

Adsorption–Photometric Determination of Cationic Surfactant Traces

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Abstract—A procedure has been developed for the adsorption–photometric determination of cationic surfactants in natural water. The procedure is based on the adsorption preconcentration of the cationic surfactants on silica gel, the reaction of the concentrate with the anionic reagent bromothymol blue to form ion pairs on a solid surface, and the photometric determination of excess bromothymol blue in solution. The analytical range is $(0.5–5) \times 10^{-5}$ M for a 50-mL sample.

Recently, the production and use of synthetic surfactants have been growing steadily. Therefore, their concentration in environmental objects, particularly, in natural water, increases. Though synthetic surfactants exhibit no explicit toxicity (except for bactericidal cationic surfactants), they facilitate the accumulation of other toxic substances in the surface films of the hydrosphere because of adsorption processes. At the same time, transformation products of surfactants themselves can be toxic [1, 2]. Cationic surfactants are among the most toxic synthetic surfactants. It is necessary to tighten analytical control over them. Since the maximum permissible concentrations for some cationic surfactants do not exceed 0.2 mg/L, the development of rapid and highly sensitive methods for the determination of their traces is required [2, 3], because most of the known methods for the analysis of water are less sensitive. In particular, all versions of titrimetry allow the determination of no less than $\geq 1 \times 10^{-3}$ M surfactants [2, 4].

Preconcentration by solvent extraction, adsorption, or chromatography is used to reduce the detection limits of various methods for the determination of surfactants. Extraction–photometry is one of the simplest and most sensitive methods (the detection limit is $\geq 1 \times 10^{-5}$ M). The sensitivity of the extraction–fluorimetric method (the detection limit of $\geq 5 \times 10^{-6}$ M) is somewhat higher [1, 2]. The main drawbacks of these two hyphenated methods are insufficient detection limits resulting from the relatively low (usually no more than 6) distribution ratios in these systems [5–7] and sanitary limitations for the operations involving volatile organic solvents. These drawbacks can be removed by replacing liquid extraction by adsorption on various solid supports.

As experience has shown, methods for the determination of surfactants with adsorption preconcentration are more sensitive than extraction methods [2, 4–9]. Various versions of hyphenated methods are used, particularly, the preconcentration of colored ion pairs of

surfactants with color reagents on membrane filters followed by solid-phase spectrophotometric determination (the detection limit reaches 1×10^{-5} M) [2, 8]. The competitive adsorption of cationic surfactants and the cationic methylene blue dye on silica gel was used in [5]. The decrease in the adsorption of methylene blue was proportional to the concentration of cationic surfactants in solutions (the detection limit was 1×10^{-5} M). Chromatomembrane preconcentration followed by the extraction–photometric determination of anionic surfactants (the detection limit is reduced to 1×10^{-6} M) was used in [6, 9].

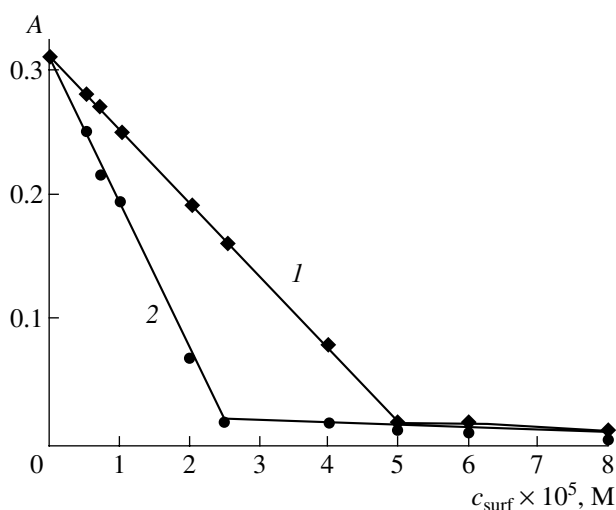
Thus, adsorption preconcentration opens up possibilities for the development of new sensitive, rapid, environmentally safe, and labor-saving methods of analytical control over synthetic surfactants in natural water.

We showed in [10] that, when an anionic dye interacts with the silica gel surface with a preadsorbed cationic surfactant, stoichiometric (in accordance with the charge of the reacting components) ion pairs of the cationic surfactant and the anionic dye are formed and retained on the surface. The excess dye remains in the aqueous phase and can be determined by photometry.

