Solid-phase reagents for the determination of anionic surfactants in water

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Sorption–spectrometric methods for the determination of anionic surfactants (A Surf) in natural and waste water using silica gel (SG) loaded with ion-pair associates of high molecular weight quaternary ammonium salts (QAS) and anionic dyes were developed. For this purpose, the interaction of Methyl Orange (MO), sodium picrate (Picr) and fluorescein (Fl) with didecylaminoethyl-β-tridecylammonium iodide (I) and *N*-methyl-*N,N,N′,N′,N′*-pentadecylethyldiammonium diiodide (II) immobilized on the surface of SG was investigated. SG loaded with I-MO and I-Fl associates was used for the determination of sodium dodecyl sulfate (SDS) in natural and waste water using absorbance, diffuse reflectance spectrometric and luminescence methods. Detection limits were 0.05 and 0.01 ppm, respectively. Humic and fulvic acids at levels < 0.5 ppm did not interfere with SDS determination. Water with higher acid contents was analysed using SG modified with the II-Picr associate at pH 2. Visual test scales for SDS determination in water at one fifth of the maximum admissible concentration (MAC) level was prepared.

***Keywords:** Adsorption onto silica gel; quaternary ammonium salt; anionic dye; anionic surfactant determination*

Synthetic anionic surfactants (A Surf) are one of the most toxic pollutants in natural water. The spectrophotometric and spectro-fluorimetric methods for A Surf determination at the maximum admissible concentration (MAC) level are based on ion-pair extraction with cationic metal chelates such as bis[2-(5-tri-fluoromethyl-2-pyridylazo)-5-diethylaminophenolato]-cobalt(III)[1] or basic dyes, *e.g.,* Methylene Blue, Ethyl Violet and Rhodamine B and 6G.[2–6] The sensitivity of these methods is 0.002–0.2 ppm. Inorganic anions, long-chain organic anions, non-ionic and cationic surfactants and especially humic and fulvic acid interfere with A Surf determination. A more selective extraction–spectrophotometric method for A Surf determination at levels > 0.03 ppm has been reported, based on their previous sorption separation using fibrous materials.[7] However, this method is fairly tedious and time consuming (the time for a single analysis is more than 1 h). All the described methods need toxic organic solvents.

Rapid techniques for A Surf determination in water that do not require toxic solvents have been developed. For example, filter-paper impregnated with a mixed aluminum–zinc hydroxide was used for the analysis of water with > 0.02 ppm A Surf content.[5] The A Surf was collected on the paper as products from their reaction with Rhodamine B, the paper was extracted with ethanol and the extract quantified photometrically. However, humic and fulvic acid interfered with A Surf determination.

High molecular weight quaternary ammonium salts (QAS) have found wide application in trace analysis.[8] The flow-injection spectrophotometric determination of A Surf has been described, based on the formation of a stable ion-pair associate

with QAS.[9] However, this method is indirect; the detection limit is 0.03 ppm. Didecylaminoethyl-β-tridecylammonium iodide immobilized on silica gel (SG) has been used for the preconcentration and determination of anionic metal complexes.[10] This sorbent was not applied to the determination of other anions.

In the present work, the possibility of the sorption–spectrometric determination of A Surf in natural and waste water using SG loaded with ion-pair associates of anionic dyes (Methyl Orange, sodium picrate and fluorescein) with QAS (didecylaminoethyl-β-tridecylammonium iodide and *N*-methyl-*N,N,N′,N′,N′*-pentadecylethyldiammonium diiodide) was studied.

Experimental

Apparatus

UV/VIS spectra were measured using a Specord M-40 spectrophotometer (Carl Zeiss Jena, Jena, Germany) and 1 cm quartz cells. A Model EV-74 potentiometer with a glass electrode was used for pH measurements. The luminescence intensity was measured with a Model DRK-120 luminescence spectrophotometer with a mercury vapour lamp (Kiev, Ukraine) and 1 cm quartz cells.

