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Influence of the Molecular Weight of Nonionic Detergents on Their Removal from Aqueous Solutions by Foaming

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Abstract

Ethoxylated nonylphenol (Rokaphenol NX-8) with a mean content of 9 oxyethylene groups was subjected to fractionation by adsorption column chromatography. The fractions obtained with a different mean polyether chain length as well as nonseparated Rokaphenol were removed from their aqueous solutions of various concentrations in a foaming column. A correlation was found between the effect of foaming and the oxyethylation degree; namely, the lower the content of oxyethylene groups in the compounds, the better the result of foaming. This is true, however, merely in the case of compounds which dissolve well in water. If the content of oxyethylene groups is so low that it diminishes the solubility of the detergent in water, foaming proceeds much more poorly.

INTRODUCTION

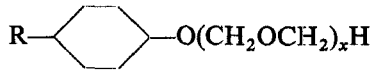
In our previous publications on the removal of nonionic detergents by foaming (*1*, *2*), no consideration was given to their molecular size. Because of the fact that adsorption at the phase boundary "aqueous solution of the surface-active agent/air" is connected with the HLB value (i.e., means with the molecular structure of the detergent), it was decided to investigate whether there is any dependence of the foaming effect on the polyether

chain length in the case of ethoxylated alkylphenols with the same alkyl radical.

EXPERIMENTAL

Preparation of Fractions with a Different Molecular Weight

A nonionic product named Rokaphenol NX-8 was used for the tests. It can be expressed as



where R is a nonyl radical and x is approximately 9.

The product was subjected to analysis by TLC under conditions which

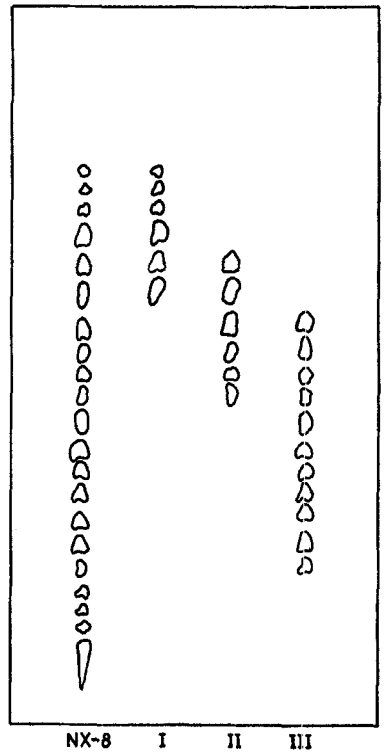


FIG. 1. Thin-layer chromatogram of Rokaphenol NX-8 and its three fractions as obtained by column separation.

TABLE 1

Properties of Rokaphenol NX-8 and of the Fractions Obtained by Its Separation

	Rokaphenol NX-8	Fractions		
		I	II	III
Content of free polyglycol (%)	3.38	—	—	—
Hydroxyl value	85.5	106.2	82.3	66.3
Content of oxyethylene groups (%)	62.0	55.5	62.4	73.2
Mean molecular weight	656	528	682	847
Mean number of oxyethylene groups	9.3	6.7	9.7	14.1

ensured the best possible separation of the components according to their oxyethylene groups content. As far as the methods which have been described are concerned (*3–7*), the best results were obtained when methyl ethyl ketone saturated with water (about 11.4% water) had been used for the development of the chromatograms (*8–12*).

The plates were developed twice and the chromatograms were visualized with the aid of a modified Dragendorff's reagent (*11–13*).

By applying the above described separation conditions, the Rokaphenol NX-8 was found to contain about 21 components differing from one another by their oxyethylene groups.

Preparative separation of Rokaphenol into components was carried out in a 60-g silica-gel (200 mesh) filled column. Approximately 2 g of the sample were separated during one operation. Methyl ethyl ketone saturated with water (about 1 liter for each separation) was used (*14–16*). The separation was controlled by TLC. The separations obtained were connected so as to receive three main fractions which differed distinctly from one another by their mean content of oxyethylene groups. Figure 1 shows a chromatogram of those three fractions. As may be seen, each fraction contains several consecutive homologs. The mean number of oxyethylene groups in the fractions was determined. In addition, the mean molecular weight and the content of free polyglycols in each fraction (*17*) were determined. Table 1 gives the results of the analyses.

Foaming of Rokaphenol and Its Fractions of Different Molecular Weights

The Rokaphenol aqueous solution as well as solutions of Fractions I, II, and III obtained by column separation of Rokaphenol were subjected to foaming.

