

Study of nonionic detergents. I. Preparation and characterization of surface-active substances of the poly(oxyethylene alkylphenol) type

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By reaction of ethylene oxide with *p*-octylphenol or *p*-nonylphenol twenty-two nonionic surface-active compounds of the poly(oxyethylene alkylphenol) type, containing different number of oxyethylene units in their molecule, were prepared.

The considerable surface activity of some poly(oxyethylene alkylphenols) stimulated an extensive investigation of the detergents of this type.

The advantage of the detergents belonging to the above group of compounds is their nonionic character and accompanying properties, such as the stability in acid and alkaline media and the increased efficiency in comparison with the ionic surface-active compounds. This means, from the pharmaceutical point of view, a marked increase of the safety during parenteral and peroral application of preparations and the decrease of irritability at their local application.

The preparation of poly(ethylene oxide) adducts of phenol and alkylphenols was the subject of numerous studies and patents and was reviewed in several monographs [1–4].

Technology of the production of poly(oxyethylene alkylphenols) is generally based on the reactions of phenols with ethylene oxide; the reaction product is usually a mixture of compounds containing different number of oxyethylene units in their molecules. The products of side reactions are poly(oxyethylenes).

The aim of this work was to prepare surface-active compounds derived from *p*-octyl- and *p*-nonylphenol with a variable length of the polyoxyethylene chain.

Experimental

p-Octylphenol, *p*-nonylphenol, ethylene oxide, and potassium hydroxide were standard commercial chemicals.

Preparation of poly(oxyethylene alkylphenols)

The addition of ethylene oxide to *p*-octyl- and/or *p*-nonylphenol (10 moles) was carried out in a 5-l laboratory stainless steel double jacket autoclave equipped with a stirrer and a thermometer. Solid potassium hydroxide (0.7% w/w) was added as a catalyst. After closing the autoclave the air was replaced by nitrogen and the mixture was heated up to 136–142°C. Ethylene oxide in the mixture with nitrogen was then introduced under stirring until the pressure in the autoclave reached 3.5 pk cm⁻². The theoretical amount of ethylene oxide necessary for the formation of the required product was divided

into the three parts (1/4, 1/2, 1/4) and each part was introduced when the pressure in the autoclave dropped from 3.5 to 1.4 kPa. The amount of the ethylene oxide consumed in the reaction was represented by the weight increase of the reaction mixture. Before opening the autoclave the reaction mixture was bubbled through nitrogen in order to remove unchanged ethylene oxide.

Using the described procedure we prepared the poly(ethylene oxide) adducts of *p*-octylphenol containing an average number of 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, and 40 ethylene oxide units and adducts of *p*-nonylphenol with an average number of 2, 3, 4, 6, 8, 10, 15, 25, 30, 35, and 45 ethylene oxide units.

The lower adducts were viscous, sirupy liquids of light yellow colour. The products with an average number of 20–30 ethylene oxide units had the consistence of a paste and the products containing over 30 ethylene oxide units were waxy substances. The water solubility of the product increased with the increasing number of ethylene oxide units. The adducts with less than 5 ethylene oxide units were practically water insoluble.

The rough characterization of the prepared poly(oxyethylene alkylphenols) was done by determining the hydroxyl number, the amount of free poly(oxyethylenes) and by estimation of the average number of ethylene oxide units in their molecule. The hydroxyl number was determined using the method of *Ogg et al.* [5]. The amount of the free poly(oxyethylenes) was determined by the method of *Weibull* [6]. The characterization of the prepared adducts is in Tables 1 and 2.

Discussion

Conditions used for the preparation of poly(oxyethylene alkylphenols) were largely based on the methods employed in the industrial production of these compounds as well as on the knowledge of the reaction mechanism [7–9]. The best results were achieved when working at temperatures around 140°C and pressures of 3–5 kPa.

The course of polyaddition reactions of ethylene oxide with phenols, first of all their velocity and the lengthening of the poly(ethylene oxide) chain, depends largely on the character and on the concentration of the catalyst used. In the acid catalysts there occurs a secondary decomposition of the formed poly(oxyethylene alkylphenols) into the products of lower molecular weight [10, 11]. The base catalysts proved themselves to be the best, especially the hydroxides of alkali metals used in concentrations around 1% in the reaction mixture. The kinetics of the base-catalyzed addition was studied by *Patat* and co-workers [12–16], *Bobleter* [17], and *Ishii et al.* [18]. These authors independently found that the rate of the addition of the first ethylene oxide molecule to phenol (phenolate anion) was dependent on the catalyst concentration. The phenol functions as proton donor in the reaction. *Ishii* [18] postulated that, in the polar solvents facilitating the ionic dissociation and at temperatures above 120°C, the reaction may be of simple nucleophilic character.

