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CHROMATOGRAPHIC STUDIES ON THE EXTRACTION OF POLYOXY-ETHYLENE ALKYLPHENYL ETHER NON-IONIC SURFACTANTS FROM WATER AT TRACE LEVELS

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SUMMARY

The extraction of polyoxyethylene non-ionic surfactants of the type $RO(CH_2CH_2O)_nH$, (where R is a *p-tert.*-nonylphenyl group and n is the degree of polymerization) from water at trace levels with some organic phases has been studied by gas chromatography. Of the solvents tested, 1,2-dichloroethane appears to be suitable as a non-fractionating phase for extracting these polydisperse non-ionic surfactants. The evaluation of the distribution constants of monodisperse compounds ($6 \leqslant n \leqslant 11$) by a spectrophotometric procedure confirmed the gas chromatographic results.

INTRODUCTION

The solvent extraction of the polyoxyethylene non-ionic surfactants from water at trace levels has been applied in the determination of these substances[1–6]. Various solvents and conditions have been proposed, but until now no quantitative and systematic approach has been made in order to define the criteria for choosing the best two-phase extraction system. This is due in part to the difficulty that these surfactants, which in most instances have the general formula $RO(CH_2CH_2O)_nH$, where R denotes an alkyl or alkylaryl group and n is the degree of polymerization, are produced industrially as mixtures of oligomers with a range of n, which can be characterized by determining the molecular weight distribution by chromatographic techniques[7–11], at least up to a certain value. In dealing with extraction procedures, a further difficulty is that the hydrophile–lipophile balance varies with n, the hydrophile character increasing up to a limit with increase in n (ref. 12).

The aim of this work was to compare the properties of some solvents in extracting polyoxyethylene non-ionic surfactants. The study was restricted to industrial surfactants with R = *p-tert.*-nonylphenyl. Of these compounds, the monodisperse oligomers with n = 3–11 were separated at a high level of purity by liquid–solid adsorption chromatography (monodisperse compounds with $2 \leqslant n \leqslant 9$ have already been separated chromatographically, without the physical data being given[13]). Their distribution coefficients between solvent and water were determined with a spectro-

photometric procedure. Temperature-programmed gas–liquid chromatography (GLC) was used for choosing the best extraction solvent by means of a comparison of the molecular weight distributions of the surfactant before and after the extraction. In view of their applicability to the analysis of waters, all experiments were carried out at an initial surfactant concentration of up to 2 mg/l in the aqueous phase. In this phase, the equilibrium concentrations are below the critical micellar concentration (CMC) of these compounds, as the distribution coefficient is constant only below the CMC[14].

EXPERIMENTAL

Apparatus

A Pye-Unicam double-column chromatograph with flame-ionization detectors was used. Stainless-steel columns (35 cm × 1/8 in. I.D.) were packed with 80–100-mesh Gas-Chrom Q coated with 3 % (w/w) GE SE-30, GC grade (Applied Science Labs., State College, Pa., U.S.A.). Fractionation was carried out with a linear temperature programme from 130° to 350° at the rate of 10°/min, and with injector and detector temperatures of 375° and 400°, respectively. The flow-rates of the gases were nitrogen 40, hydrogen 40 and air 300 ml/min. The effective peak number was 0.6 for C_{22}/C_{23} n-alkanes[15].

Spectrophotometric measurements were carried out with a Unicam SP 500 instrument with various silica cell path lengths at 20°. Absorbance spectra were also measured with a Perkin-Elmer 402 spectrophotometer.

The monodisperse oligomers ($3 \leqslant n \leqslant 11$) were obtained by preparative gradient elution adsorption chromatography with an LKB Ultrorac 7000 fraction collector at 20°. By means of a glass column (2.5 cm I.D.), about 100 mg of oligomer at 80 % purity was obtained, which was fractionated in another column (1 cm I.D.). The pure compounds were obtained by selecting systematically the purest 10-ml fractions by GLC. In both instances 30–50-μm silica gel (AR grade, Mallinckrodt, St. Louis, Mo., U.S.A.) was used as an adsorbent, packed in a column of length 21 cm in the first instance and 30 cm in the second. Mixtures of acetone in dichloromethane were used as the eluent, with the linear gradients $A = 0.083V$ (first column) and $A = 0.040V$ (second column), where A is the concentration of acetone (% v/v at 20° before mixing), and V (ml) is the volume of the eluent at the top of the column.

