Preconcentration and Rapid Spectrophotometric Determination of Polyoxyethylene Non-ionic Surfactants in Waters as Potassium Picrate Active Substances

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Preconcentration and Rapid Spectrophotometric Determination of Polyoxyethylene Non-Ionic Surfactants in Waters as Potassium Picrate Active Substances†

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The polyether chain of the polyoxyethylene non-ionic surfactants co-ordinates potassium cation in an aqueous solution and the positive complex is extracted into 1,2-dichloroethane as an ion-pair with picrate, which is the anionic chromophore for the spectrophotometric determination at 378 nm. Previous extraction of the non-ionics from the polluted waters by means of 1,2-dichloroethane eliminates the interference of the accompanying anionic surfactants and allows the determination of the Potassium Picrate Active Substances (PPAS).

A rapid procedure for the extraction and determination of PPAS in waters at levels from 100 down to $5 \mu g/l$ is proposed. The validity of the method for the absolute determination of commercial polydisperse surfactants of the type $R(OCH_2CH_2)_{\bar{n}}OH$ ($\bar{n}$ is the number-average degree of polymerization), derived from ethoxylation of primary alcohols from C_{10} to C_{18}, is discussed.

KEY WORDS: Polyoxyethylene non-ionic surfactants, Potassium Picrate Active Substances.

Non-ionic surfactants of the type $R(OCH_2CH_2)_nOH$, where R is a hydrophobic group and n is the degree of polymerisation, are widely used in household and industrial detergent formulations and are found at trace level (0.01–1 mg/kg) in waters receiving untreated urban liquid wastes. For instance, in coastal sea waters from gulf of Trieste (Northern Adriatic Sea) values ranging from 0.01 to 0.2 mg/kg have been determined with chromatographic[1,2] and spectrophotometric methods.[3,4] Surfactant

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concentration is usually referred to a standard substance: the mono-disperse hexaoxyethylene n-dodecylether, $C_{12}H_{25}(OCH_2CH_2)_6OH(C_{12}E_6)$ was already suggested for many reasons.[4]

The extraction and spectrophotometric determination at 378 nm of polyoxyethylene non-ionics as potassium picrate active substances (PPAS) has been recently suggested.[4] Potassium cation is coordinated by the open chain polyether of the surfactant in the aqueous phase and the positively charged complex is extracted into 1,2-dichloroethane by use of picrate as chromophoric, ion-pairing agent.[5] Reaction mechanisms have been also discussed by studying the reactivity of monodisperse surfactants with $R = p$-*tert*-nonylphenyl $(n = 4–15)$[6] and with $R = n$-dodecyl $(n = 3–14)$.

In this paper the extension of the method to the determination as PPAS of some commercial ethoxylated primary alcohols from C_{10} to C_{18} and with various number-average degree of polymerisation $(\bar{n})$ is considered, in order to define the influence of the length of the hydrophobic chain on the reactivity as PPAS. Mixtures of these biodegradable surfactants are likely present in waters receiving urban liquid wastes polluted by detergents. Their determination down to a level of 0.005 mg/kg is quite important for assessing water quality. The reactivity as PPAS of the surfactants with $R = n$-dodecyl $(3.8 \leqq \bar{n} \leqq 28)$ has already been considered.[7]

EXPERIMENTAL

Apparatus

The absorbance of organic extract was measured in matched silica cells (1 or 2 cm path length) with a Varian Superscan 3 instrument. The pH of the aqueous phases was determined with a Beckman 4500 pH-meter calibrated with Fisher certified buffer solution. Molecular weights are determined with a Hewlett–Packard Mechrolab vapour pressure osmometer at 37°C in 1,2-dichloroethane $(1 \times 10^{-3} m)$.

Reagents

1-2-Dichloroethane, E. Merck, extra-pure grade, freshly distilled.

Potassium nitrate solution (2.5 M): Dissolve 25.38 g of Riedel-De Haën potassium nitrate with water and dilute to 100.0 ml.

