An Improved Method for the Spectrophotometric Determination of Polyoxyethylene Non-Ionic Surfactants in Waters as Potassium Picrate Active Substances in Presence of Cationic Surfactants

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An Improved Method for the Spectrophotometric Determination of Polyoxyethylene Non-Ionic Surfactants in Waters as Potassium Picrate Active Substances in Presence of Cationic Surfactants †‡

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A new method, free from interference of cationic surfactants, is proposed for the determination of polyoxyethylene non-ionics in waters at ultra-trace levels. The procedure involves (i) a pre-extraction from water sample with dichloromethane, and (ii) the determination of non-ionics as potassium picrate active substances (PPAS). In aqueous phase the polyether chain reacts reversibly with potassium cation (in large excess) to form a positive complex, which is extracted and concentrated in 1,2-dichloroethane (1,2-DCE) through ion-pairing with the chromophoric picrate. The yellow colour of ion-pairs extracted into organic layer disappears immediately by extraction with water, which lowers drastically the concentration of reagents. The difference between the absorbances gives the PPAS attributable to polyoxyethylene non-ionics only, because PPAS due to cationics are not extractable. The method was tested in sea waters polluted by urban liquid wastes.

KEY WORDS: Polyoxyethylene non-ionic surfactants, cationic surfactants, water analysis, ion pairing.

INTRODUCTION

Some years ago the use of potassium picrate was suggested as a reagent for the spectrophotometric determination of polyoxyethylene non-ionic surfactants in waters as potassium picrate active substances (PPAS).[1] The cation (in large excess) is coordinated by the polyether chain in the aqueous phase and the positive complex is extracted and concentrated in a suitable organic phase (1,2-dichloroethane, 1,2-DCE) through ion-pairing with picrate, which is the chromophore at 378 nm (c $= 18664 \, cm^{-1} \, mole^{-1}$) for $C_6H_2(NO_2)_3O^-$ in 1,2-DCE at 20°C).[2,3] Pre-extraction of the filtered water sample with 1,2-DCE allows the determination at trace levels and the separation from common interfering substances (anionic surfactants, hydrocarbons, soaps, and so on).[4]

Although the method was tested in progressively refined versions,[5,6] the determination of polyoxyethylene non-ionic surfactants as PPAS is, however, sensitive to the interference of cationics if they co-exist in polluted waters.

In this paper a simple method *free* from the interference of cationic surfactants is suggested.

The procedure is improved and shortened both in the pre-extraction with dichloromethane (DCM), as well as in the final spectrophotometric determination, which is suitable for the determination of non-ionics in an enlarged range of concentration (200 to 2 μg/l). The procedure is tested on biodegradable surfactants of the type $R(OCH_2CH_2)_nOH$, where R is a linear alkyl group and $\bar{n}$ is the number-average degree of polymerisation. 1,2-Dichloropropane (1,2-DCP) is also studied as an alternative extracting organic phase in the final spectrophotometric determination, although with 1,2-DCP the recovery of ion-pairs is lower than that observed with 1,2-DCE.

EXPERIMENTAL

Apparatus

The absorbance spectrum of the organic extract was recorded in matched silica semi-micro cells (1 or 2 cm path length) with a Varian Superscan 3 instrument at 20°C. First-derivative spectra $(dA/d\lambda)$ were also obtained with the same instrument. The pH of the aqueous phase was measured at the same temperature with a Beckman 4500 pH-meter calibrated with Fischer Certified buffer solutions. Water and other solvents were distilled in roto-evaporators under a reduced pressure.

Reagents

Sodium chloride, BDH AnalaR.

Water, bi-distilled.

Dichloromethane (DCM), Ridel-De Haën ACS, freshly distilled and stored in the dark.

1,2-Dichloroethane (1,2-DCE), E. Merck, extra-pure grade, freshly bi-distilled and stored in the dark.

1,2-Dichloropropane (1,2-DCP) Fluka *puriss.*, freshly bi-distilled and stored in the dark.