Reagents

All chemicals were of analytical-reagent grade. Distilled water was further distilled once before use.[11] Methyl Orange (MO), sodium picrate (Picr) and fluorescein (Fl) were obtained from Merck (Darmstadt, Germany); 5.0 mmol l^{-1} solutions were used. Sodium dodecyl sulfate (SDS) solution (1.0 mmol l^{-1}) was prepared by dissolving the reagent (98%) (Merck) in water. Silica gel L 40/100 was from Chemapol (Prague, Czech Republic). The QAS didecylaminoethyl-β-tridecylammonium iodide (**I**) and *N*-methyl-*N,N,N′,N′,N′*-pentadecylethyldiam-monium diiodide (**II**) were synthesized as described elsewhere[12] and were used for preparing the modified silica gel. Modified silica gels (**I**-SG and **II**-SG) with QAS contents of 0.12 and 0.012 mmol g^{-1}, respectively, were obtained as described in ref. 10. Humic and fulvic acid obtained by a standard method[13] from river water were used for preparation of their aqueous solutions.

Procedure

Sorption of anionic dyes onto *I*-SG and *II*-SG

I-SG or **II**-SG (0.2 g) was stirred with 50 ml of an aqueous solution containing a known amount of the dye (0.05–0.5 mmol l^{-1}) for 10–40 min at the appropriate pH. The mixture was then centrifuged and the solid product dried at 80 °C. The residual MO and Picr in the aqueous solution were measured spectrophotometrically at 440 and 364 nm, respectively. The equilibrium concentration of Fl in solution was determined by measuring the luminescence intensity at 496 nm.

Desorption of anionic dyes from the surface of loaded silica gel

I-SG modified with MO (MO-**I**-SG) or Fl (FI-**I**-SG) or **II**-SG modified with Picr (Picr-**II**-SG) (0.05 g) was stirred with 50 ml of 0.01–0.1 mmol l^{-1} aqueous SDS solution at the appropriate pH for 10–60 min. The mixture was then centrifuged and the amount of dye removed by SDS from the surface of the silica gel into solution was measured by spectrophotometric or luminescence (Fl) methods.

Results and discussion

Modification of I-SG and II-SG by anionic dyes

The sorption of MO, Picr and Fl from aqueous solutions onto **I**-SG and **II**-SG was studied. The effect of pH on the sorption of the dyes was examined. It was found that MO and Picr were adsorbed at pH 4–9 and Fl at pH 8–9. The effect of time on the sorption of the dyes is shown in Fig. 1. It was found that equilibrium of adsorption of the dyes was reached in 30 min (MO and Fl) and 20 min (Picr).

Sorption isotherms were evaluated in order to quantify the affinity of the adsorbents for the dyes. The results are shown in Fig. 2. The maximum amounts of MO and Fl adsorbed on the surface of **I**-SG are 0.12 and 0.02 mmol g^{-1}, respectively. The maximum amounts of Picr adsorbed on the surface of **I**-SG and **II**-SG are 0.12 and 0.025 mmol g^{-1}, respectively. Thus, MO (Picr): I = 1 : 1 and Picr: II = 2 : 1 associates are formed on the QAS-SG surface under optimum conditions. The small amount
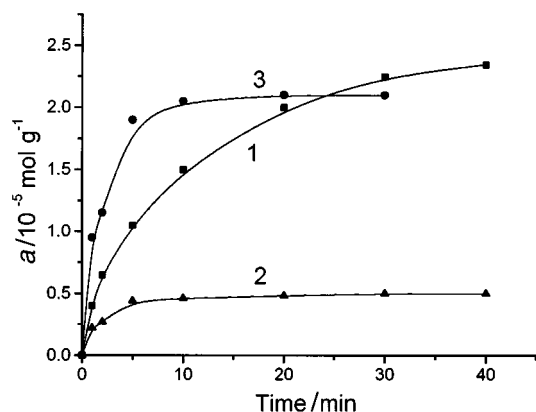