Potassium picrate solution (0.01 M): Dissolve 0.267 g of potassium picrate re-crystallized from an aqueous solution and dried under phosphorus(V) oxide in aqueous potassium hydroxyde $(2 \times 10^{-4} M)$ up to 100.0 ml.

Hydrochloric acid (0.1 M) from BDH AnalaR.

Sodium hydroxyde (0.1 M) from BDH AnalaR

Commercial surfactants

The following polydisperse surfactants ($C_m E_{\bar{n}}$, where m is the number of carbon atoms of the aliphatic straight chain and $\bar{n}$ is the number-average degree of polymerisation) from various industrial origin were considered: $C_{10}E_{\overline{3.1}}$, $C_{12}E_{\overline{3.8}}$, $C_{12}E_{\overline{7.1}}$, $C_{12}E_{\overline{8.0}}$, $C_{12}E_{\overline{8.9}}$, $C_{12}E_{\overline{10.2}}$, $C_{12}E_{\overline{11.1}}$, $C_{12}E_{\overline{12.0}}$, $C_{12}E_{\overline{14.6}}$, $C_{12}E_{\overline{17.3}}$, $C_{12}E_{\overline{27.5}}$, (Chemische Werke Hüls, Marl, Kreis Recklinghausen, DBR), $C_{16}E_{\overline{2.3}}$, $C_{16}E_{\overline{10.3}}$, $C_{16}E_{\overline{16.5}}$, $C_{16}E_{\overline{18.2}}$, $C_{18}E_{\overline{2.7}}$, $C_{18}E_{\overline{10.0}}$, $C_{18}E_{\overline{17.5}}$, $C_{18:1}E_{\overline{2.0}}$, $C_{18:1}E_{\overline{2.2}}$, $C_{18:1}E_{\overline{7.1}}$, $C_{18:1}E_{\overline{7.8}}$, $C_{18:1}E_{\overline{9.5}}$, $C_{18:1}E_{\overline{18.1}}$, $C_{18:1}E_{\overline{19.0}}$, ($C_{18:1}$ refers to oleyl group) were also considered together with $C_{13}E_{\overline{11.9}}$, and $C_{13}E_{\overline{13.6}}$, where C_{13} refers to a branched-chain tridecyl group (Atlas Europol, Ternate, Milan, Italy).

All compounds were previously dried at 80°C/0.1 mm. with phosphorus(V) oxide. Aqueous stock solutions containing 10 mg/l were prepared *daily* by weighing the surfactant on a Mettler M5 microbalance. The substance was transferred into a 1 l-volumetric flask by dissolution with 5 ml of 95%-ethanol and the volume was made up to the mark with water. "Solutions" of surfactants with $\bar{n} \sim 2$ appeared to be slightly turbid for some hours. These emulsions were used immediately.

With gas liquid chromatography it was previously controlled that polydispersions derive from the ethoxylation of nearly pure alcohols. Therefore $\bar{M}_{VPO} = M_0 + \bar{n}_{VPO} 44.05$, where $\bar{M}_{VPO}$ is the number-average molecular weight determined by vapour pressure osmometry (VPO), M_0 is the molecular weight of the starting alcohol and $\bar{n}_{VPO}$ is the number-average degree of polymerisation. The chromatographic peaks of ethoxylated branched chain primary C_{13}-alcohol are slightly enlarged for the presence of positional isomers in the alkyl group. Chromatographic data on the molecular-weight distribution of some surfactants $C_{12}E_{\bar{n}}$ have already appeared.[7]

Procedures

Calibration graphs: In a 50-ml calibrated flask add aliquots of the standard solution to 20.00 ml of potassium nitrate solution, in order to have 0.10–2.00 mg/l of surfactant in the final volume of aqueous phase. Mix and add 10.0 ml of the potassium picrate solution, making the volume up to the mark with water (pH ~ 10). Transfer the mixed solution into a pear-shaped separating funnel with a PTFE stop-cock, add 5.00-ml of 1,2-dichloroethane and shake vigorously for 3 min. Transfer the organic layer into a conical centrifuge tube fitted with a polyethylene stop-cock and centrifuge at 2000 g for 5 min. Measure the absorbance (*A*) of the organic extract at 378 nm in a 1-cm (or 2-cm) cell against the reagent blank.

