no. 11, p. 1218 [*J. Anal. Chem.* (Engl. Transl.), vol. 55, no. 11, p. 1096].
13. Mar'yanov, B.M., *Zh. Anal. Khim.*, 1986, vol. 41, no. 9, p. 1698.
14. Fisher, A.V., *Zh. Anal. Khim.*, 1985, vol. 40, no. 3, p. 493.
15. Fialkov, Yu.D., Zhitomirskii, A.N., and Tarasenko, Yu.A., *Fizicheskaya khimiya nevodnykh rastvorov* (Physical Chemistry of Nonaqueous Solutions), Leningrad: Khimiya, 1973.