Fig. 1 Kinetics of MO (1), Fl (2) and Picr (3) sorption on **I**-SG (1,2) and **II**-SG (3). Concentration of dyes: 1×10^{-5} (1,3); 4×10^{-6} (2) mol l^{-1}; pH 5.5 (1,3) and 8.0 (2); volume, 50 ml.
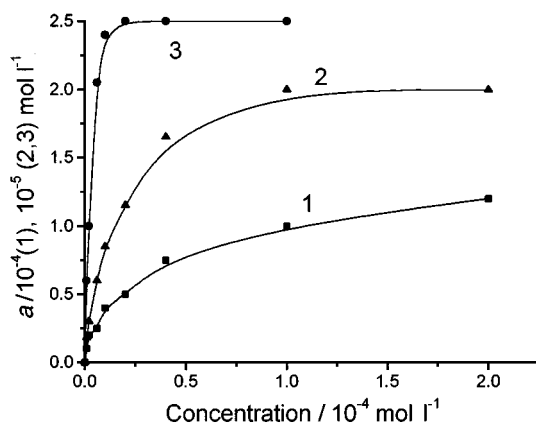

Fig. 2 Sorption isotherms of MO (1), Fl (2) and Picr (3) on **I**-SG (1,2) and **II**-SG (3). Content of QAS on SG surface: 1.2×10^{-4} (**I**) and 1.2×10^{-5} (**II**) mol g^{-1}; mass of sorbent, 0.02 g; volume, 50 ml.

of Fl on the surface of **I**-SG is the result of incomplete dissociation of the dye in aqueous solution at pH 8–9.[14]

The isotherms are formally described by a Langmuir equation with conditional constants (10^4 l mol^{-1}): of 1.4 (MO), 5.1 (Fl) and 16.6 (Picr).

Desorption of dyes by anions

The desorption of the dyes from the QAS-SG surface by aqueous solutions of inorganic and organic anions was studied using dye-**I**-SG.

The process is based on anion exchange of the dye at the QAS-SG/solution interface according to the reaction:

$$\text{Dye-}\mathbf{I}\text{-SG} + \text{An}^{n-} \rightarrow \text{An-}\mathbf{I}\text{-SG} + n \text{ Dye}^- \qquad (1)$$
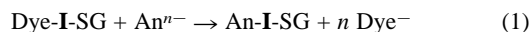
It can be described by an effective exchange constant when the amount of dye on the surface decreases by not more than 1–2% during the exchange process:

$$K = [\text{Dye}]^n/[\text{An}^{n-}] \qquad (2)$$

where $[\text{An}^{n-}] = C_{\text{An}} - [\text{Dye}^-]$. The concentration of the dominant anion (C_{An}) at the appropriate pH was calculated by using the initial anion concentration and dissociation constants of acids.[15] The values of the effective exchange constant (K) for different inorganic and organic ions are given in Table 1. The data obtained showed that the dyes were hardly removed from the surface of **I**-SG by short-chain organic and inorganic ions, except for thiocyanate ions. The maximum replacement effect was observed for organic ions, especially for long-chain organic anions such as A surf.

In order to choose the optimum dye for the spectrophotometric determination of A Surf, the dependence of MO and Picr removal from the loaded SG surface on SDS concentration was studied. It was found that the sensitivity coefficient (dA/dC for the range of linearity of the calibration graph) using MO-**I**-SG was more than two-fold higher than that for Picr-**I**-SG. Thus, MO-**I**-SG was used in all further work.

The pH dependence of the desorption of the dyes from the modified SG surface by SDS is shown in Fig. 3. The optimum pH range of Fl desorption from the surface Fl-**I**-SG by SDS is 8–9, since silica dissolves in aqueous solutions at pH > 10. MO-**I**-SG can be used at 4 < pH < 9 because **I** and MO are partly washed from the surface at pH < 3[10] and the blank value is not constant. **II** and Picr are not desorbed at pH $\geqslant$ 2, so Picr-**II**-SG can be used in a weakly acidic medium.