Extraction of surfactants from waters: Centrifuge at 2000 g for 5 min the water sample, transfer a 1000-g aliquot into a 2-l, pear-shaped separating funnel with PTFE tap and stop-cock, and extract first with 15.0 ml, then twice with 10.0 ml of 1,2-dichloroethane shaking for 3 min. Collect the organic layers into a 50-ml separating funnel and extract first with 2.0 ml of hydrochloric acid, then with 2.0 ml of sodium hydroxide for 1 min. Transfer the organic phase into a 50-ml calibrated flask, evaporate to dryness at $45 \pm 1°C$ under a stream of nitrogen and treat the residue as indicated in the previous section.

Statistical data processing

Linearity of the calibration graphs was tested by the analysis of the variance (ANOVA) for the linear regression, using the F-ratio as a criterion of adequacy. F is the ratio between the variance attributable to regression and the variance attributable to deviation from regression.[8] Computations were performed on an Olivetti P6040 desk Calculator.

RESULTS AND DISCUSSION

Advantages of 1,2-dichloroethane as an extracting phase of PPAS

1,2-dichloroethane, chloroform and benzene were often proposed for the extraction of polyoxyethylene non-ionic surfactants as Cobalt Thiocyanate Active Substances (CTAS).[9–15] The comparison of the absorbance spectrum of PPAS extracted into 1,2-dichloroethane with that of PPAS extracted into chloroform and benzene appears in Figure 1. All spectra were obtained by extracting the surfactant $C_{12}E_{\overline{10.2}}$ from an aqueous phase at 1.00 mg/l concentration. 1,2-dichloroethane, chloroform and benzene have an absorbance maximum at 378, 371 and 359 nm respectively. At these wavelengths Beer's law is obeyed at least up to 1.0 mg/l of surfactant in the aqueous phase.

Figure 2 shows the advantages of 1,2-dichloroethane over chloroform and benzene as an organic phase for the extraction of surfactants $C_{12}E_{\bar{n}}$ ($3.8 \leq \bar{n} \leq 27.5$) as PPAS. With 1,2-dichloroethane the absorbance increases with $\bar{n}$ up to a plateau at which a nearly complete extraction is reached.[7] With chloroform and benzene the same trend is observed but with a lower sensitivity, already noted in the use of ammonium tetraisothiocyanatocobaltate(II) reagent.[16]