Reference compounds and reagents

Monodisperse compounds with $3 \leqslant n \leqslant 11$ were separated from a commercial polydispersion having a number-average degree of polymerization of $\bar{n} = 3.3, 5.4$ and 6.5. Fig. 1 shows the variation of the refractive index with n.

The GLC purity of the compounds is shown in Table I. Aqueous stock solutions containing 20 mg/l were prepared from these monodisperse compounds. At 20°, these solutions are stable for a few days; after a week 5 % biodegradation was observed spectroscopically with oligomers with $n = 8$ and 11, from the reduction of the slope of the calibration line. More dilute solutions (10–1 mg/l) were prepared daily by dilution.

Stock solutions of polydisperse surfactants are stable for up to a month; no explanation of this different behaviour is available at present, but it may be tentatively
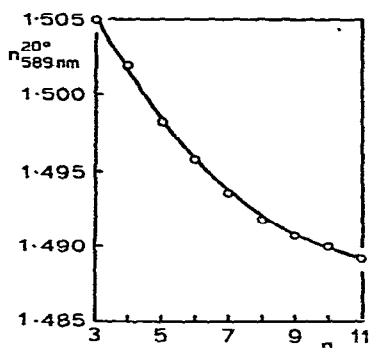
Fig. 1. Plot of refractive index ($n_{589\,nm}^{20^\circ}$) *versus* degree of polymerization (n) of the monodisperse surfactants $RO(CH_2CH_2O)_nH$ ($R = p\text{-}tert.\text{-nonylphenyl}$).

TABLE I

GLC PURITY (% OF PEAK AREA) OF THE MONODISPERSE OLIGOMERS $RO(CH_2CH_2O)_nH$ ($R = p\text{-}tert.\text{-NONYLPHENYL}$)

n is the degree of polymerization; $n_{589\,nm}^{20^\circ}$ is the refractive index.

n	Purity (%)	Oligomers present as impurities (%)	$n_{589\,nm}^{20^\circ}$
3	95.28	3.84 ($n =$ 2)	1.5051
		0.40 ($n =$ 4)	
4	98.05	1.35 ($n =$ 3)	1.5019
		0.60 ($n =$ 5)	
5	89.37	3.79 ($n =$ 3)	1.4982
		6.84 ($n =$ 4)	
6	93.96	4.38 ($n =$ 5)	1.4958
		1.66 ($n =$ 7)	
7	95.26	0.90 ($n =$ 5)	1.4936
		3.83 ($n =$ 6)	
8	94.93	5.07 ($n =$ 7)	1.4919
9	92.93	7.17 ($n =$ 8)	1.4908
10	92.00	6.85 ($n =$ 9)	1.4900
		1.09 ($n = 11$)	
11	98.00	1.89 ($n = 10$)	1.4892

suggested that the relative stability of the polydispersion is due to the presence of nonylphenol, which like phenol[16], can act as a bacteriostat at trace bacterial levels. These solutions were conveniently prepared by transferring 20 mg (exactly weighed) of the polydisperse non-ionic surfactant with 2.0 ml of 95% ethanol into a 1000-ml calibrated flask and making the volume up to the mark. From this solution, a 2 mg/l solution was prepared daily.

1,2-Dichloroethane (extra pure), chloroform (pro analysi) (both freshly distilled) and diethyl ether (pro analysi) (E. Merck, Darmstadt, G.F.R.) were used as extracting organic phases. Chromatographic-grade acetone and other analytical-grade reagents were also used.

Extraction procedure

The polydispersion with $\bar{n} = 6.5$ was used in two-phase extraction experiments.

At 25°, 50 ml of the 2 mg/l solution was equilibrated with 50 ml of organic phase by shaking for 5 min in a 250-ml separating funnel with PTFE stop-cocks. An aliquot of the organic layer was transferred into a centrifuge tube fitted with a polyethylene stop-cock and centrifuged for 5 min at 1000 g. The clear layer was then evaporated to dryness under a stream of nitrogen in a conical centrifuge tube to avoid oxidation. The residue was transferred into a conical glass vial with about 0.1 ml of extracting solvent. An aliquot of this solution was then injected into the gas chromatograph.