In this work, we have developed an adsorption–photometric procedure for the determination of traces of cationic surfactants in natural water using the anionic bromothymol blue dye of the sulfophthalein series with the adsorption preconcentration of the corresponding cationic surfactant on silica gel.

EXPERIMENTAL

We used ethonium (a bis-quaternary ammonium salt) $[(\text{CH}_3)_2\text{RN}^+(\text{CH}_2)_2\text{N}^+\text{R}(\text{CH}_3)_2] \cdot 2\text{Cl}^-$ (ETCl₂), where R is CH₂COOC₁₀H₂₁, and cetylpyridinium chloride (CPCI) differing by the charge and structure of their hydrocarbon chains. Cationic surfactant solutions were prepared by dissolving accurately weighed por-



Calibration plots for the adsorption-photometric determination of (1) cetylpyridinium chloride and (2) ethonium.

tions of pharmaceutical grade substances in water. A stock 1×10^{-3} M solution of bromothymol blue was prepared by dissolving 0.0625 g of bromothymol blue of analytical grade in 100 mL of 0.15% Na_2CO_3 in water.

To maintain a constant ionic strength, we used 0.1 M NaCl as a supporting electrolyte. The absorbances were measured with a KFK-2 photometer at 490 nm and 1 cm path length. We used Silicagel L 5/40 for chromatography (Chemapol, Czech Republic) silica gel.

RESULTS AND DISCUSSION

Preliminarily, we studied the adsorption interaction of ethonium and cetylpyridinium chloride with silica gel and optimized the conditions for the quantitative extraction of these cationic surfactants in the range 1×10^{-5} – 1×10^{-4} M.

It was found that the equilibration time in the corresponding adsorption systems is 30 min. The quantitative extraction of the cationic surfactants is achieved at a mass ratio of the solid and liquid phases of 1 : 500 (0.1 g of silica gel per 50 mL of the analyte solution). As for the dependence of adsorption on pH, it was found that the cationic surfactants are extracted almost quantitatively (97–98%) at pH from 4 to 8. At higher acidity (pH down to 2), the adsorption slightly decreases (to 75%). This is caused by the absence of the electrostatic component of the adsorption interaction, because a zero-charge point is attained at the silica gel surface. At the same time, it is known that the alkaline hydrolysis of cationic surfactants can proceed at $\text{pH} > 8$ [11]; therefore, studying the adsorption of the cationic surfactants in this pH range is of no use. Hence, the adsorption of cationic surfactants was performed at pH 4.

It is known [12] that, in acid solutions (from 4 M to pH 7), anionic bromothymol blue dye exists as the Y^{2-} ion. At pH 2.7–2.8, bromothymol blue quantitatively associates with cationic surfactants to form stoichiometric ion pairs in accordance with their charge. Association in the bromothymol blue–cationic surfactant systems causes a slight hypsochromic shift in the absorption spectra ($\Delta\lambda = 20$ nm, $\lambda_{\text{bromothymol blue}} = 480$ nm, $\lambda_{\text{ion pair}} = 460$ nm) [13, 14]. During association in solutions, the visible aggregation of neutral molecules begins within approximately 5 min, causing opacity. Because of this, we did not study the adsorption of the cationic surfactant–dye ion pairs by silica gel from solutions. The experiment was designed so that the ion pairs formed immediately on the silica gel surface. To do this, cationic surfactants are adsorbed at optimum conditions; next, the obtained concentrate is placed in a bromothymol blue solution of an exactly known concentration at pH 2.7. Previously, it was found that bromothymol blue at pH 2.7 is not adsorbed by silica gel; this is probably caused by the high density of the negative charge of its ions. Under these conditions, the absorbances of the dye solutions separated from the concentrate after 20 min decrease in proportion to the amount of the preadsorbed cationic surfactant. The obtained plots are shown in the figure. The shape of these plots (a distinct kink) as well as the general concept of the adsorption properties of silica gel allow one to conclude that cationic surfactant–bromothymol blue ion pairs are formed on a silica gel surface at pH 2.7. Ion pairs are electroneutral, hydrophobically hydrated particles [15]. At the same time, the surface charge of silica gel at pH 2.7 is close to a zero-charge point, which also decreases the hydrophilic hydration of surface groups. Therefore, the affinity and strength of the adsorption interaction of silica gel and the ion pairs at pH 2.7 caused by van der Waals interaction increases, and the ion pairs are adsorbed quantitatively; this is supported by the experiment. The unreacted bromothymol blue remains in solution.