Potassium picrate-potassium nitrate reagent solution: first prepare and purify the following solutions:

i) Potassium nitrate solution (2.50 M): Dissolve 253.8 g of potassium nitrate (Riedel-De Haën Analytical grade) with water and dilute to 1000.0 ml. Purify the solution by extraction with DCM (100 ml, at least three times), remove the solvent from the solution by a current of ultra-pure nitrogen.

ii) Potassium picrate solution (0.010 M): Dissolve 2.67 g of potassium picrate (prepared from picric acid, C. Erba analytical grade), re-crystallized from an aqueous solution and dried under phosphorous(V) oxide, in aqueous potassium hydroxyde 2×10^{-4} M up to 1000.0 ml. Purify this solution as indicated in (i). Then, in a 1000-ml calibrated flask add 400 ml of (i), then 190 ml of water, mix gently and add 200 ml of (ii), making the volume up to the mark with water. This reagent must have pH ~ 10.5.

Above described solutions are prepared and purified separately, because it is supposed that they are also utilized for the preparation of the calibration lines (see later). Otherwise, the purification with DCM is simply performed on the single mixed reagent, following the instruction given under (i).

Hydrochloric acid (0.1 M), from BDH AnalaR.

Sodium hydroxide (0.1 M), from BDH AnalaR.

Surfactants: Polydisperse surfactants having the formula $R(OCH_2CH_2)_{\bar{n}}OH$ were considered, and in particular those with $R=$ dodecyl ($C_{12}E_{\overline{3.8}}$, $C_{12}E_{\overline{7.1}}$, $C_{12}E_{\overline{8.0}}$, $C_{12}E_{\overline{8.9}}$, $C_{12}E_{\overline{10.2}}$, $C_{12}E_{\overline{11.1}}$, $C_{12}E_{\overline{12.0}}$, $C_{12}E_{\overline{14.6}}$, $C_{12}E_{\overline{17.3}}$, $C_{12}E_{\overline{27.5}}$ obtained from Chemische Werke Hüls, Marl, Kreis Recklinghausen, DBR), $R=$ hexadecyl ($C_{16}E_{\overline{2.3}}$, $C_{16}E_{\overline{10.3}}$, $C_{16}E_{\overline{16.5}}$, $C_{16}E_{\overline{18.2}}$), $R=$ octadecyl ($C_{18}E_{\overline{2.7}}$, $C_{18}E_{\overline{10.0}}$, $C_{18}E_{\overline{17.5}}$) and $R=$ oleyl ($C_{18:1}E_{\overline{2.0}}$, $C_{18:1}E_{\overline{2.2}}$, $C_{18:1}E_{\overline{7.1}}$, $C_{18:1}E_{\overline{7.8}}$, $C_{18:1}E_{\overline{9.5}}$, $C_{18:1}E_{\overline{18.1}}$, $C_{18:1}E_{\overline{19.0}}$). The value of $\bar{n}$ was calculated from the number-average molecular weight obtained by vapour pressure osmometry. Aqueous stock solutions containing from 5 to 30 mg/l were prepared daily by weighing the surfactant (previously dried at

80°C/0.1 mm with phosphorous (V) oxide) on a Mettler M5 microbalance. The substance was transfered into a 1000-ml volumetric flask by dissolution with 5 ml of 95%-ethanol and the volume was completed with water. Emulsions obtained with surfactants having $\bar{n} \sim 2$ were used immediately.

Procedures

Pre-extraction and concentration of surfactants from water: Filter a water sample through a 0.7 μm glass fiber paper (Whatman GF/F) and transfer a 500-ml aliquot into a pear-shaped, 1000-ml separating funnel with PTFE stop-clock. Add 5.8 g of sodium chloride, dissolve and extract first with 15.0, then 10.0 ml of DCM (3 min shaking time). Collect organic layers into a pear-shaped, 50-ml separating funnel and extract for 1 min with 1.0 ml of 0.1 M sodium hydroxide solution. Transfer the organic layer to a funnel and extract with 0.1 M hydrochloric acid solution. Transfer the washed organic phase to a pear-shaped 100-ml flask and evaporate to dryness at <40°C under a stream of ultrapure nitrogen.