Determination of monodisperse non-ionic surfactants in aqueous solution

The determination of the concentration of monodisperse non-ionic surfactants in aqueous solution was carried out by a spectrophotometric method, based on the coordination reaction between the polyoxyethylene surfactant and an alkaline earth metal cation and on the extraction into 1,2-dichloroethane of the positive complex with the chromophoric picrate anion[6]. The method was substantially modified by using potassium as a coordinating cation, which forms complexes that are more stable than those obtained with sodium[17].

The procedure consists in dissolving the dried surfactant in 0.25 ml of ethanol plus 25.0 ml of an aqueous solution 2 M in potassium nitrate and 0.1 M in potassium hydroxide in a 50-ml calibrated flask at 20°. Then 10.0 ml of 0.01 M of picric acid solution are added and the volume is made up to the mark with water. A blank extracted with reagents only is prepared. The solutions are mixed and allowed to stand for 12 h. The liquid is transferred into a separating funnel with PTFE stopcocks, 5.0 ml of 1,2-dichloroethane are added and the mixture is shaken vigorously fc⁻ 5 min. The organic layer is transferred dropwise into a conical centrifuge tube fitted with a polyethylene stop-cock and centrifuged as indicated above. The absorbance of the clear organic extract is measured at 378 nm in a 1-cm (or 2-cm) cell against the blank.

The calibration lines were obtained by extracting 50 ml of aqueous solutions containing increasing concentrations of the surfactant from 0.1 to 1 mg/l by the same procedure. Fig. 2 shows the calibration lines for monodisperse surfactants with $6 \leqslant n \leqslant 11$. The compounds with $3 \leqslant n \leqslant 5$ react so slightly that they cannot be utilized for accurate analytical determinations. The absorbance of the reagent blank against the solvent is constant (for $b = 1$, $A = 0.01$).

Determination of distribution coefficients

The determination of the distribution coefficient was carried out by equilibrating 50.0 ml of an aqueous solution containing 2.00 mg/l of monodisperse oligomer with 50.0 ml of organic phase (1,2-dichloroethane or chloroform) in a 250-ml separating funnel with PTFE stop-cocks for 5 min at 25°. Then 25.0 ml of the clear, centrifuged organic layer were evaporated to dryness in a 50-ml calibrated flask under a stream of nitrogen at 60°. The residue was processed as described under *Determination of monodisperse non-ionic surfactants in aqueous solution.*

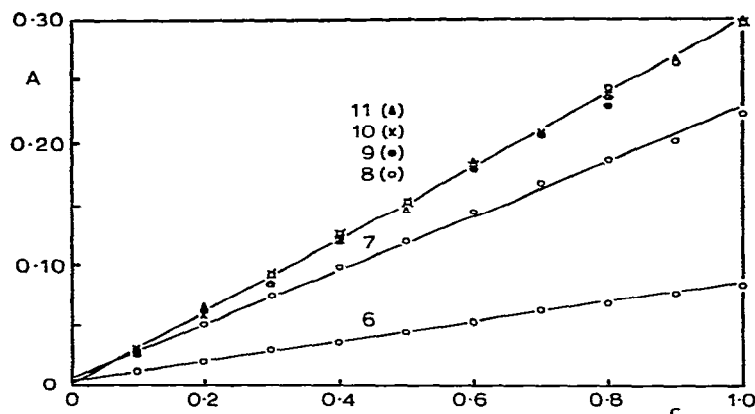Let $\beta = a_O/a_A$ be the distribution coefficient between the organic (O) and

Fig. 2. Calibration lines at 20° for the monodisperse surfactants $RO(CH_2CH_2O)_nH$ ($R = p\text{-}tert.$-nonylphenyl). The numbers indicate the degree of polymerization. c is the concentration (mg/l) of surfactant in the aqueous phase; A is the absorbance ($b = 1$ cm). Observed points are interpolated by straight lines. Regression equations: $n = 6$, $A = 0.080c + 0.004$ ($F = 2710$); $n = 7$, $A = 0.221c + 0.008$ ($F = 1802$); $n = 8\text{-}10$, $A = 0.0296c + 0.002$ ($F = 22234$). The goodness of fit of the linear regression is given in parentheses by the value calculated according to the F-test.

aqueous (A) phases. As the ionic strength is zero and the surfactant concentration is at the trace level, the system is very close to ideal. With non-ionic surfactants, the activity coefficient can be assumed to be unity. Hence the value of β can be determined from the equilibrium concentration of the surfactant in the organic phase (c_O) and the aqueous phase (c_A), calculated by difference: $\beta = c_O/(c - c_A)$, where c is the total initial concentration (the direct determination in the aqueous phase was unsuccessful, owing to the very low concentration involved).

