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BIODEGRADATION OF NONIONIC SURFACTANTS OF TETRONIC TYPE UNDER STATIONARY CONDITIONS

I. THE EFFECT OF SURFACTANT STRUCTURE ON THE BIODEGRADATION COURSE

The effects of average molecular weight \overline{M}_n of tetronic-type block copolymers and of the content of ethylene in a macromolecule on their biodegradability under stationary conditions in the presence of mixed bacterial populations have been examined. The copolymer was the only energy and carbon source for bacteria. Its concentration amounted to 1%. The biodegradation course was estimated from the loss of copolymer mass, changes in its \overline{M}_n and the contents of carbonyl groups as well as of neutral fraction and amine groups. It has been stated that in the case of technical preparations containing polyoxyalkylene glycols as side-products, the presence of the latter affects significantly biodegradation process. For this reason it is diffucult to estimate the separate effects of the components of the main copolymer structure.

1. INTRODUCTION

The biodegradation of nonionic surfactants is the subject of numerous papers [15]. This dynamically growing group of surfactants comprises, among others, block copolymers of alkylene oxides, mainly propylene and ethylene oxides which are based on monoand multifunctional initiators and usually do not contain the typical hydrophobic hydrocarbon groups [11]. This factor, combined with the possibility of a wide modification of a macromolecule, makes the above-mentioned copolymers an interesting object in the studies of biodegradation on the one hand and may provide difficulties in the observation of this process, due to the structure of this compound being not typical, on the other hand.

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It seems that it is one of the reasons for which the biodegradability of nonionic copolymers of alkylene oxides is not yet known. So far the investigations have been performed on copolymers of pluronic type [1, 2, 6] of the general formula:

$$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x(\text{CHCH}_2\text{O})_y(\text{CH}_2\text{CH}_2\text{O})_z\text{H}.$$

$$|$$
 CH_3

The effect of the average molecular weight \overline{M}_n of copolymere on its biodegradability may be inferred indirectly from the literature data concerning polyoxyethylene and polyoxypropylene glycols, which are the structural elements of a copolymer macromolecule [7, 15, 16]. From the data it follows also that the biodegradation rate of the corresponding polyglycols depends to a high extent on the conditions and the time of adaptation of bacterial strains used in the experiment. The molecules of the above-mentioned copolymers and polyglycols do not contain any other heteroatoms (e.g. nitrogen) except for oxygen. It is also known from other sources that the introduction of amine or amide groups into aliphatic [4] and aromatic [8] compounds reduces the biodegradation rate. Thus, it seemed of interest to investigate some problems connected with biodegradation of block copolymers of tetronic type, described by the formula

and containing in the macromolecule centre two basic nitrogen atoms. It has been shown earlier [9] that these compounds are substantially less susceptible to chemical oxidation than the copolymers of pluronic type.

This paper offers discussion of the results of investigations on the influence of a copolymer macromolecule structure, i.e. of its \overline{M} , and the ratio of hydrophilic polyoxyethylene to hydrophobic polyoxypropylene grouping on the biodegradation degree under stationary conditions in presence of mixed bacterial populations. The copolymers used were technical products which besides the main compound (1) contained also copolymers of pluronic type and polyoxyethylene glycols formed during consecutive stages of synthesis and constituting a neutral part of the product [10].

The experiments were conducted at a high concentration of surfactants that, as a rule, amounted to 1 percentage by weight and was the only available source of carbon and energy for the bacteria. This concentration allowed us to isolate the biodegradation products in amounts required for analysis, bearing in mind, however, that such a high concentration may affect negatively bacterial cells.

In order to measure a progress of degradation and changes occurring in a macromolecule the following criteria have been assumed:

- a) amount of product remaining after a defined biodegradation time,
- b) changes in concentrations of characteristic functional groups formed during the process,
 - c) changes in \overline{M}_n ,
 - d) changes in content of neutral fraction,
 - e) changes in amine content in the product.