The kinetics of the desorption of the dyes by SDS are presented in Fig. 4. It was shown that equilibrium was reached in 30 min for MO-**I**-SG and Fl-**I**-SG and in 40 min for Picr-**II**-SG for a 50 ml sample volume. The blank values were stable under the conditions studied.

Analytical application of modified sorbents

Mo-**I**-SG, Fl-**I**-SG and Picr-**II**-SG were examined as solid-phase reagents for SDS determination in dilute solutions. The

Table 1 Conditional constants of MO (1) and Fl (2) exchange with inorganic and organic ions on the surface of **I**-SG. The values of MO and Fl adsorption were 0.05 and 0.02 mmol g^{-1}, respectively. pH 6 (1) and 8 (2)

| Inorganic anion	pK		Organic anion	pK	
	1	2		1	2
Cl$^-$	4.0	4.0	Acetate	5.0	3.6
HCO$_3^-$	3.4	3.4	Tartrate	9.6	9.9
NO$_3^-$	3.8	3.0	Citrate	10	14
SCN$^-$	1.5	1.8	EDTA	13	14
SO$_4^{2-}$	13	9.8	SDS	0.75	1.5

method was based on removal of the dyes from the surface of loaded SG into an aqueous solution by SDS. The amount of dyes in solution can be determined by spectrophotometric (MO, Picr) or luminescence (Fl) methods.

The influence of foreign ions on the results of SDS determination with the modified sorbents was examined. No interference was observed for alkali, alkaline earth and heavy metals at their average content in natural water, for inorganic and short-chain organic ions at concentrations <1 mmol l^{-1} and for long-chain organic anions (humic and fulvic acid) at contents of less than 0.5 and 10 ppm, respectively. Hence, the modified sorbents were applied to SDS determination in natural and waste water.

Determination of SDS using Mo-I-SG

Absorbance method

Water samples (50 ml) with SDS contents of 5–500 μg at pH 5–7 were stirred for 30 min with 0.05 g of MO-I-SG and then centrifuged. The concentration of MO removed into solution was determined spectrophotometrically by means of a calibration graph which was prepared under the same conditions using standard SDS solutions. The equation of the calibration graph was $A_{440} = 0.1C(\text{ppm}) + 0.14$. The calibration graph was linear in the range 0.1–10 ppm SDS and the detection limit was 0.05 ppm. The results of SDS determination in synthetic solutions and sewage are presented in Table 2.
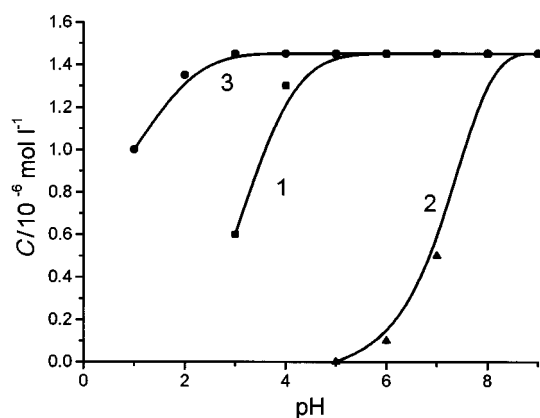
Fig. 3 Effect of pH on MO (1), Fl (2) and Picr (3) removal from **I**-SG (1,2) and **II**-SG (3). Concentration: SDS, 2×10^{-5} mol l^{-1}. Dye content on the surface (mol g^{-1}): 5×10^{-5} (1), 5×10^{-6} (2), 1×10^{-5} (3).
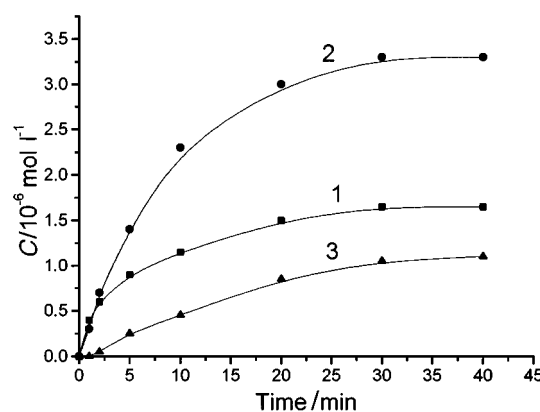
Fig. 4 Kinetics of MO (1), Fl (2) and Picr (3) removal from **I**-SG (1,2) and **II**-SG (3) surfaces by SDS. Concentration: SDS, 5×10^{-5} (1, 3) and 2×10^{-5} (2) mol l^{-1}. pH = 5.5 (1,3) and 8.0 (2). Dye content on the surface (mol g^{-1}): 5×10^{-5} (1), 1×10^{-5} (2,3). Phase volume, 50 ml.