Calibration graphs

The absorbance (A) of the organic extract is proportional to the surfactant concentration (c') existing in aqueous phase before the
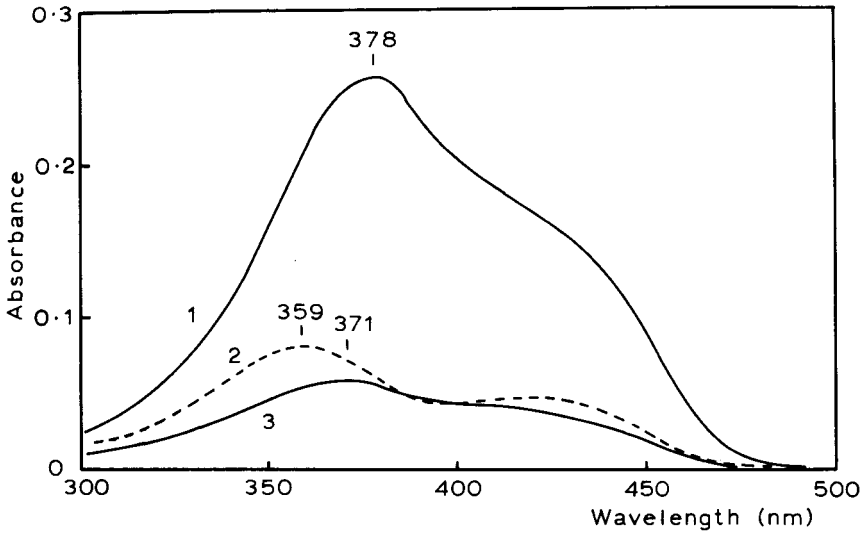
FIGURE 1. Absorbance spectra $(b = 1\,cm)$ of PPAS extracted in 1,2-dichloroethane (1), benzene (2) and chloroform (3) at $20^\circ C$. In all cases 50.0 ml of an aqueous phase having c' $= 1.00\,mg/l$ of surfactant $C_{12}E_{10.2}$ are extracted, according to the procedure described under *Calibration graphs*.
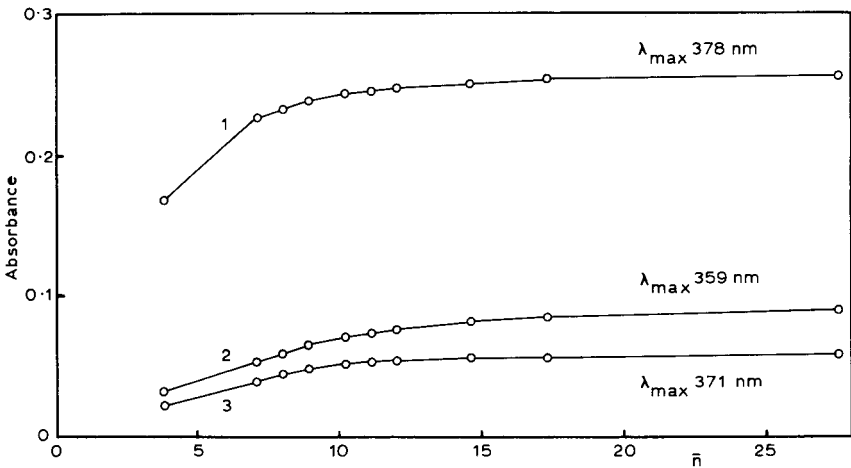

FIGURE 2 Absorbance $(b = 1\,cm)$ of PPAS extracted in 1,2-dichloroethane (1), benzene (2) and chloroform (3) with surfactants $C_{12}E_n$ at $20^\circ C$. In all cases $c' = 1.00\,mg\,l$.

extraction, at least up to $c' = 2.0$ mg/l. The interpolating straight lines pass through the origin ($A = a'bc'$, where b is the optical path length, cm). Table I summarizes the values of the slope (a') of the calibration lines obtained at 20°C (For the surfactants $C_{12}E_{\bar{n}}$ linearity has been already

TABLE I

Slope of the calibration graphs (a') for some C_mE_n surfactants extracted as PPAS at 20°C. In all cases $a' = A/bc'$ was determined in the range $0.1 \leqq c'$ $\leqq 2.0$ mg/l from N observations processed by linear regression.

Surfactant				
m	$\bar{n}$	a'	N	F
10	3.1	0.140	14	19870
12	3.8	0.167	18	26754
	7.1	0.227	16	32680
	8.0	0.234	14	29880
	8.9	0.240	14	34560
	10.2	0.243	14	33274
	11.1	0.246	15	42701
	12.0	0.248	16	40024
	14.6	0.250	16	38475
	17.3	0.256	14	31160
	27.5	0.257	14	30870
13	11.9	0.244	12	36760
	13.6	0.247	12	37038
16	2.3	0.062	18	10014
	10.3	0.222	14	37946
	16.5	0.228	14	30262
	18.2	0.230	14	28797
18	2.7	0.053	18	8063
	10.0	0.206	16	40240
	17.5	0.218	16	36542
18:1	2.0	0.043	18	6853
	2.2	0.046	18	7441
	7.1	0.195	16	41679
	7.8	0.202	14	46702
	9.5	0.212	12	37406
	18.1	0.233	12	34210
	19.0	0.224	14	42675