Spectrophotometric determination of PPAS: Re-dissolve the residue with 2.50 ml of 1,2-DCE (or 1,2-DCP), add 25.00 ml of potassium picrate-potassium nitrate reagent, close the flask tightly and shage *vigorously* for 3 min (ensure occasionally that the aqueous phase has a pH $\sim$ 10–10.5 after the extraction). Transfer the organic layer into a 10-ml conical centrifuge tube and centrifuge at 2000 g for 3 min. Measure the spectrophotometric absorbance (A_T) at 378 nm of the clear organic layer. Recover the layer in a pear-shaped, 50-ml separating funnel with PTFE stop-cock, add 2.50 ml of water and shake for 1 min. Transfer the organic layer into a 10-ml conical centrifuge tube, centrifuge for 3 min at 2000 g and read again the spectrophotometric absorbance (A_W). Measure also the absorbance (A_0) of a blank processed in the same manner on a residue of 15 + 10 ml of DCM.

Calibration graphs: In pear-shaped 100-ml separating funnels add aliquots of the standard solution to 10.00-ml of potassium nitrate solution (i), in order to have 0.1–4 (or 0.1–2) mg/l of surfactants in the final 25.0-ml volume of aqueous phase. Add water to reach *exactly* 15.0 ml, swirl and add 10.00 ml of potassium picrate solution (ii).

Mix by swirling, add 2.50-ml of 1,2-DCE (or 1,2-DCP) and shake for 3 min. Transfer the organic layer into a 10-ml centrifuge tube and centrifuge at 2000 g for 3 min. Measure the spectrophotometric absorbance against the solvent at 378 nm. Run a blank in parallel. The PPAS-absorbance only due to surfactant is obviously the difference between

them, and is plotted as a function of the concentration (c') of surfactant existing in the aqueous phase.

Calculations: The value of PPAS is expressed as $\mu g/l$ of standard surfactant and is calculated as follows:

$$PPAS \ (\mu g/l) = 50 \, f_S \, [A_T - (A_0 + A_W)]/a'_S$$

where: $50 = 1000/20$ is a concentration factor; f_S is the recovery factor of the standard surfactant ($f_S = 100/R$, where R (%) is the recovery of the Table I for DCM); A_T is the absorbance measured at 378 nm ($b = 1$ cm) at 20°C on the 2.5 ml of organic phase; A_0 is the absorbance of the corresponding reagent blank: A_W is the absorbance of the organic phase after water extraction; a'_S is the slope of the calibration line of the selected standard extracted in 1,2-DCE (or in 1,2-DCP): the slope corresponds to the absorbance of the standard at a concentration $c' = 1.00$ mg/l in 25.0 ml of the aqueous phase (Table II). Of course, control that the A_T-value does not exceed the limiting concentration of the validity of the Beer's law.

Example: If the extraction of the PPAS is made up with 1,2-DCE and the standard is $C_{12}E_{\overline{10.2}}$: $f_S = 100 \ 93.5 = 1.07$; $a'_S = 0.243$. With $b = 1$ cm, PPAS ($\mu g/l$) $= 50 \times 1.07/0.243 \ [A_T - (A_0 + A_W)]$.

Statistical data processing

No detailed test of linearity was performed on data from calibration graphs. However, the upper limit of concentration for the validity of Beer's law was approximately determined by comparing the intercept of the calibration line with zero: If a significative difference between them existed, it was assumed to be due to curvature. As an approximate index of fitting to a straight line, the F-ratio derived from the analysis of the variance for the linear regression of A on c' was chosen. Computations were performed on an Olivetti P6040 desk calculator.[7]