The figure shows that the plots of the solution absorbance vs. initial concentration of the cationic surfactants are linear at 5×10^{-6} – 5×10^{-5} M for cetylpyridinium chloride and 5×10^{-6} – 2.5×10^{-5} M for ethonium. Therefore, these plots can be used as calibration graphs for the determination of the corresponding cationic surfactants. This method is indirect; therefore, the plots do not begin at the origin of the coordinates, and the zero concentration of the cationic surfactant corresponds to the initial concentration of bromothymol blue in the operational solution.

The kinks in the plots show that the ion pairs are formed on the silica gel surface. It follows from the plots that the kink corresponds to 5×10^{-5} M cetylpyridinium chloride and 2.5×10^{-5} M ethonium for adsorption from 50 mL of solution. The corresponding molar

Table 1. Determination of cationic surfactants in model solutions (0.1 g of silica gel, $\tau = 30$ min, $c_{\text{bromothymol blue}} = 5.00 \times 10^{-5}$ M, total salt content 12 g/L, $P = 0.95$, $n = 5$)

Cationic surfactant	Added, $c \times 10^5$, M	Found, $c \times 10^5$, M	RSD, %
Cetylpyridinium chloride	0.00	0.02 ± 0.02	6.4
	0.50	0.48 ± 0.02	3.8
	1.00	0.98 ± 0.01	1.2
	5.00	5.02 ± 0.01	0.2
	10.00	10.07 ± 0.01	0.1
Ethonium	0.00	0.01 ± 0.01	2.1
	0.50	0.49 ± 0.01	1.7
	1.00	1.07 ± 0.01	1.1
	2.50	2.52 ± 0.02	0.5
	5.00	4.99 ± 0.01	0.2

The proposed indirect adsorption-photometric determination of cationic surfactant traces was verified using model solutions with a maximum salinity of up to 12 g/L (Table 1). At total 12 g/L, the salt content was 0.45 g/L CaCl_2 , 0.6 g/L MgCl_2 , 0.19 g/L KCl, 0.08 g/L Na_2SO_4 , 10.48 g/L NaHCO_3 , and 0.08 g/L NaOH. The results show that the high salt concentration affects only slightly the sensitivity of the proposed procedure in the region of trace concentrations of cationic surfactants.

An increase in the volume of the cationic surfactant solution of up to 250 mL causes no changes in the corresponding absorbances and decreases the detection limit by a factor of 5. Further increase in the solution volume results in substantial errors caused by the loss of the suspended silica gel during filtration.

The developed procedure was tested on real samples in the analysis of natural and mineral water samples differing in the total salt content and by the added-found method (Tables 2 and 3). The performance characteristics show that the procedure exhibits no systematic errors and has a reasonably high precision. The results obtained by simultaneously spiking the analyte with cationic surfactants of different classes (cetylpyridin-

ratios are $Y : \text{CPCl} = 1 : 2$ and $Y : \text{ETCl}_2 = 1 : 1$ according to the stoichiometry of the following equilibria:

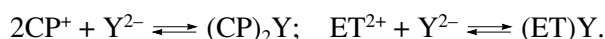


Table 2. Determination of cationic surfactants in natural water (0.1 g of silica gel, $\tau = 30$ min, $c_{\text{bromothymol blue}} = 5.00 \times 10^{-5}$ M, $P = 0.95$, $n = 5$)

Sample	Cationic surfactant added	Added, $c \times 10^{-5}$, M	Found, $c \times 10^{-5}$, M	RSD, %
Tap water, Odessa	–	–	0	–
	Cetylpyridinium chloride	1.00	0.98 ± 0.03	2.5
		2.50	2.47 ± 0.02	0.6
	Ethonium	1.00	1.02 ± 0.05	4.3
		2.00	2.03 ± 0.02	0.6
	Cetylpyridinium chloride + ethonium	$0.50 + 0.50$	$1.48 \pm 0.02^*$	1.2
$1.00 + 1.00$		$2.97 \pm 0.01^*$	0.4	
Water from Turunchuk River, Odessa Region*	–	–	0	–
	Cetylpyridinium chloride	1.00	1.06 ± 0.05	4.0
		2.50	2.51 ± 0.01	0.4
	Ethonium	1.00	0.98 ± 0.04	3.0
		2.00	1.97 ± 0.01	0.6
	Cetylpyridinium chloride + ethonium	$0.50 + 0.50$	$1.50 \pm 0.02^*$	1.4
		$1.00 + 1.00$	$3.02 \pm 0.01^*$	0.3
	Water from Lake Yalpus, Odessa Region*	–	–	0.50 ± 0.01
Cetylpyridinium chloride		1.00	1.50 ± 0.04	2.2
		2.50	2.97 ± 0.04	1.2
Ethonium		1.00	1.50 ± 0.01	0.2
		2.00	2.48 ± 0.01	0.4
Cetylpyridinium chloride + ethonium		$0.50 + 0.50$	$1.98 \pm 0.02^*$	0.8
	$1.00 + 1.00$	$3.52 \pm 0.01^*$	0.2	