tested up to $c' = 1.0$ mg/l).[7] At least considered in the range of $\bar{n}$, the linearity of the calibration graphs is demonstrated by the ANOVA for the linear regressions: the F- value is higher than 2000 for all surfactants. The linearity of Beer's law *at trace levels* of non-ionic surfactants has also been

demonstrated from equilibrium expressions.[6] It is noteworthy that surfactants with $\bar{n} \sim 2$ can also be determined as PPAS, since these polydisperse materials still contain a fraction of reactive compounds. Figure 3 shows the variation of slope of the calibration lines as a function of $\bar{n}$. At least in the range of $\bar{n}$, the slope increases with $\bar{n}$ showing nearly the same trend in all surfactants. This seems to come to a limiting value. Within the range C_{12} to C_{18} the hydrophobic group slightly affects the calibration graphs by decreasing the sensitivity as the length of the group increases.
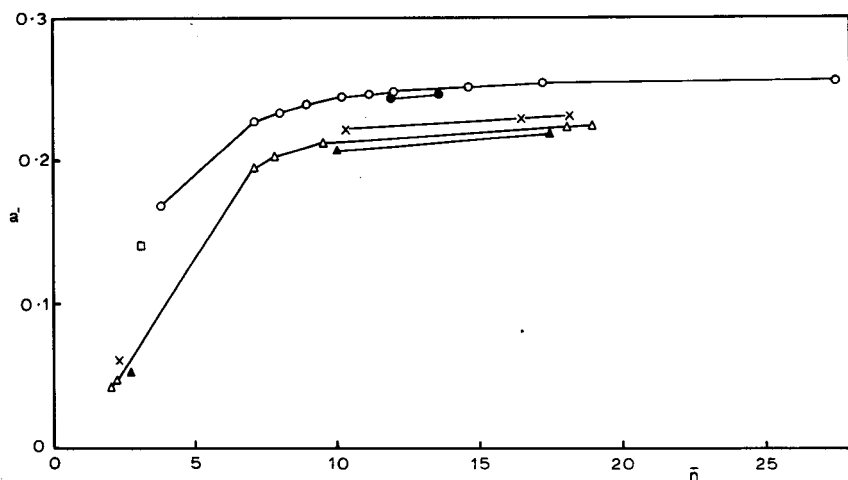
FIGURE 3   Trend of the slope of the calibration line (a') as a function of $\bar{n}$ for surfactants $C_m' E_{\bar{n}}$. $C_{10} E_{3.1}^-$ (open square), $C_{12} E_{\bar{n}}$ (open circles), $C_{13} E_{\bar{n}}$ (dark circles), $C_{16} E_{\bar{n}}$ (crosses), $C_{18} E_{\bar{n}}$ (dark triangles), $C_{18:1} E_{\bar{n}}$ (open triangles).

In the range $9 \leq \bar{n} \leq 19$ all surfactants show a trend parallel to that of $C_{12} E_{\bar{n}}$, which is well defined up to $\bar{n} = 27.5$ for availability of standards. In the surfactants with C_{12}, C_{13}, C_{16} and C_{18}, the decrease of a' with m is approximately given by a value of 0.006 for every carbon atom added to the chain. The slope of the surfactants $C_{18:1}$ is slightly higher than that of C_{18}.

In mixtures from C_{12} to C_{16} (as in surfactants derived from the ethoxylation of alcohols from hydrogenated coconut fatty acids in which C_{12} predominates), the calibration graphs of $C_{12} E_{\bar{n}}$ surfactants can be approximately used for the determination of these mixtures as PPAS. When $\bar{n} \geq 10$ their absolute determination is also possible as the slope is nearly constant.

In constructing calibration graphs the procedure has been accelerated by a systematic study on the time required to complete complexing and ion-pairing steps. Both reactions can be considered as instantaneous for practical purposes, since the recovery of surfactants $C_{12}E_{3.8}$ and $C_{12}E_{27.5}$ at $c' = 1.00$ mg/l is complete at least down to 2 min of reaction time.