Addition reactions of ethylene oxide with compounds containing active hydrogen proceed in dependence on the relative acidity of the starting compound and that of the products. During the reaction with ethylene oxide the phenol is more acidic than the arising product and the equilibrium constant for this reaction of proton exchange is considerably high. Consequently, polyaddition reactions start to proceed only after transforming all of the phenol taken into the reaction to a monoadduct. In this stage of reaction the product has a character of chemical individuality — monoglycol ether of the corresponding phenol. In the second phase of reaction in the absence of free phenols the products having different lengths of the poly(oxyethylene) chain arise. The further addition of ethylene oxide occurs randomly, since there are no differences in the acidity

Table 1

Characterization of the prepared poly(oxyethylene *p*-octylphenols) of general formula $C_8H_{17}-C_6H_4-O-(CH_2CH_2O)_n-H$

No.	Formula	<i>M</i>	Consistency	Hydroxyl number calculated/found	Number of ethylene oxide units added		Free poly(oxyethylenes) [%]
					calculated from hydroxyl number	calculated from weight increase	
1	$C_{18}H_{30}O_3$	294.44	sirup	190.5 185.4	2.05	2.00	0.3
4	$C_{22}H_{38}O_5$	382.54	sirup	146.6 157.8	3.72	4.01	1.6
6	$C_{26}H_{46}O_7$	470.65	sirup	119.1 130.5	5.47	5.87	
4	8 $C_{30}H_{54}O_9$	558.76	sirup	100.4 121.2	6.63	8.17	3.4
	10 $C_{34}H_{62}O_{11}$	646.87	sirup	86.7 97.7	8.87	10.10	5.3
6	15 $C_{44}H_{82}O_{16}$	867.13	sirup	64.7 84.7	11.21	15.03	7.0
7	20 $C_{54}H_{102}O_{21}$	1087.40	paste	51.6 70.2	14.69	20.77	8.9
8	25 $C_{64}H_{122}O_{25}$	1307.74	paste	42.9 62.0	17.29	24.69	9.6
9	30 $C_{74}H_{142}O_{31}$	1527.94	wax	36.7 58.6	18.80	30.40	11.6
10	35 $C_{84}H_{162}O_{35}$	1748.11	wax	32.1 53.1	21.15	36.20	13.8
11	40 $C_{94}H_{182}O_{41}$	1968.47	wax	28.5 50.7	22.47	39.40	14.9

Table 2

Characterization of the prepared poly(oxyethylene *p*-nonylphenols) of general formula $C_9H_{19} - C_6H_4 - O - (CH_2CH_2O)_n - H$

No.	Formula	<i>M</i>	Consistency	Hydroxyl number calculated/found	Number of ethylene oxide units added		Free poly(oxyethylenes) [%]	
					calculated from hydroxyl number	calculated from weight increase		
1	2	C ₁₄ H ₃₂ O ₃	308.51	sirup	181.8 194.4	1.87	2.02	0.4
2	3	C ₂₁ H ₃₀ O ₄	352.52	sirup	159.1 163.8	2.91	3.09	0.8
3	4	C ₂₃ H ₄₀ O ₅	390.57	sirup	141.4 132.0	4.29	3.96	1.5
4	6	C ₂₇ H ₄₈ O ₇	484.68	sirup	115.7 122.7	5.66	6.01	2.5
5	8	C ₃₁ H ₅₆ O ₉	572.79	sirup	97.9 106.1	7.38	7.92	3.6
6	10	C ₃₅ H ₆₄ O ₁₁	660.89	sirup	84.8 111.5	7.90	9.71	5.3
7	15	C ₄₅ H ₈₄ O ₁₆	881.16	sirup	63.6 88.0	10.80	14.60	7.3
8	25	C ₆₅ H ₁₃₄ O ₂₆	1321.70	paste	42.4 65.3	16.24	24.84	9.8
9	30	C ₇₅ H ₁₄₄ O ₃₁	1541.96	wax	36.3 57.9	18.84	29.34	13.1
10	35	C ₈₅ H ₁₆₄ O ₃₆	1763.23	wax	31.8 52.9	21.05	33.29	14.3
11	45	C ₁₀₅ H ₂₀₄ O ₄₆	2202.77	wax	25.4 44.1	25.79	42.46	16.8

of hydroxyl end groups of the poly(oxyethylene) chain of different length. At the same time, in dependence on the reaction conditions, poly(oxyethylenes) of different molecular weights are formed. The resulting product is a mixture of poly(ethylene oxide) adducts of phenol and poly(oxyethylenes) both containing poly(oxyethylene) chains of different length. The composition of the final reaction products can be thus expressed only by an average summary chemical formula and by an average molecular weight. The content of the free poly(oxyethylenes) in the reaction product is one of the factors unfavourably influencing the quality and the properties of the projected poly(ethylene oxide) adducts of phenol [19, 20].

The characterization of poly(ethylene oxide) adducts of phenol having the character of polydisperse mixtures cannot be accomplished by using the standard methods generally used for the characterization and evaluation of surface-active compounds. Therefore it was of interest to find a rapid, economically convenient method for the evaluation of poly(oxyethylene alkylphenols). From aspects of the above criteria, the determination of the hydroxyl number proved to be the most suitable.