RESULTS AND DISCUSSION

Pre-extraction with DCM

Figure 1 shows the advantage of DCM over 1,2-DCE in the pre-extraction of $C_{12}E_{\bar{n}}$ surfactants ($3.8 \leq \bar{n} \leq 27.5$) from a 500-ml sample of water containing 50 $\mu g/l$ of non-ionics, following the described procedure. The final spectrophotometric determination was performed with 1,2-DCE.
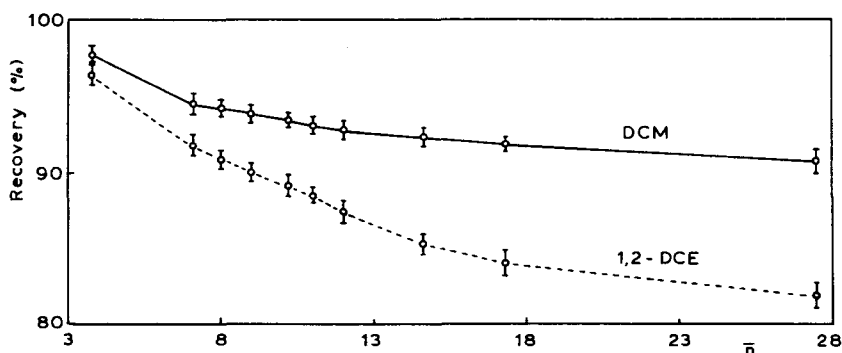
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FIGURE 1   Recovery (%) in the pre-extraction with DCM and 1,2-DCE from a 500-ml sample of water containing $50\,\mu g/l$ of $C_{12}E_{\bar{n}}$ surfactants $(3.8 \leq \bar{n} \leq 27.5)$. The spectrophotometric determination was performed with 1,2-DCE. The circle indicates the arithmetic mean, the segment the root mean square deviation evaluated from 4 determinations.

The recovery with DCM is systematically higher than that observed with 1,2-DCE, already suggested as an extracting phase.[8] Moreover Table I indicates that the recovery with DCM is at least 88.2% even for surfactants having a long polyether chain and with the proposed extraction conditions. It is important to note that a recovery of 90% of $C_{12}E_{\overline{10.2}}$ is reached with the first extraction of 500 ml-sample with 15.0 ml of DCM, but a further extraction with 10.0 ml is needed for a better analytical repeatability. With the surfactant $C_{12}E_{\overline{10.2}}$, sometimes chosen as a practical standard substance, the recovery is 93.5%. The extreme values observed from all surfactants considered in this research correspond only to a systematic deviation of about $\pm 5\%$ of the value indicated for the $C_{12}E_{\overline{10.2}}$. Therefore, the use of this polydisperse standard is recommended in practice to determine the concentration of non-ionics from PPAS-values with noticeable accuracy.

Other important analytical advantages of DCM over 1,2-DCE are (i) better repeatability (see Figure 1), (ii) lower reagent blanks ($A_0 \leq 0.005$ with $b = 1$ cm), whereas the instability of 1,2-DCE in air at $>40°C$ increases slightly A_0 (this solvent must be used freshly and doubly distilled with particular care during evaporation), (iii) lower boiling point allowing a rapid evaporation at $<40°C$. Moreover, DCM is less harmful in the laboratory atmosphere (Maximale Arbeitsplatzkonzentration, MAK, of DCM is 360 mg/m^3, of 1,2-DCE 80 mg/m^3).[9]

The early procedure of washing the DCM-extract with an acid and with a basic solution was maintained.[1] This treatment does not change the

TABLE I

Recovery $(R, \%)$ at 20°C of some $C_m E_{\bar{n}}$ surfactants from a 500 ml-sample of water, containing 50 μg/l. $\bar{x}$ $\pm s$, arithmetic mean and root mean square deviation from 4 determinations

| | $C_m E_{\bar{n}}$ | | $R(\%)$ | |
| | | | DCM | 1,2-DCE |
m		$\bar{n}$	$\bar{x} \pm s$	$\bar{x} \pm s$
12		3.8	97.7 ± 0.6	96.4 ± 0.7
		7.1	94.6 ± 0.6	91.9 ± 0.7
		8.0	94.3 ± 0.5	90.9 ± 0.6
		8.9	93.9 ± 0.5	90.1 ± 0.6
		10.2	93.5 ± 0.4	89.2 ± 0.7
		11.1	93.2 ± 0.5	88.5 ± 0.5
		12.0	92.8 ± 0.6	87.5 ± 0.6
		14.6	92.4 ± 0.6	85.3 ± 0.7
		17.3	91.9 ± 0.5	84.1 ± 0.8
		27.5	90.8 ± 0.8	81.8 ± 0.9
18:1		2.0	98.0 ± 2.1	n.d.
		2.2	98.3 ± 1.3	n.d.
		7.1	95.8 ± 0.5	89.1 ± 0.6
		7.8	95.4 ± 0.6	n.d.
		9.5	94.0 ± 0.4	n.d.
		18.1	88.8 ± 0.5	n.d.
		19.0	88.2 ± 0.7	n.d.

recovery of $C_{12}E_{\overline{10.2}}$ appreciably. However, no systematic study was performed on the possibility to eliminate these washings, when the PPAS are determined with the method proposed in this paper.