Extraction of the surfactants from water sample

Pre-extraction of polyoxyethylene non-ionic surfactants from polluted water by means 1,2-dichloroethane has been found to be an essential step in order to concentrate and purify the analyte. The negative interference of anionic surfactants, which compete with picrate as pairing agent, is

TABLE II

Recovery (%) of surfactant $C_{12}\overline{E_{28}}$ in successive extractions (at 20°C) of 250 ml of aqueous solution (0.20 mg/l) with various volumes of 1,2-dichloroethane. (Two determinations).

Recoveries at every extraction step: Order of extraction	Volume of organic phase					
	25 ml		10 ml		5 ml	
1	82.9	83.7	78.7	78.1	73.6	72.9
2	12.4	12.0	13.9	14.1	15.5	17.1
3	2.3	3.0	3.1	3.2	4.3	4.6
Sum	97.6	98.7	95.7	95.4	93.4	94.6

Cumulative recoveries:

	Volume of organic phase					
	3 × 25 ml		3 × 10 ml		3 × 5 ml	
	96.5	97.3	95.6	94.8	94.1	93.0

eliminated at least up to a 1/10 ratio non-ionic/anionic surfactant,[4] which satisfies the needs for analysis of waste waters. Advantages of 1,2-dichloroethane over other used organic phases have been already discussed.[17]

Preliminary systematic experiments on 250-ml size samples of water having known amounts of surfactant have been performed in order to study the extent of recovery into the organic phase under various experimental conditions. The effect of pH of the aqueous phase has been also considered. Table II reports the recovery of the surfactant in successive extractions of an aqueous phase initially containing 0.20 mg l^{-1}. In this two-phase system three extractions give at least a 93%-recovery of the surfactant, even when the organic-to-aqueous phase ratio is unfavourable. The pH of the aqueous phase does not affect the recovery at least in the range 3–12.

In further experiments on 1 l-volume samples, an organic-to-aqueous phase ratio of 1/67 has been adopted in the first extraction, then 1/100 in the two successive extractions, with the aim of lowering both reagent blank and time required for the analysis. The repeated analysis of aqueous solutions of some $C_mE_{\bar{n}}$ surfactants at a level of 50 μg/l has given the intra-laboratory repeatability shown in Table III. The coefficient of variation ranges from about 1 to 3 %, whereas the recovery (evaluated from the arithmetic mean) ranges from 88.4 to 96.8 %; however in typical

TABLE III

Recovery of surfactants $C_mE_{\bar{n}}$ from 1-l sample of solution containing 50 μg/l. $\bar{x} \pm s$, arithmetic mean and root-mean square deviation evaluated from N parallel determinations (two operators). The recovery of surfactant $C_{12}E_{10.2}$ at 5.0 μg/l level is indicated in italics.

Surfactant					
m	$\bar{n}$	N	$\bar{x} \pm s$ (μg/l)	Recovery (%)	Correction factor
12	3.8	4	48.4 ± 0.5	96.8	1.03
	7.1	6	45.7 ± 0.4	91.4	1.09
	8.9	4	45.3 ± 0.6	90.6	1.10
	10.2	6	45.2 ± 0.7	90.4	1.11
		6	*4.4 ± 0.3*	*88.0*	*1.14*
	12.0	4	45.0 ± 0.5	90.0	1.11
	14.6	4	45.4 ± 0.8	90.8	1.10
	27.5	5	45.1 ± 0.6	90.2	1.11
18	10.0	4	44.6 ± 0.9	89.2	1.12
	2.7	4	44.2 ± 1.2	88.4	1.13

surfactants for detergents the recovery varies just from 88 to 92%, with 90% as an average. Therefore the factor 1.11 is an acceptable working value for correcting accuracy. At a level of 5.0 μg/l a recovery of 88% is also observed, but the coefficient of variation approaches 7%, so that the factor 1.11 is used in this case too.