2. EXPERIMENTAL

Surfactants used in the reported work were obtained by a successive three-stage addition of propylene and ethylene oxides to ethylenediamine in the presence of NaOH as a catalyst. The latter was removed from the raw product by means of a cation exchanger WOFATIT KPS, according to [9]. Characteristics of the products are given in tab. 1.

Table 1

Characteristics of the examined surfactants of tetronic type
Charakterystyka badanych surfaktantów typu tetroników

Symbol of preparation*	\overline{M}_n determined	Contents	Contents	Neutral fraction	
		of ethylene oxide [wt - %]	of nitrogen [wt - %]	Content [wt - %]	\overline{M}_n
2400/20	2840	16.3	0.45	9.1	1760
1800/40	2780	37.2	0.60	19.3	1300
1000/70	2760	70.2	0.84	24.4	1570
1000/40	1560	37.5	1.68	9.9	730
2000/40	3560	44.7	0.34	29.7	1780

^{*} First and second digits of the symbol denote the approximate value of \overline{M}_n of hydrophobic grouping and the approximate value of weight percentage of the ethylene oxide in a molecule, respectively.

Biodegradation was conducted in 5 dm³ bottles aerated with a membrane pump at the temperature of 293 K. The bottles were filled with approx 1 dm³ of a sterile nutrient solution of pH = 7.0, prepared according to [14] and containing 1 cm³ of solution of microelements prepared according to [5]. The nutrient solution was inoculated with bacterial strain. The extinction of the medium was equal to 0.055 at the wavelength of 550 nm. Thereupon the compound investigated was added to the bottle volume of which was next completed with the nutrient solution to 5050 cm³. Concentration of the compound subject

to biodegradation was usually 1% by volume although some tests were carried out with 0.5% solutions when using at the same time a smaller volume of the compound. Adaptation of mixed bacterial populations was conducted for 3 months in nutrient solution, the copolymer examined being there the only source of carbon. Maximum concentration of the latter amounted to 1%. Inoculum was taken from surface waters of the rivers Ślęza and Oława as well as from municipal wastewater from sewage pumping station at Szczytniki in Wrocław. After adaptation the bacteria were transferred to the solid medium and after a 48 h culturing they were used for inoculation of nutrient solution.

From the culture investigated 300 cm³ samples were taken at the given time intervals and the bacteria removed by centrifugation. The biomass was then washed twice with cold water. The mixture of supernatant and washings was supplemented with NaCl (30 g $/100 \text{ cm}^3$ of solution) and the degradation products were extracted by shaking with chloroform ($1 \times 100 \text{ cm}^3$ and $7 \times 50 \text{ cm}^3$) in a separator. From the mixed extracts the solvent was removed on a rotation evaporator (temperature of water bath 343 K) to achieve a constant mass (1 h at ca 1.9 kN/m² and 3 h at ca 0.7 kN/m²).

In some samples of biodegradation products, neutral fraction was separated from the basic one by ion sorption method using a macroporous cation exchanger Amberlyst 15, according to [10]. The average molecular weight \overline{M}_n of the samples examined was determined by the vapour osmometric method, using a thermcelectric osmometer produced by Hitachi-Perkin Elmer, model 15, according to [9].

Total amines were determined by titrating the solution in glacial acetic acid with perchloric acid [13]. The content of tertiary amine was determined in a similar way, the amines of lower orders being previously acetylated with acetic acid anhydride [3].

IR spectra were obtained by using the Perkin Elmer made apparatus, model 621, and applying 4% solution of samples in CCl₄ of pro analysis purity. The width of the sample cell was 2.63 mm, and the working range of the spectrum was 1500–1850 cm⁻¹. To determine the absorption intensity the basic line method was used. When the absorption was determined from the height of peak at the band maximum, this line was parallel to the wavelength axis and tangent to the absorption curve at the wavenumber 1820 cm⁻¹. When the measurements were made by the weight method, based on the band area, this line was tangent to the band contour at 1710 cm⁻¹ and 1790 cm⁻¹.