Spectrophotometric determination with 1,2-DCP

1,2-DCP can substitute 1,2-DCE in the final spectrophotometric determination, though with a lower sensitivity. Figure 2 shows the first-derivative spectrum of $C_{12}E_{\overline{10.2}}$ as PPAS extracted in these organic phases. The spectra coincide at the absorbance maximum.

Table II summarizes the a'-values of the calibration graphs with both solvents.

With 1,2-DCP the absorbance (A, corrected for the reagent blank) of the PPAS in the organic extract is proportional to the surfactant concentration (c') existing in the aqueous phase before the extraction, at least up to $c' = 2.0$ mg/l. For some surfactants, linearity holds up to 4.0 mg/l.
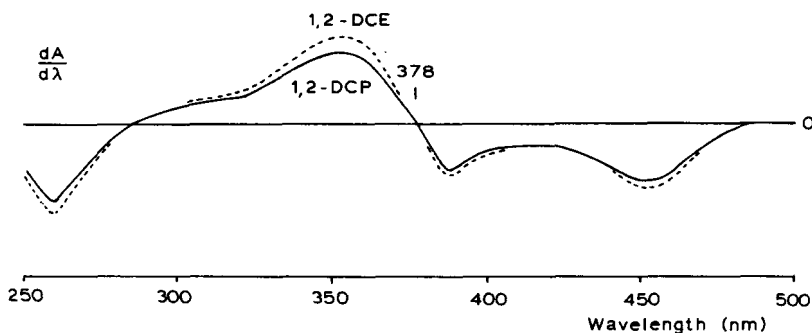
FIGURE 2   First-derivative spectra of $C_{12}E_{\overline{10.2}}$ surfactant extracted as PPAS into 1,2-DCE and 1,2-DCP.

TABLE II

Comparison of the slope of the calibration graph (a') for some $C_mE_{\bar{n}}$ surfactants extracted as PPAS at 20°C with 1,2-DCE (see literature 6) and 1,2-DCP. $a' = A/bc'$ was determined in the range $0.1 \leqq c' \leqq 2.0$ mg/1 or in the range $0.1 \leqq c' \leqq 4.0$ mg/1 (*) from N observations ·processed by linear regression

$C_mE_{\bar{n}}$		1,2-DCE	1,2-DCP		
m	$\bar{n}$	a'	a'	N	F
12	3.8	0.167	0.109	14	21123
	7.1	0.227	0.173*	12	35005
	8.0	0.234	0.187*	14	48626
	8.9	0.240	0.195*	12	29932
	10.2	0.243	0.201*	14	48862
	11.1	0.246	0.202*	12	46032
	12.0	0.248	0.203*	14	34419
	14.6	0.250	0.205*	12	29802
	17.3	0.256	0.209*	12	30582
	27.5	0.257	0.219*	14	59870
16	2.3	0.062	0.033	12	5210
	10.3	0.222	0.174*	14	32126
	16.5	0.228	0.184*	14	38175
	18.2	0.230	0.187*	12	29680
18	2.7	0.053	0.029	12	5860
	10.0	0.206	0.155*	14	37500
	17.5	0.218	0.168*	12	40037
18:1	2.0	0.043	0.022	12	5870
	2.2	0.046	0.025	12	6100
	7.1	0.195	0.146*	14	46712
	7.8	0.202	0.152*	12	49510
	9.5	0.212	0.159*	12	38750
	18.1	0.223	0.175*	12	36125
	19.0	0.224	0.176*	14	40016