RESULTS AND DISCUSSION

Table II summarizes the results of the gas chromatographic analysis of the polydispersion with $\bar{n} = 6.5$ (standard mixture, extracted with some solvents). In order to attain the maximal accuracy and precision, the oligomer with $n = 5$ was used as an internal standard in all of the chromatograms, as it is not cut off by volatility limits and is also near to the maximum of the molecular weight distribution. The distributions are shown in Fig. 3. Up to $n = 5$, there is no significant difference among the various extracting phases, although the chlorinated hydrocarbons tend to extract more the $n = 4$ substances. Diethyl ether has an appreciable preferential efficiency in the range $n = 6\text{-}8$; chloroform extracts less the higher oligomers. The values obtained with 1,2-dichloroethane approach closely those of the standard distribution. From Table II, it can be seen that 1,2-dichloroethane also gives a better reproducibility than with the other extracting phases. In the single-extraction procedure adopted, chloroform and 1,2-dichloroethane have the further advantage of having a lower water solubility than diethyl ether.

Table III gives the distribution constants of some monodisperse oligomers ($7 \leqslant n \leqslant 11$) between water and organic solvents (chloroform and 1,2-dichloroethane). The values obtained with chloroform are systematically lower than those obtained

TABLE II

MOLECULAR WEIGHT DISTRIBUTION OF THE SURFACTANT $RO(CH_2CH_2O)_nH$ (R = *p-tert.*-NONYLPHENYL, $\bar{n}$ = 6.5) EXTRACTED FROM WATER WITH SOME SOLVENTS AT 25°

n is the degree of polymerization. The value A_n/A_5 is calculated as the ratio of the gas chromatographic peak areas of an n-mer and the pentamer, used as an internal standard. s is the root-mean square deviation from four analyses. Reference polydispersion (A), extracted with diethyl ether (B), chloroform (C) and 1,2-dichloroethane (D). Initial organic to aqueous phase ratio = 1:1. Initial concentration of the surfactant in the aqueous phase, 2.0 mg/l.

| n	Elution temperature (°C)	$A_n/A_5 \pm s$			
		A	B	C	D
1	139	0.032 ± 0.003	0.043 ± 0.005	0.038 ± 0.005	0.033 ± 0.002
2	150	0.156 ± 0.013	0.144 ± 0.010	0.171 ± 0.012	0.147 ± 0.009
3	161	0.464 ± 0.014	0.468 ± 0.018	0.459 ± 0.006	0.496 ± 0.013
4	180	0.850 ± 0.009	0.831 ± 0.010	0.938 ± 0.019	0.911 ± 0.016
5	198	1	1	1	1
6	216	1.035 ± 0.012	1.117 ± 0.015	1.011 ± 0.004	1.017 ± 0.008
7	232	0.962 ± 0.010	1.054 ± 0.009	0.923 ± 0.011	0.991 ± 0.005
8	246	0.807 ± 0.014	0.884 ± 0.015	0.744 ± 0.016	0.783 ± 0.007
9	261	0.566 ± 0.013	0.565 ± 0.014	0.480 ± 0.016	0.546 ± 0.013
10	274	0.345 ± 0.010	0.290 ± 0.019	0.245 ± 0.019	0.341 ± 0.016
11	286	0.166 ± 0.008	0.122 ± 0.009	0.097 ± 0.013	0.141 ± 0.009
12	297	0.064 ± 0.005	0.040 ± 0.007	0.029 ± 0.010	0.055 ± 0.006
13	308	0.037 ± 0.008			
14	318	0.020 ± 0.009			
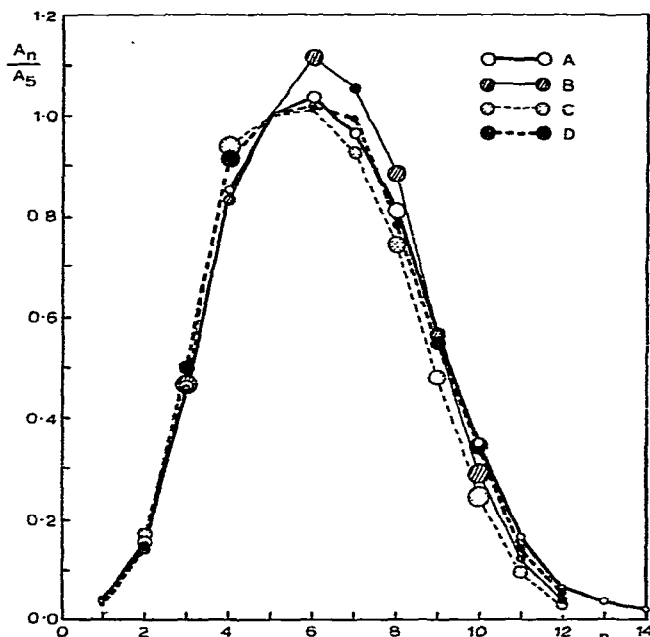
Fig. 3. Comparison of various solvents in extracting the polydisperse non-ionic surfactant $RO(CH_2CH_2O)_nH$ (R = *p-tert.*-nonylphenyl, $\bar{n}$ = 6.5) from water at 25°. Organic to aqueous phase ratio = 1:1. Concentration of the surfactant in the aqueous phase, 2 mg/l; A_n/A_5 is the ratio of the gas chromatographic peak areas of an n-mer and the pentamer, used as an internal standard. Reference polydispersion (A), extracted with diethyl ether (B), chloroform (C) and 1,2-dichloroethane (D). The radius of the circles is proportional to the root-mean square deviation (see Table II).