3. RESULTS AND DISCUSSION

During biodegradation conducted under stationary conditions in the presence of mixed bacterial populations, the loss of surfactant mass is relatively low (figs. 1 and 2). It does not exceed several percent and varies in cycles. Initial loss of mass, with the maximum occurring after 2-5 days, was particularly distinct. At the same time the mass loss does not depend simply on the ethylene oxide content in the molecule (series I, $\overline{M}_n = \text{const:} 1000/70 > 2400/20 > 1800/40$) or on the mean molecular weight of polymer (series II:

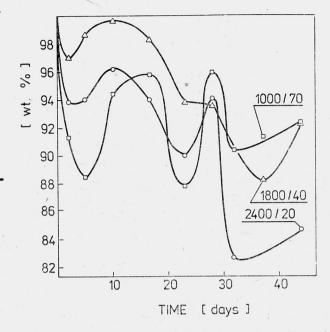


Fig. 1. Amount of the extracted product obtained from the solutions of surfactants of the tetronic type versus biodegradation time for copolymers with varying contents of ethylene oxide in a molecule (series I)

Rys. 1. Zależność ilości produktu wydzielonego podczas ekstrakcji z roztworów surfaktantów typu tetroników poddanych biodegradacji od czasu procesu. Kopolimery o zmiennej zawartości tlenku etylenu w cząsteczee (seria I)

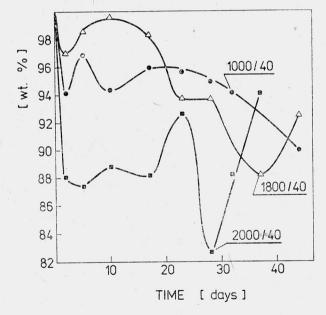


Fig. 2. Amount of the extracted product obtained from the solutions of surfactants of tetronic type versus biodegradation time for copolymers with varying average molecular weight (series II)

Rys. 2. Zależność ilości produktu wydzielonego podczas ekstrakcji z roztworów surfaktantów typu tetroników poddanych biodegradacji od czasu procesu. Kopolimery o zmiennej średniej masie cząsteczkowej (seria II)

2000/40 > 1000/40 > 1800/40). This loss does not simply depend either on the content of neutral fraction in the starting polyether nor on the nitrogen content in the molecule, though in both series of copolymers the highest mass loss at the first stage is observed for substances with the highest contents of this fraction (1000/70 - 24.4%) and 2000/40 - 29.7%). It should be noticed that at high concentration of surfactant subject to biodegradation and with the method applied, the influence of surface adsorption on the mass loss value may be neglected [1].

The changes in the copolymer spectrum occurring with biodegradation are particularly distinct for the bands characteristic of carbonyl groups, i.e. for the bands within 1710–1790 cm⁻¹ with the maximum at 1730 cm⁻¹ (ester and carboxyl groups, aldehydes, and ketons) and for that with the maximum at 1675 cm⁻¹ (amide groups [12]). These cases are exemplified in fig. 3. Some amounts of carbonyl groups present in non-biodegraded copolymer result from oxidation during the catalyst removal as well as during extraction process.

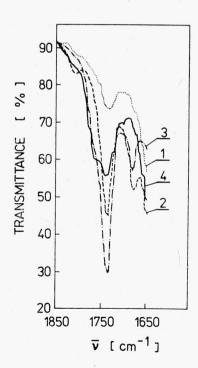
Changes in the absorption of the band with the maximum at about 1730 cm⁻¹ (figs. 4 and 5), as the most characteristic ones, have been determined from its area by the weight method. These changes have also a cyclic character; at the initial biodegradation stage the increase in concentration of carbonyl groups is, in general, closely related to the decreasing loss in copolymer mass. A distinct dependence of the concentration of carbonyl