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For all surfactant, the interpolating straight line passes through the origin. Table II summarizes the values of the slope $(a' = A/bc')$ of the calibration lines obtained at 20°C with 1,2-DCE[6] and 1,2-DCP.
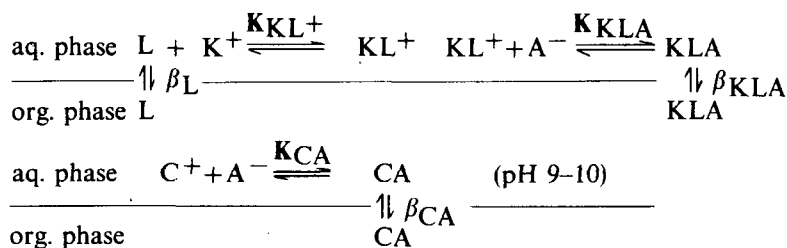
All a'-values of 1,2-DCP are systematically lower than the corresponding values of 1,2-DCE. Therefore, when a high sensitivity is required (water samples with less than 0.1 mg/l non-ionics), the use of 1,2-DCE is mandatory in the final spectrophotometric determination. However, the use of 1,2-DCP implies a number of practical advantages, such as lower volatility, lower harmfulness (MAK of 1,2-DCP is 350 mg/m^3)[9] and lower reagent blank values (about 1/3 of those obtained with 1,2-DCE).

Possible sources of PPAS as reagent blank (A_0) were found in purified water, especially when it is obtained by ionic exchange (traces of cationic resin react as PPAS); and in potassium nitrate, depending on source. The blank-value can be reduced if the KNO_3 stock solution is extracted with DCM (solvent is eliminated by bubbling through ultrapure nitrogen). The same method of purification is applicable to potassium picrate-potassium nitrate reagent solution.

Interference of cationic surfactants

In a recent study[4] on possible interferences in the pre-extraction with 1,2-DCE and determination of non-ionics as PPAS, it has been shown that cationics positively interfere even at a very low interfering substance to analyte ratio (3/100). Although the use of cationics is restricted to a few special industrial applications (for instance, textile industries), all methods proposed up to now based on the final spectrophotometric determination of PPAS do not resolve the basic problem of this interference.

The equilibria involved in a two-phase extraction of monodisperse surfactant ligand (L) reacting 1:1 with picrate (A^-) and in presence of an interfering cationic surfactant (C^+) are the following (a ratio of organic to aqueous phase of 1:1 is simply assumed):

$$
\begin{array}{l}
\text{aq. phase} \quad L + K^+ \underset{}{\overset{K_{KL^+}}{\rightleftharpoons}} KL^+ \quad KL^+ + A^- \underset{}{\overset{K_{KLA}}{\rightleftharpoons}} KLA \\
\rule{5cm}{0.4pt} \updownarrow \beta_L \rule{6cm}{0.4pt} \updownarrow \beta_{KLA} \\
\text{org. phase} \quad L \qquad\qquad\qquad\qquad\qquad\qquad\qquad KLA
\end{array}
$$

$$
\begin{array}{l}
\text{aq. phase} \quad C^+ + A^- \overset{K_{CA}}{\rightleftharpoons} CA \qquad (pH\ 9\text{--}10) \\
\rule{6cm}{0.4pt} \updownarrow \beta_{CA} \rule{2cm}{0.4pt} \\
\text{org. phase} \qquad\qquad\qquad CA
\end{array}
$$

β_L, β_{KLA} and β_{CA} are the distribution constants of L, KLA and CA, K_{KL^+}, K_{KLA} and K_{CA} are the formation constants of KL^+, KLA and CA,

respectively, at the equilibrium and at a constant ionic strength. The total concentration c of both L and C^+ at trace levels in the aqueous phase is $< 1 \times 10^{-6}$ M.

As the extraction is performed at a constant alkaline pH, the equilibrium concentration of A^- is also constant and the side reaction of protonation can be neglected. It is also assumed that the ionisation of KLA and CA in the organic phase is negligible. Using A^- as chromophore, both KL^+ and C^+ are obviously extracted into organic phase and determined as sum of KLA and CA respectively.

However, ion-pairing is completely different in the two cases.

In the first case, A^- is paired with the KL^+-complex formed in aqueous phase by coordination of solvated K^+-ion with the polyethylene chain (L). This reaction approaches completeness only if K^+ (as KNO_3) is in a large excess ($[K^+]_{aq} \geqq 1$ M) together with the pairing anion ($[A^-]_{aq} \geqq 0.02$ M) when $c_L \sim 1 \times 10^{-6}$ M in the aqueous phase.