TABLE III

DISTRIBUTION COEFFICIENTS BETWEEN AQUEOUS AND ORGANIC PHASES AT 25°
OF THE MONODISPERSE NON-IONIC SURFACTANTS RO(CH$_2$CH$_2$O)$_n$H (R = *p-tert.*-NONYLPHENYL)

The composition of the aqueous and organic phases is that resulting from equilibrium at 25°. n is the degree of polymerization; $\bar{\beta}_n \pm s$ is the distribution coefficient $\pm$ root-mean square deviation calculated from N determinations; C_v is the coefficient of variation.

n	*Chloroform*			*1,2-Dichloroethane*		
	N	$\bar{\beta}_n \pm s$	C_v (%)	N	$\bar{\beta}_n \pm s$	C_v (%)
7	6	11.8 $\pm$ 1.0	$\pm$ 8.5	6	20.2 $\pm$ 2.5	$\pm$12.4
8	5	11.0 $\pm$ 1.3	$\pm$11.8	4	19.1 $\pm$ 3.8	$\pm$20.0
9	4	9.74 $\pm$ 0.54	$\pm$ 5.5	8	18.0 $\pm$ 2.6	$\pm$14.4
10	5	8.80 $\pm$ 1.17	$\pm$13.3	5	15.0 $\pm$ 1.8	$\pm$12.0
11	6	9.20 $\pm$ 1.16	$\pm$12.6	7	14.4 $\pm$ 2.8	$\pm$19.4

with 1,2-dichloroethane, the latter being a better extracting phase than the former for these non-ionic surfactants. This conclusion is in accordance with the observation[18] that 1,2-dichloroethane is also better than chloroform in extracting the polydisperse surfactants coordinated with NH$_4$$^+$ and precipitated with Co(NCS)$_4$$^{2-}$.

The values obtained with both chloroform and 1,2-dichloroethane decrease only slightly with increasing n. This can be seen in Fig. 4, which shows the regression lines of the relationship log $\bar{\beta}_n$ *versus n*. With both solvents the slope of the interpolating line is nearly the same. In the extraction of polydisperse surfactants, both solvents are acceptable as $\bar{\beta}_n$ varies slightly with n. Assuming the extrapolation of the interpolating line towards higher n is valid, the intercept on the abscissa (n_0) gives the value of n at which $\bar{\beta}_n = 1$; for $\bar{\beta}_n < 1$, the polyoxyethylene surfactants are no longer concentrated from the aqueous phase. For chloroform this value is $n_0 = 41$, and for 1,2-dichloroethane $n_0 = 40$. Therefore, the fractionation of the monodisperse compounds between the two phases is negligible, at least with common surfactants.
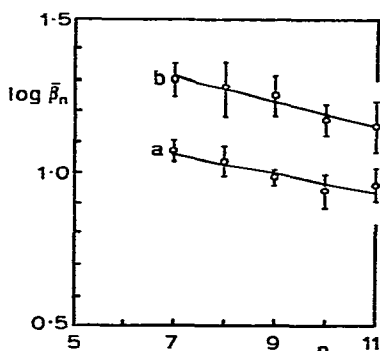