Fig. 3. Fragment of IR spectrum of biodegraded tetronic type (1800/40 surfactant)

Biodegradation time amounting to 0, 2, 32, and 44 days is shown in curves 1, 2, 3, and 4, respectively

Rys. 3. Fragment widma IR produktu biodegradacji surfaktantu 1800/40 typu tetroniku

Czas biodegradacji: 0 dni (1), 2 dni (2), 32 dni (3) i 44 dni (4)



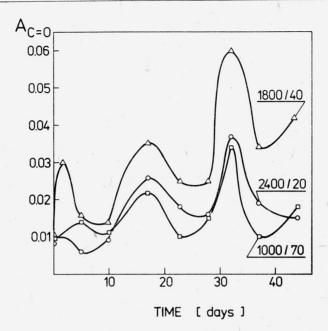


Fig. 4. Band absorbance with the maximum at the wave number 1730 cm⁻¹ versus biodegradation time of surfactants of the tetronic type (series I) (absorbance calculated from the band area)

Rys. 4. Zależność absorbancji pasma z maksimum przy liczbie falowej 1730 cm⁻¹ (dla surfaktantów typu tetroników serii I poddanych biodegradacji) od czasu procesu (absorbancja obliczona z powierzchni pasma)

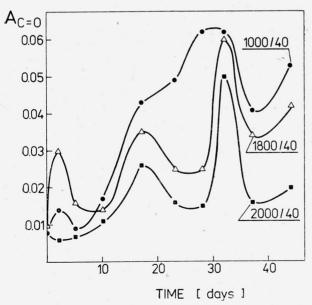


Fig. 5. Band absorbance with the maximum at the wave number 1730 cm⁻¹ versus biodegradation time of surfactants of tetronic type (series II) (absorbance calculated from the band area)

Rys. 5. Zależność absorbancji pasma z maksimum przy liczbie falowej 1730 cm⁻¹ (dla surfaktantów typu tetroników serii II poddanych biodegradacji) od czasu procesu (absorbancja obliczona z powierzchni pasma)

groups on the \overline{M} value of preparation subject to biodegradation, thereby on the content of neutral fraction, has been observed after a longer time of biodegradation in the series II in which the ethylene oxide content in a molecule was similar. The highest changes in the \overline{M}_n value appear mainly in the initial period (fig. 6); the position of the minimum fairly well coincides with the first maximum of the loss of extracted preparation and corresponds to a small content of carbonyl groups. The decrease of \overline{M}_n is the greatest in preparations with the greatest content of neutral fraction (1000/70 and 2000/40). After a longer time of biodegradation a small increase of \overline{M}_n is generally observed.

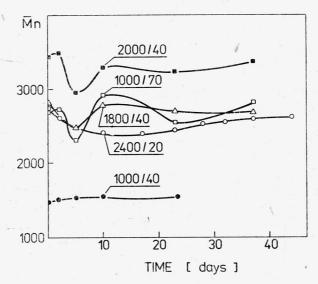


Fig. 6. Average molecular weight of the biodegradation products of tetronic type surfactants versus biodegradation time

Rys. 6. Zależność średniej masy cząsteczkowej produktów biodegradacji surfaktantów typu tetroników od czasu procesu

From the comparison of changes in the loss of copolymer mass in the initial period of its biodegradation (2–5 days) with the decrease of the \overline{M}_n value occurring in this period, it follows that the degradation of polyether molecule results not only in the stripping of its end fragment. On the other hand, the fact that the \overline{M}_n value does not decrease during the first two days of biodegradation, observed in preparations 2000/40 and 1000/70 characterized by the highest contents of polyoxyalkylene glycols which are the components of the neutral fraction, may suggest that bacteria utilize first of all polyglycols showing value of \overline{M}_n lower as compared to that of the main copolymer. This suggestion is consistent with the literature data concerning the effect of the \overline{M}_n value of polyglycols on the rate

of their biodegradation, which have been mentioned in the introduction. Thus, the observed dependences may be due to superposition of two opposite processes: degradation (decreasing \overline{M}_n) and utilization of low-molecular products by bacteria (increasing \overline{M}_n). The fact that after 2–5 days the amounts of extracted polyether increase seems to indicate that the bacterial growth is inhibited and that some bacteria are destroyed releasing the molecules of polyether which were accumulated in their cells. The readaptation of bacteria may occur in further stages of biodegradation.