As all reactions are reversible, the concentration of KLA in the organic phase may be reduced to very low values, when the concentration of K^+ is drastically reduced in the aqueous phase. Actually, PPAS derived from polyoxyethylene non-ionic surfactants disappear when the organic phase containing KLA is extracted with water. Figure 3 shows that at 20°C an equivalent volume of water is needed for the nearly complete disappearance ($< 1\%$) of PPAS at least up to 1 mg/l of $C_{12}E_{\overline{10.2}}$.

In the second case, PPAS due to CA resist to further extraction with water, since the equilibrium involved is only connected to the distribution between the two phases and CA is nearly exclusively concentrated in the organic phase.
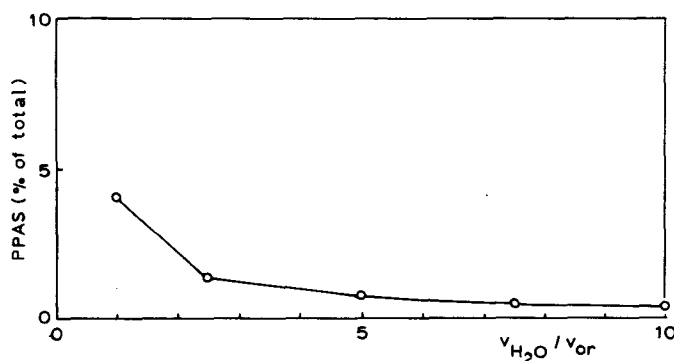

FIGURE 3   PPAS (%) remaining in the organic phase (1,2-DCE) after extraction with water (v_{H_2O}/v_{or} is the ratio of water to organic phase). PPAS were extracted with 2.50 ml of 1,2-DCE from 25.0 ml of aqueous phase containing 1.00 mg/l of $C_{12}E_{\overline{10.2}}$.
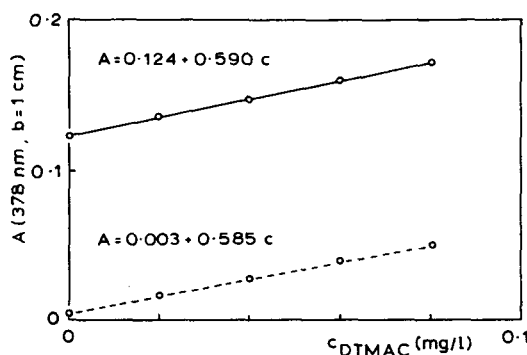
FIGURE 4 PPAS-absorbance of 1,2-DCE-extracts from aqueous phases containing a fixed concentration of $C_{12}E_{\overline{10.2}}$ (0.50 mg/l) and increasing concentration of DTMAC. Continuous line: PPAS measured *before* extraction with water. Interrupted line: PPAS measure *after* extraction with water ($v_{H_2O}/v_{or} = 1$). Parameters of lines were evaluated by linear regression (in both cases $R^2 = 0.9993$).

Figure 4 presents some data supporting these suggestions. The figure reports the absorbance of PPAS observed in 5.00 ml of 1,2-DCE with a fixed concentration of $C_{12}E_{\overline{10.2}}$ and with increasing concentrations of cationic surfactants (DTMAC, dodecyl trimethylammonium chloride, Eastman). PPAS derived from DTMAC have the same λ_{max} of PPAS due to polyether non-ionics.[3]

At least up to the concentration of DTMAC of 0.08 mg/l in the aqueous phase, the absorbance of the PPAS due both to non-ionic and to cationic surfactants increases linearly with DTMAC-concentration. Also the absorbance of the PPAS after extraction with water increases linearly with DTMAC-concentration, with practically the same slope. The difference between intercepts corresponds exactly to the PPAS due to the non-ionic surfactants only.

The procedure is a simple proof for the presence of polyoxyethylene non-ionic surfactants in the final spectrophotometric determination and can probably substitute the time-consuming separation techniques based on ion-exchange chromatography.[10,11]

Applications

Determination of polyoxyethylene non-ionic surfactants in polluted sea water has been carried out.