Magnesium sulphate has been used as a salting-out agent for polyoxyethylene non ionics.[18,19] It decreases also the solubility of the 1,2-dichloroethane in the aqueous phase (for instance, at 25°C the solubility is 8.58 g/l in water,[20] 5.49 in 0.08 M magnesium sulphate.)[21] Figure 4 shows the recoveries observed with the addition of solid magnesium sulphate to 1-l-volume of a solution containing 50.0 μg/l of $C_{12}E_{10.2}$. The addition increases only slightly the recovery up to 92% and becomes uneffective impractical beyond 0.2 moles of added magnesium

sulphate. The proposed method does not consider any addition of this salt.

In analyzing real samples of sea water from Trieste harbour, the repeatability is nearly the same as that observed in determining the PPAS of aqueous solutions of standard surfactants. In 6 parallel determinations of a sample containing $2.3 \pm 0.3\,\mu g/l$ PPAS (expressed as $C_{12}E_6$), the coefficient of variation raises to 13 %, but that level represents the detection limit, as the reagent blank is half of the absorbance registered.
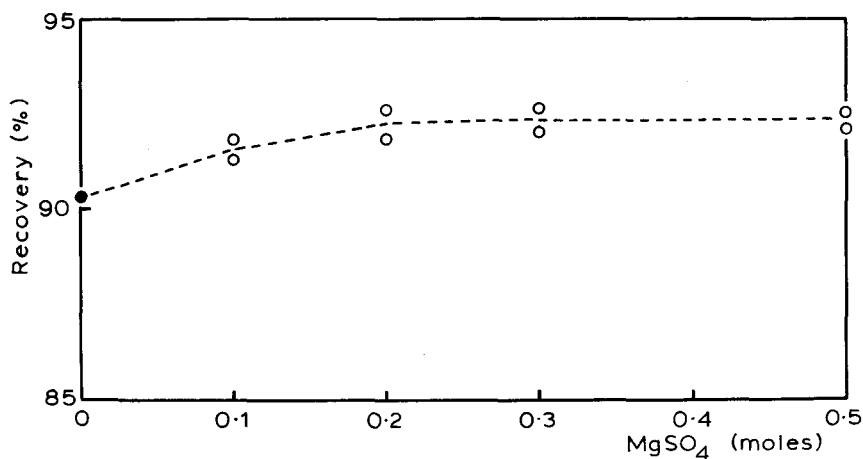

FIGURE 4   Recovery (%) of the surfactant $C_{12}E_{\overline{10.2}}$ as a function of the amount (moles) of magnesium sulphate added to 1 l-volume of aqueous solution containing $50\,\mu g/l$ of surfactant. The darkened circle indicates the arithmetic mean evaluated from 6 parallel determinations (see Table III).

CONCLUSIONS

The potassium picrate technique has distinct advantages over methods using potassium and barium tetraiodobismutate(III)[22,23] as precipitating agent. This holds particularly for surfactants having a polyoxyethylene chain ($C_{12}E_{\bar{n}}$ with $n < 6$) which is too short for precipitation. The same can be said for surfactants having R = p, tert-nonylphenyl. The limit of applicability of the methods based on this reagent has been confirmed on surfactants $C_{12}E_{\bar{n}}$,[24] and it holds likely for other precipitating reagents suggested for the determination of polyoxyethylene non-ionic surfactant, despite the improved sensitivity reached in recent methods by using atomic absorption spectroscopy.[24,25,26]

Surfactants with low $\bar{n}$ can be determined with the proposed method with a remarkable repeatability. The method can probably be adapted to

the determination of low reacting polyoxyethylene surfactants in various matrices of commercial products, like detergents. The calibration over an enlarged range of concentration represents a further advantage in analyzing polluted waters, that are often characterized by a wide range of variability in surfactant concentration. In a 1-1 sample of water PPAS from 5 up to $100\,\mu g/l$ can be determined.

Acknowledgement

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