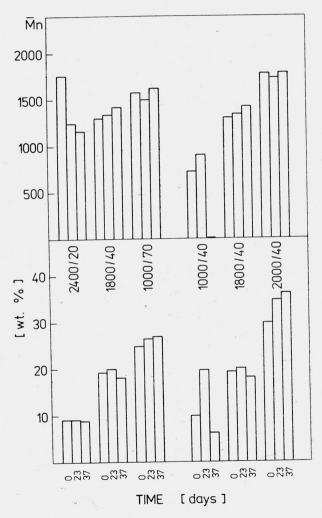


Fig. 7. Changes in content of neutral fraction and its mean molecular weight in tetronic type surfactants subject to biodegradation

Rys. 7. Zmiany zawartości i średniej masy cząsteczkowej frakcji obojętnej w biodegradowanych surfaktantach typu tetroników

In most substances only slight changes in contents of neutral fraction are observed (fig. 7). The same refers to the \overline{M}_n of this fraction, except for the preparation 2400/20, where substantial decrease of \overline{M}_n results from small percent of neutral fraction in the product and relatively high value of \overline{M}_n .

It should be emphasized that, theoretically, biodegradation process with the period examined could be exclusively based on the neutral fraction, since — as a rule — the loss of the preparation mass is lower than the content of this fraction. Considering the fact

Changes in the contents of amine groups in tetronic-type surfactants subject to biodegradation

Zmiany zawartości grup aminowych w surfaktantach typu teroników poddanych biodegradacji

Preparation	D' 1 1 1	Contents of amine groups [mVal/g]				
	Biodegradation time	Raw	Adduct free			
	[days]	Sum of amines	Tertiary amines	from neutral		
	0	0.57	0.60	0.64		
	17	0.62	0.61	_		
2400/20	23	0.58	0.60	0.65		
	32	0.59	0.59	_		
	37	0.56	0.60	0.67		
	0	0.46	0.44	0.58		
	17	0.46	0.43	_		
1800/40	23	0.43	0.43	0.59		
	32	0.39	0.39	_		
	37	0.46	0.45	0.56		
	0	0.30	0.27	0.42		
	17	0.30	0.40	_		
1000/70	23	0.32	0.32	0.46		
	32	0.31	0.30			
	37	0.32	0.30	0.44		
	0	1.11	1.11	1.18		
	17	1.13	1.47	_		
1000/40	23	0.92	0.55	1.18		
	32	0.90	0.97			
	37	1.03	1.04	1.22		
	0	0.24	0.24	0.32		
	17	0.24	0.23			
2000/40	23	0.24	0.22	0.32		
	32	0.21	0.21			
	37	0.22	0.21	0.34		

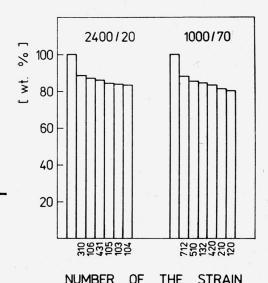


Fig. 8. Amount of products obtained by extraction from solutions of tetronic type surfactants subject to 5 day biodegradation, depending on the bacterial strains employed

The amount of polyether extracted from solution not subject to biodegradation is 100%

Rys. 8. Zależność ilości produktów wydzielonych podczas ekstrakcji z roztworów surfaktantów typu tetroników poddanych 5-dniowej biodegradacji od użytego szczepu bakterii