Method of diffuse reflectance spectrometry with MO preconcentration

Water samples (250 ml) with SDS contents of 1.5–150 μg were stirred with MO-I-SG as described above. The MO desorbed was recovered from solution with 0.2 g of I-SG for 30 min. The amount of MO adsorbed on the surface of **I**-SG was determined by diffuse reflectance spectrometry. The equation of the calibration graph was: $R_{440} = 0.39C$ (ppm) $+ 0.35$. The calibration graph was linear in the range 0.02–3 ppm SDS. The detection limit was 0.015 ppm, which is three times lower than that of the spectrophotometric method. Water samples with low contents of humic and fulvic acid were examined. The results of SDS determination in synthetic solutions and waste water are presented in Table 2.

Determination of SDS using Fl-I-SG

Water samples (50 ml) with SDS contents of 1–150 μg at pH 8–9 were stirred for 30 min with 0.05 g of Fl-**I**-SG and centrifuged. The amount of Fl removed by SDS into solution was determined by a luminescence method. The calibration graph was prepared by using the same procedure and standard SDS solutions. The equation of the calibration graph was: I(real units) $= 150C$ (ppm) $+ 41$. The calibration graph was linear in the range 0.02–3.0 ppm SDS. The detection limit (0.01 ppm for a 50 ml water sample) was similar to that of diffuse reflectance spectrometry and five times lower than that of the spectrophotometric method. The results of SDS determination in model solutions and natural water are presented in Table 3.

Humic acid at concentrations above 0.5 ppm and fulvic acid at concentrations above 10 ppm interfere with the determination of SDS with MO-**I**-SG and Fl-**I**-SG as a result of the dissociation of their carboxyl groups at pH > 2.5.[16] Their influence can be removed by using Picr-**II**-SG in a weakly acidic medium.

Determination of SDS using Picr-II-SG

Water samples (50 ml) containing 5–500 μg of SDS at pH 2 were stirred for 40 min with 0.05 g of Picr-**II**-SG and centrifuged. The amount of Picr removed by SDS into the aqueous solution was determined spectrophotometrically. The calibration graph for SDS determination was prepared under the same conditions using standard SDS solutions. The equation of the calibration graph was: $A_{364} = 0.12C$ (ppm) $+ 0.11$. The calibration graph was linear in the range 0.1–10 ppm SDS and the detection limit was 0.05 ppm. The results of SDS

Table 2 Results of SDS determination in synthetic solutions and water with MO-**I**-SG using spectrophotometric (1) and diffuse reflectance spectrometric (2) techniques. Sample volume, 50 (1) and 250 (2) ml; mass of sorbent = 0.05 (1) and 0.2 (2) g; $n = 4$; $p = 0.95$

| | | | SDS/mg l^{-1} | | |
No.	Sample	Method	Added	Found $x \pm \Delta x$	RSD
1	Synthetic solution*	1	1.5	1.50 ± 0.08	0.05
2	Synthetic solution*	1	3.0	2.9 ± 0.2	0.06
3	Synthetic solution*	2	0.14	0.15 ± 0.02	0.10
4	Synthetic solution*	2	0.28	0.28 ± 0.03	0.09
5	Waste water	1	0	3.0 ± 0.3	0.06
6	Waste water	2	0	2.5 ± 0.2	0.05
7	Waste water	1	3.5	6.3 ± 0.6	0.06
8	Waste water	2	3.5	5.7 ± 0.5	0.06
9	Waste water	1	10.6	13.6 ± 0.6	0.05
10	Waste water	2	10.6	13.1 ± 0.5	0.05