* For solutions spiked with cetylpyridinium chloride + ethonium mixture, the determination was performed with the calibration plot for cetylpyridinium chloride.

Table 3. Determination of cationic surfactants in mineral water (0.1 g of silica gel, $\tau = 30$ min, $c_{\text{bromothymol blue}} = 5.00 \times 10^{-5}$ M, $P = 0.95$, $n = 5$)

Sample	Cationic surfactant added	Added, $c \times 10^5$, M	Found, $c \times 10^5$, M	RSD, %
Kuyal'nik, total salt concentration 3.0–4.0 g/L	–	–	0	–
	Cetylpyridinium chloride	1.0	1.05 ± 0.04	3.5
		2.5	2.54 ± 0.02	7.0
	Ethonium	1.0	1.08 ± 0.04	3.4
		2.0	2.04 ± 0.02	0.8
	Cetylpyridinium chloride + ethonium	0.50 + 0.50	$1.54 \pm 0.03^*$	1.8
1.00 + 1.00		$3.04 \pm 0.01^*$	0.5	
Luzhanskaya-7, total salt concentration 6.5–9.0 g/L	–	–	0	–
	Cetylpyridinium chloride	1.00	1.05 ± 0.04	3.2
		2.50	2.56 ± 0.01	0.6
	Ethonium	1.00	0.99 ± 0.04	3.1
		2.00	1.95 ± 0.05	2.4
	Cetylpyridinium chloride + ethonium	0.50 + 0.50	$1.51 \pm 0.02^*$	0.9
1.00 + 1.00		$3.06 \pm 0.01^*$	0.5	
Polyana Kvasova, total salt concentration 6.5–12 g/L	–	–	0	–
	Cetylpyridinium chloride	1.00	1.01 ± 0.07	6.6
		2.50	2.50 ± 0.01	0.4
	Ethonium	1.00	1.07 ± 0.04	3.0
		2.00	2.06 ± 0.02	0.9
	Cetylpyridinium chloride + ethonium	0.50 + 0.50	$1.55 \pm 0.02^*$	1.2
1.00 + 1.00		$2.98 \pm 0.01^*$	0.4	

* See note to Table 2.

ium chloride and ethonium) indicate that this procedure can be used for the determination of not only a single surfactant but the total amount of different cationic surfactants as well.

Procedure of the adsorption–photometric determination of cationic surfactants. Portions (50 mL) of the water under study are placed in 100-mL beakers, and pH is adjusted to 4 by adding HCl and NaOH. The solutions are quantitatively transferred to 100-mL conical flasks with 0.1 g of silica gel and are shaken in a shaking apparatus for 30 min. The concentrates are separated from the solutions and quantitatively transferred to conical flasks with 25 mL of 5×10^{-5} M bromothymol blue at pH 2.7. The flasks are shaken in a shaking apparatus for 20 min. The suspension is centrifuged for 7 min at 12000–15000 rpm. The absorbance of the centrifugates is measured at 490 nm and 1 cm path length.

A calibration plot is constructed by placing various amounts of 1×10^{-4} M solution of a cationic surfactant in 100-mL beakers and diluting to 50 mL with distilled water. The surfactants are determined by the procedure described above.

The detection limits of the proposed adsorption–photometric procedure is 5×10^{-6} M or ca. 0.4 mg/L for 50-mL portions.

The rectilinear sections of the plots used as calibration graphs correspond to the regression equations $A = 0.3084 - 0.0945c_{\text{surf}}$ for cetylpyridinium chloride and $A = 0.3059 - 0.1159c_{\text{surf}}$ for ethonium. The correlation coefficients are 0.9956 and 0.9967, respectively.

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