Ilość polieteru wydzielonego z roztworu nie poddanego degradacji wynosi 100%

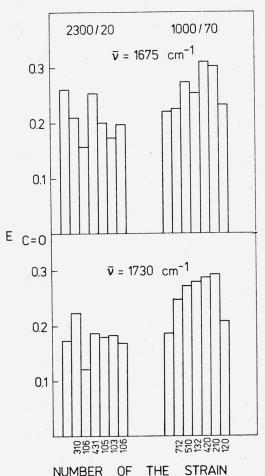


Fig. 9. Absorbance of bands with the maxima at 1675 cm⁻¹ and 1730 cm⁻¹ (calculated from the height of bands) for tetronic type surfactants subject to 5 day biodegradation, depending on the bacterial strain used

First column corresponds to the preparation not subject to biodegradation

Rys. 9. Zależność wartości absorbancji pasm z maksimum przy 1675 cm⁻¹ i 1730 cm⁻¹ (obliczone z wysokości pasma) dla surfaktantów typu tetroników poddanych 5-dniowej biodegradacji od użytego szczepu bakterii

Pierwszy słupek odpowiada preparatowi nie poddanemu biodegradacji

that the changes in the amount of neutral fraction are slight and that the content of amine groups in the adduct does not increase distinctly (tab. 2), this loss — reaching several percent — may, however, show that the bacterial activity would lead to the disintegration of copolymer molecules and, consequently, to the consumption of the polyglycol fragment and that containing amine nitrogen occurring in further biodegradation process.

Results presented in tab. 2 show that the type of amine group does not change essentially, thus that the processes occurring in a macromolecule do not cause any changes in the character of this group, except for the preparation 1000/40 in which distinct differences in the content of tertiary amine have been observed after 17 and 23 days of degradation. The above differences do not seem to be the result of analytical error, since substantial differences in the percent of neutral fraction have been observed for this substance after 23 days of degradation.

In view of the fact that in presence of mixed bacterial populations biodegradation degree of surfactants is rather low, some additional tests of biodegradation have been performed on the preparations 2400/20 and 1000/70 using different bacterial strains. Biodegradation time amounting to 5 days corresponded to the first maximum of mass loss in the series discussed previously. In this case, the loss was also small (see fig. 8), hence it follows that the compounds of tetronic type are resistant to the destructive activity of bacteria.

The two copolymers contained a certain number of carbonyl groups formed during processing. The absorbance values presented in fig. 9 for the bands with the maxima at 1730 cm⁻¹ and 1675 cm⁻¹ (the sequence of strains applied like in fig. 8) show that the biodegradation degree determined via extraction is not directly proportional to the change in the concentration of the groups being determined. This fact may be due to different predisposition of bacteria to utilize the oxidized fragments of macromolecule.

From the comparison of results obtained for copolymers of tetronic type with those for the pluronic type [1, 6], it follows that in both cases the mass loss and concentration of carbonyl groups as functions of biodegradation time take significantly different courses. No cyclic changes in these characteristic parameters have been observed for surfactants of pluronic type and the concentration of carbonyl groups showed a decreasing tendency. The above facts seem to be caused by different structures of both the types of copolymers, connected with the kind of polymerization initiator, thus by different compositions of by-products. In case of tetronic type the differences between the structure of the copolymer itself and side-products are much higher and may result from the fact that in the adaptation process the mixed bacterial population would be adapted first of all to polyoxyalkylene glycols. The latter — because of a considerably smaller average molecular weight — are a more available source of carbon and energy.

4. CONCLUSIONS

1. Biodegradation process of technical surfactants of tetronic type, conducted by mixed bacterial population under stationary conditions and assessed on the basis of co-

polymer mass loss and from the changes of some of its characteristic properties, exhibits a high complexicity. For this reason it is difficult to draw explicite conclusions concerning the influence of the copolymer structur (i.e. content of ethylene oxide in a molecule and average molecular weight) on its biodegradability.