The difference between the calculated and found hydroxyl numbers indicates the approximate degree of the product contamination by lower molecular weight poly(oxyethylene). Besides, the hydroxyl number enables to calculate the length of poly(oxyethylene) chains expressed as the number of ethylene oxide units per one mole of phenol. The calculated value can be then compared with the result based on the weight increase of the product and with the number of units of the ideal product.

The characterization of the prepared poly(oxyethylene) *p*-octyl- and *p*-nonylphenols is given in Tables 1 and 2. The qualitatively satisfying products were only those containing in average less than 10 oxyethylene units. The experimentally found values of the hydroxyl numbers and the numbers of ethylene oxide units added are in a fairly good agreement with the theory. The differences become more apparent in the products containing more than 10 ethylene oxide units and increase with the increasing molecular weight of the product. For example, in the compound $C_9H_{19}-C_6H_4-O-(CH_2CH_2O)_{45}-H$ the weight increase during the reaction indicated the addition of 42.46 ethylene oxide units and the value of hydroxyl number was 44.1 mg KOH in contrast to the theoretical value of hydroxyl number 25.4 mg KOH. The value of hydroxyl number found indicates the presence of 26 ethylene oxide units. This fact may lead to a conclusion that the conversion of the starting compounds to desired poly(oxyethylene alkylphenol) did not proceed quantitatively. This possibility can be, however, ruled out since the course of the addition of ethylene oxide was checked by measuring the weight increase of the reaction mixture. The found higher values of the hydroxyl number, when compared with the theoretical value based on the average summary composition, lead inevitably to the conclusion that the final reaction product contains high content of free poly(oxyethylene) thus making the precise determination of the composition of the reaction product impossible. The knowledge of the hydroxyl number can be sufficient parameter for the characterization of the product only in the case of poly(oxyethylene alkylphenols) containing less than 10 ethylene oxide units in their molecule.

The high percentage of free poly(oxyethylene) in the products of higher average molecular weight was confirmed also by using the specific method of Weibull [6] based on the distribution of poly(oxyethylene alkylphenols) and poly(oxyethylene) between 30% solution of NaCl in water and ethyl acetate. The separation of these two constituents by usual purification techniques is, due to their physical and chemical similarities, accompanied with considerable difficulties. The separation is, in some cases, also complicated by the formation of emulsion systems by surface-active glycols.

References

1. Schick, M. J., *Nonionic Surfactants*. Marcel Dekker Inc., New York, 1967.
2. Stüpel, H., *Syntetische Wasch- und Reinigungsmittel*. Konradin Verlag, Stuttgart, 1957.
3. Schönfeldt, N., *Oberflächenaktive Anlagerungsprodukte des Äthylenoxids*. Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1959.
4. Fajngold, S. I., *Sinteticheskie sredstva iz neftyanovo i slancevovo syrja*, p. 200. Nedra, Leningrad, 1964.
5. Ogg, C. L., Porter, W. L., and Willitts, C. O., *Ind. Eng. Chem.* **17**, 394 (1945).
6. Weibull, B., *Dokument CIA 3/69 E* (Comité international des dérivés tensio-actifs. Lisabon, 1968).
7. Flory, P., *J. Amer. Chem. Soc.* **62**, 1561 (1940).
8. Kuriyama, K., *Kolloid. Z.* **180**, 55 (1960).
9. Nakagawa, T., Kuriyama, K., and Inove, H., *J. Colloid. Sci.* **15**, 268 (1960).
10. Drew, H. F. and Schaeffer, J. R., *Ind. Eng. Chem.* **50**, 1253 (1958).
11. Nagase, K. and Sakaguchi, K., *Kogyo Kagaku Zasshi* **64**, 1199 (1961).
12. Patat, F., Cremer, E., and Bobleter, O., *J. Polym. Sci.* **12**, 489 (1954).
13. Patat, F. and Wojtech, B., *Makromol. Chem.* **37**, 1 (1960).
14. Wojtech, B. and Patat, F., *Z. Phys. Chem.* **25**, 39 (1960).
15. Patat, F., *Pure Appl. Chem.* **4**, 333 (1962).
16. Patat, F., *Inter. Symp. Macromol. Chem.*, p. 333. Montreal, 1961.
17. Bobleter, O., *Monatsh. Chem.* **87**, 483 (1956).
18. Ishii, Y., Nishikawa, Y., and Kato, H., *Kogyo Kagaku Zasshi* **63**, 2177 (1960); *Chem. Abstr.* **57**, 8523 (1962).
19. Gaylord, N. G., *Polyethers, Part I*, 112 (1963).
20. Staudinger, H., *Die hochmolekularen organischen Verbindungen*. Springer-Verlag, Berlin, 1932 (1960).

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