* Concentrations: Cl$^-$, NO$_3^-$, SO$_4^{2-}$, CO$_3^{2-}$ = 1×10^{-3} mol l^{-1}; humic acid = 0.5 mg l^{-1}; fulvic acid = 5.0 mg l^{-1}.

determination in synthetic solutions and natural water are presented in Table 3. The method can be applied to SDS determination in natural water at fulvic acid concentrations up to 150 ppm. Humic acid did not interfere under these conditions.

Visual test scales for SDS determination

Visual scales for SDS determination were prepared. The scale for tap water analysis was obtained by stirring standard solutions (V = 50 ml) containing 0, 0.036, 0.072, 0.144, 0.360 and 0.720 mg of SDS at pH 5–7 with 0.05 g of MO-**I**-SG for 30 min. The desorbed MO was recovered from solution by stirring with 0.2 g of **I**-SG for 30 min. The scale for natural water analysis was obtained by using Picr-**II**-SG at pH 2 following the described procedure. The amount of dye on the surface of **I(II)**-SG was determined visually. The maximum relative standard deviation of the test determinations did not exceed 0.50. The scales were stable for more than 1 year. The visual method permits the SDS content in water to be monitored at one fifth of the MAC level.

Table 3 Results of SDS determination in synthetic solutions and natural water by spectrophotometric (1) and fluorescence (2) methods, using Picr-**II**-SG (1) and Fl-**I**-SG (2). Sample volume, 50 ml; mass of sorbent = 0.05 g; pH = 2 (1) and 8 (2); n = 4; p = 0.95

No.	Sample	Method	Added	Found $x \pm \Delta x$	RSD
			SDS/mg l^{-1}		
1	Synthetic solution*	1	0.20	0.21 ± 0.03	0.09
2	Synthetic solution*	1	0.50	0.52 ± 0.04	0.05
3	Synthetic solution*	1	1.00	1.50 ± 0.08	0.05
4	Synthetic solution†	2	0.27	0.25 ± 0.06	0.10
5	Synthetic solution†	2	1.36	1.40 ± 0.05	0.04
6	Natural water 1	1	0	0.51 ± 0.03	0.04
7	Natural water 1	1	0.50	1.04 ± 0.08	0.05
8	Natural water 1	1	1.00	1.54 ± 0.05	0.04
9	Natural water 2	2	0.27	0.25 ± 0.05	0.12
10	Natural water 2	2	0.54	0.68 ± 0.10	0.10

* Concentrations: Cl$^-$, NO$_3$$^-$, SO$_4$$^{2-}$, CO$_3$$^{2-}$ = 1 × 10^{-3} mol l^{-1}; humic acid = 10 mg l^{-1}; fulvic acid = 150 mg l^{-1}. † Concentrations: Cl$^-$, NO$_3$$^-$, SO$_4$$^{2-}$, CO$_3$$^{2-}$ = 1 × 10^{-3} mol l^{-1}; cationic surfactants = 1 × 10^{-6} mol l^{-1}; non-ionic surfactants = 1 × 10^{-5} mol l^{-1}.

Conclusions

MO, Fl and Picr formed stable ion-pair associates with high molecular weight QAS loaded on SG. The dyes were hardly removed from the immobilized associate by inorganic and short-chain organic ions but were easily replaced by long-chain organic anions, especially A Surf. This phenomenon was used to develop sorption–spectrometric and visual test methods for SDS determination in tap, natural and waste water.

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