Further research is planned with the aim of controlling the intralaboratory repeatability of the method applied to samples of polluted sea waters.
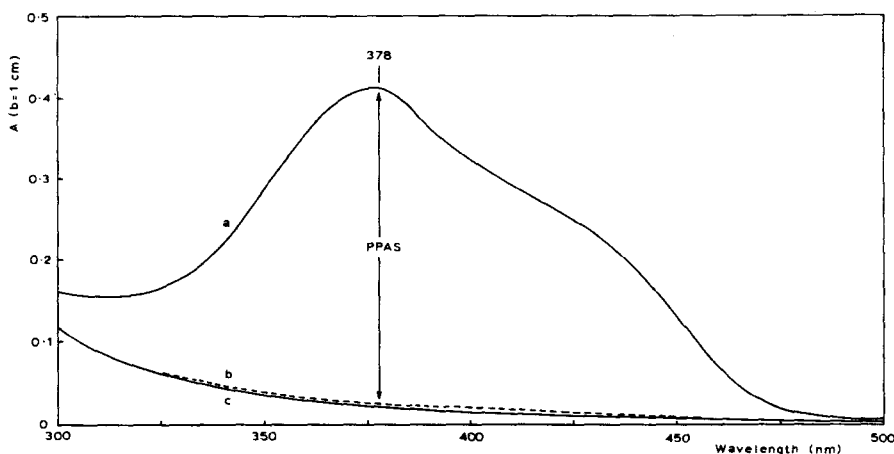
FIGURE 5   Absorbance spectrum due to PPAS of a sea water sample containing $85\,\mu g/l$ of polyoxyethylene non-ionic surfactants expressed as $C_{12}E_{\overline{10.2}}$. Trace a: spectrum of PPAS of 2.5-ml extract in 1,2-DCE. Trace b (interrupted line): spectrum of the same organic phase extracted with 2.5 ml of water. Trace c (continuous line): spectrum of an organic phase obtained without addition of potassium picrate solution.

Figure 5 shows the absorbance spectra of the extracts (into 1,2-DCE) obtained from a typical sample of polluted sea water. This sample, collected in proximity of an outlet in the harbour of Trieste (Northern Adriatic Sea), is polluted by urban waste waters containing hydrocarbons too. Trace a indicates the absorbance spectrum of PPAS against pure solvent, trace b that of the same organic phase but after extraction with water. Note that PPAS are no longer present in the latter, and the background absorbance is very close to that observed in a "blank extraction", that is, an extraction processed in parallel but without picrate addition (trace c). Table III summarizes the results obtained by the analysis of two samples of sea water from the harbour of Trieste. Intra-laboratory repeatability is about $\pm 0.77\,\mu g/l$ of PPAS expressed as $C_{12}E_{\overline{10.2}}$.

CONCLUSIONS

The method presents a simple and rapid procedure, which avoids the use of the exchange resins. The procedure, tested at ultra trace-levels, can also be applied to trace levels. For instance, when the spectrophotometric determination is made up with 5.00 ml of organic phase extracted from 50.0 ml of aqueous phase, the sensitivity is halved without changing correction factors and the range of linearity raises up to $400\,\mu g/l$ in the 500-ml sample.

TABLE III

Concentration (c_i) of polyoxyethylene non-ionic surfactants (expressed as $\mu g/l$ on $C_{12}E_{\overline{10.2}}$) found in polluted coastal sea water from the harbour of Trieste, Northern Adriatic Sea (sampling date June 20th, 1982). Analysis on two samples were performed in parallel

Sample site and number		PPAS ($\mu g/l$)	
		c_1	c_2
Muggia			
	1	8.1	8.6
	2	8.1	8.8
	3	6.6	5.9
	4	6.8	6.4
	5	5.7	6.6
	6	5.9	5.2
	7	4.0	3.3
	8	9.2	9.9
	9	3.3	3.7
	10	3.5	4.2
	11	3.7	4.0
	12	7.0	9.5
	13	7.0	6.4
	14	4.4	5.2
	15	4.2	3.7
	16	8.6	8.1
Scalo Legnami			
	1	29.9	30.6
	2	5.2	4.9
Porto Vecchio			
	1	85.0	88.1

Intra-laboratory repeatability $\quad s = \pm \left[\dfrac{\sum (c_1 - c_2)^2}{2N} \right]^{1/2} = \pm 0.77 \, \mu g/l.$

A sample size lower than 500-ml can likely be chosen for decreasing sensitivity, but correction factors (and repeatability) must be carefully evaluated for each selected size.

Further studies are still in progress for testing the method in waters polluted by cationic surfactants.

EAC—D

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