Fig. 4. Variation of log $\bar{\beta}_n$ with n for the monodisperse non-ionic surfactants RO(CH$_2$CH$_2$O)$_n$H (R = *p-tert.*-nonylphenyl) at 25°. Extracting organic phases: (a) chloroform, (b) 1,2-dichloroethane. The composition of the aqueous phase is that resulting from equilibrium at 25°. In the range $7 \leqslant n \leqslant 11$, the data are interpolated by linear regression with the solid lines, which have the equations: (a) log $\bar{\beta}_n = -0.031n + 1.28$; (b) log $\bar{\beta}_n = -0.040n + 1.59$. The test of significance for the regression gives the following values: (a) $F = 19.2$; (b) $F = 57.0$. The scatter of the data (log $\bar{\beta}_n$) is also reported by segments traced above and below the point corresponding to log $\bar{\beta}_n$.

For a reversible distribution equilibrium with very dilute solutions, the free energy of transfer from the aqueous to the organic phase of an oxyethylene group is about 43 cal/mole for chloroform and about 54 cal/mole for 1,2-dichloroethane. No distribution data on monodisperse *p-tert.*-nonylphenyl ethers are available. From extraction studies on monodisperse *p-tert.*-octylphenyl ethers $(1 \leqslant n \leqslant 10)$ with isooctane from an aqueous solution below the CMC^{19}, $\bar{\beta}_n$ varies linearly with n (log $\bar{\beta}_n = -0.4387n + 3.81$), at least in the range $3 \leqslant n \leqslant 10$. The substantial fractionation of this solvent is indicated by the slope, which gives a free energy of transfer of about 598 cal/mole for an oxyethylene group, and by the value of $n_0 = 8.7$.

To conclude, at trace levels 1,2-dichloroethane appears to be a useful organic solvent for the direct extraction of non-ionic surfactants from water aqueous solutions, permitting the gas chromatographic analysis of the molecular weight distribution at least up to the limit of n to which this technique is applicable.

REFERENCES

1 N. T. Crabb and H. F. Persinger, *J. Amer. Oil Chem. Soc.*, 41 (1964) 752.
2 S. J. Patterson, E. C. Hunt and K. B. E. Tucker, *J. Proc. Inst. Sew. Purif.*, (1966) 190.
3 S. J. Patterson, C. C. Scott and K. B. E. Tucker, *J. Amer. Oil Chem. Soc.*, 44 (1967) 407.
4 L. Favretto, G. Pertoldi Marletta and L. Favretto Gabrielli, *Ann. Chim. (Rome)*, 62 (1972) 478.
5 L. Favretto Gabrielli and G. Pertoldi Marletta, *Ann. Chim. (Rome)*, 63 (1973) 807.
6 L. Favretto and F. Tunis, *Analyst (London)*, 101 (1976) 198.
7 G. Pertoldi Marletta and L. Favretto Gabrielli, *Tec. Ital.*, 34 (1969) 649.
8 L. Favretto, G. Pertoldi Marletta and L. Favretto Gabrielli, *J. Chromatogr.*, 46 (1970) 255.
9 L. Favretto, *Riv. Ital. Sostanze Grasse*, 47 (1970) 187.
10 L. Favretto and B. Stancher, *J. Chromatogr.*, 108 (1975) 183.
11 B. Stancher, L. Favretto Gabrielli and L. Favretto, *J. Chromatogr.*, 111 (1975) 459.
12 P. Becher, in M. J. Schick (Editor), *Non-Ionic Surfactants*, Marcel Dekker, New York, 1967, p. 604.
13 N. T. Crabb and H. E. Persinger, *J. Amer. Oil Chem. Soc.*, 45 (1968) 611.
14 H. L. Greenwald, E. B. Kice, M. Kenly and J. Kelly, *Anal. Chem.*, 33 (1961) 465.
15 A. Murrel and S. G. Perry, *Nature (London)*, 196 (1962) 571.
16 R. D. Swisher, *Surfactant Biodegradation*, Marcel Dekker, New York, 1970, p. 96.
17 L. Favretto, *Ann. Chim. (Rome)*, in press.
18 C. Calzolari, L. Favretto and F. Tunis, *Analyst (London)*, 99 (1974) 171.
19 E. H. Crook, D. B. Fordyce and G. F. Trebbi, *J. Colloid Sci.*, 20 (1965) 191.