2. The course of biodegradation under stationary conditions may be best evaluated during first 2–5 days. Some secondary processes that occur at a longer biodegradation time may be related to the readaptation of bacteria to varying conditions of the environment.

3. As far as further investigations under stationary conditions are concerned, it would be advantageous to use individual bacterial strains allowing better biodegradation of the surfactant examined as well as to employ the preparations free of side-products.

REFERENCES

- [1] Karpińska-Smulikowska J., Badania nad biochemicznym rozkładem i toksycznością związków powierzchniowo czynnych z grupy pluroników, Wrocław Technical University, 1975.
- [2] KARPIŃSKA-SMULIKOWSKA J., PAWLACZYK-SZPILOWA M., PLUCIŃSKI J., Untersuchungen zur biologischen Abbaubarkeit nichtionischer grenzflächenaktiver Verbindungen vom Typ Pluronics mit Belebtschlamm-Verfahren, Proceedings of the VII International Congress on Surface Active Substances, Moscow, Vol. 4 (1977) pp. 238–247.
- [3] Kontrola analityczna w przemyśle chemicznym, Vol. 5, p. 246, *Analiza produktów organicznych*, PWT, Warszawa 1957.
- [4] LAMB C. B., JENKINS G. F., BOD of synthetic organic chemicals, Purdue Conf., Vol. 7 (1952), pp. 326–339.
- [5] Methods in Microbiology, Vol. 3A (1970), pp. 96-97, ed. J. J. Norris, D. W. Ribbons, New York.
- [6] PAWLACZYK-SZPILOWA M., PLUCIŃSKI J., KARPIŃSKA-SMULIKOWSKA J., STAROOJCIEC O., JANIK R., Studies on biodegradation of nonionic surface active compounds of pluronic type under stationary conditions, Wissenschaftliche Zeitschr. Techn. Univ. Dresden, Vol. 26 (1977), pp. 1178–1184.
- [7] PITTER P., Über die biologische Abbaufähigkeit der Polyäthylenoxide, Collection Czech. Chem. Commun., Vol. 38 (1973), pp. 2665–2669.
- [8] PITTER P., RICHTROVÁ L., Vztah mezi strukturou a biologickomu rozložitelnosti organických látek. IV. Biologicka rozložitelnost aromatických aminolátek, Sbornik Vys. Šk. Chem. Technol. Praze, Vol. F 19 (1974), pp. 59–75.
- [9] PLUCIŃSKI J., JANIK R., STAROOJCIEC O., Oxydation der nichtionogenen Tenside vom Pluronic- und Tetronic-Typ, Tenside Detergents, Vol. 17 (1980), pp. 186–190.
- [10] PLUCIŃSKI J., LEFLER A., PRYSTASZ H., Über die Reaktion von Propylenoxid mit Äthylendiamin, Proceedings of the VII International Congress on Surface Active Substances, Moscow, Vol. 1 (1977), pp. 299–312.
- [11] SCHMOLKA I. R., *Polyalkylene oxide block copolymers*, [in:] *Nonionic surfactants*, ed. M. J. Schick, M. Dekker Inc., New York 1967, pp. 300–394.
- [12] Sebastian M., Pluciński J., Amide group formation during oxidation of polyoxyalkylene derivatives of ethylenediamine, Polymer, Vol. 22 (1981), pp. 956–959.
- [13] SIGGIA S., Quantitative Organic Analysis via Functional Groups, ed. J. Wiley, New York-London-Sydney 1966, p. 432.
- [14] ŠIŠKINA V. N., TROČENKO J. A., Svojstva novogo štamma Hyphomicrobium ispolzujuščego odnouglerodnyje sojedinienija, Mikrobiologija, Vol. 43 (1974), pp. 765–770.

- [15] SWISHER R. D., Surfactant biodegradation, M. Dekker Inc., New York 1970.
- [16] Watson G. K., Jones N., The biodegradation of polyethylene glycols by sewage bacteria, Water Res., Vol. 11 (1977), pp. 95–100.

DEGRADACJA BIOLOGICZNA NIEJONOWYCH SURFAKTANTÓW TYPU TETRONIKÓW W WARUNKACH STACJONARNYCH

CZĘŚĆ I. WPŁYW BUDOWY SURFAKTANTU NA PRZEBIEG DEGRADACJI

Badano wpływ udziału tlenku etylenu w makrocząsteczce i średniej masy cząsteczkowej \overline{M}_n kopolimerów blokowych typu tetroników na ich podatność na biodegradację w warunkach stacjonarnych w obecności mieszanych populacji bakterii. Stężenie kopolimeru wynosiło 1%. Stanowił on jedyne źródło węgla i energii dla bakterii. Przebieg degradacji oceniano na podstawie ubytku masy kopolimeru, zmiany jego \overline{M}_n , zawartości grup karbonylowych oraz zawartości frakcji obojętnej i grup aminowych. Stwierdzono, że w preparatach technicznych, zawierających glikole polioksyalkilenowe jako produkty uboczne, obecność tych ostatnich wpływa w istotny sposób na proces biodegradacji, utrudniając ocenę wpływu poszczególnych elementów budowy właściwego kopolimeru.

BIOLOGISCHER ABBAU NICHTIONOGENER TENSIDE VON TETRONIC-TYP UNTER STATIONÄREN VERSUCHSBEDINGUNGEN

I. DER EINFLUß DER STRUKTUR DES TENSIDS AUF DEN ABBAUVERLAUF

Untersucht wurde der Anteil des Äthylenoxyds im Makromolekül und der Einfluß des Mittelwertes der Partikelmasse \overline{M}_n von blockartigen Tetronik-Kopolimeren auf die Abbaubarkaeit unter stationären Verhältnissen durch bakterielle Mischpopulationen. Die Konzentration des Kopolimers war 1%. Es war für die Mikroorganismen die einzige Energie- und Kohlenstoffquelle. Der Abbauverlauf wurde anhand der Abnahme der Kopolimerkonzentration, der Abänderung deren \overline{M}_n , des Anteils an Karbonylgruppen, der neutralen Fraktionen und der Amingruppen abgeschätzt. Man stellte fest, daß bei der Anwendung von technischen Produkten (welche polyoxyalkilene Glikole als Nebenprodukte enthalten) deren Anwesenheit hemmt den biologischen Abbau wesentlich und erschwert die Abschätzung des Einflußes der einzelnen Bausteine des Kopolimers auf den Prozeßverlauf.

БИОЛОГИЧЕСКАЯ ДЕГРАДАЦИЯ НЕИОННЫХ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ ТИПА ТЕТРОНИКОВ В СТАЦИОНАРНЫХ УСЛОВИЯХ

ЧАСТЬ І. ВЛИЯНИЕ СТРОЕНИЯ ПАВ НА ХОД ДЕГРАДАЦИИ

Исследовалось влияние участия окиси этилена в макромолекуле и молекулярной массы \overline{M}_n блок-сополимеров типа тетроников на их податливость на биодеградацию в стационарных условиях в присутствии смешанных совокупностей бактерий. Концентрация сополимера составляла 1%. Он представлял собой только источник углерода и энергии для бактерий. Ход деградации оценивался на основе убыли массы сополимера, изменения его \overline{M}_n , содержания каробнильных групп, а также содержания нейтральной фракции и аминогрупп. Выявлено, что в случае технических препаратов, содержащих полиоксиалкиленовые гликоли как побочные продукты, присутствие последних влияет существенным образом на процесс биодеградации, затрудняя оценку влияния отдельных элементов строения соответствующего сополимера.