TABLE 2

Results of Foaming Rokaphenol NX-8 Solutions and

Rokaphenol NX-8				Fraction I			
C_0 [(moles/liter) $\times 10^5$]	$\frac{C_0}{C_r}$	$\frac{C_0}{C_f}$	$\frac{V_f}{V_0} \times 100\%$	C_0 [(moles/liter) $\times 10^5$]	$\frac{C_0}{C_r}$	$\frac{C_0}{C_f}$	$\frac{V_f}{V_0} \times 100\%$
11.5	6.0	0.17	14.5	14.7	2.8	0.10	7.2
15.8	4.6	0.28	20.4	18.5	2.2	0.17	8.8
22.2	2.8	0.39	29.3	25.1	1.6	0.21	9.6
30.8	2.3	0.59	41.9	39.9	1.3	0.31	9.9
38.3	2.0	0.72	48.1	49.6	1.2	0.39	10.8

The same equipment as described in our previous paper was used for foaming (*1*). The following column working parameters were applied: height of the liquid phase $h_1 = 30$ cm, height of the column $h_c = 90$ cm, gas flow rate $V_g = 10$ liters/hr, and feeding solution flow rate $V_0 = 1.6$ liters/hr. Solutions with initial detergent concentrations ranging from 9.0 to 50.0 $\times$ 10^{-5} mole/liter were subjected to foaming.

The concentration of the detergent in the solution was determined by UV absorption spectrophotometry (*18*). Separate calibration curves were plotted for the dependence of the extinction on the concentration of each fraction. Measurements of the extinction were taken at a wavelength of 223 nm.

The concentration of the detergent in the raffinate and in the foam as well as the flow rates of the raffinate (V_r) and the foam (V_f) were measured for each of the foaming processes. The following factors were calculated on the basis of the determined magnitudes:

Decontamination factor: C_0/C_r

Water removed with the foam: (V_f/V_0) 100%

Foam enrichment factor: C_0/C_f

The results are given in Table 2 and presented graphically in Figs. 2 and 4.

From Fig. 2 it follows that the changes of the decontamination factor connected with the changes of the surfactant concentration are similar to those previously found for nonionic detergents (*1*); namely, the decontamination factor becomes lower with an increasing concentration of the detergent in the initial solution. This is true for all the fractions under

the Three Fractions Obtained by Its Separation

Fraction II				Fraction III			
C_0 [(moles/liter) $\times 10^5$]	$\frac{C_0}{C_r}$	$\frac{C_0}{C_f}$	$\frac{V_f}{V_0} \times 100\%$	C_0 [(moles/liter) $\times 10^5$]	$\frac{C_0}{C_r}$	$\frac{C_0}{C_f}$	$\frac{V_f}{V_0} \times 100\%$
11.0	5.8	0.16	13.8	9.1	3.8	0.23	19.3
13.4	4.7	0.24	18.5	11.9	3.3	0.29	23.6
22.1	2.8	0.41	28.5	17.5	2.8	0.41	32.1
31.0	2.2	0.61	43.1	23.8	2.4	0.56	43.2
38.1	2.0	0.75	51.8	29.8	2.1	0.67	48.7

investigation. At higher detergent concentrations, changes of the decontamination factor were negligible. At a concentration of about 30.0×10^{-5} mole/liter the decontamination factor attains a constant value for all fractions, amounting to approximately 2 (with the exception of Fraction I, Fig. 2).

The value of the decontamination factor is higher the higher the mean molecular weight of the substance subjected to foaming.

Only the results obtained for Fraction I foaming processes do not comply with the above conclusion. In that case the C_0/C_r values are much lower than in all the other fractions. This may be explained by a poorer solubility of Fraction I in water due to a lower oxyethylene group content. According to Wurtzschmitt (*20*) the cloud temperature of alkyl phenol adducts with an oxyethylene group content lower than seven lies below room temperature, and those with nine or more oxyethylene groups lie above it.

The results obtained for the Fraction I foaming processes may be influenced by an analytical error due to the partial dispersion of light during the spectrophotometrical determination of the detergent concentration in the solution.

The aqueous solutions which contained Fraction I were cloudy, especially at a high concentration of the detergent, i.e., mainly in solutions obtained from collapsed foam. The dependence of the foam enrichment factor (c_0/c_f) of the quantity of water removed with the foam [$(V_f/V_0)\ 100\%$] on the concentration of the initial solution is nearly a straight-line curve (Figs. 3 and 4). The lines for Fraction I are at a smaller angle than those for the other fractions. The relationship of the lines is in a sequence where the values of both factors [C_0/C_f and $(V_f/V_0)\ 100\%$] are higher the higher the mean molecular weight of the fraction subjected to foaming.

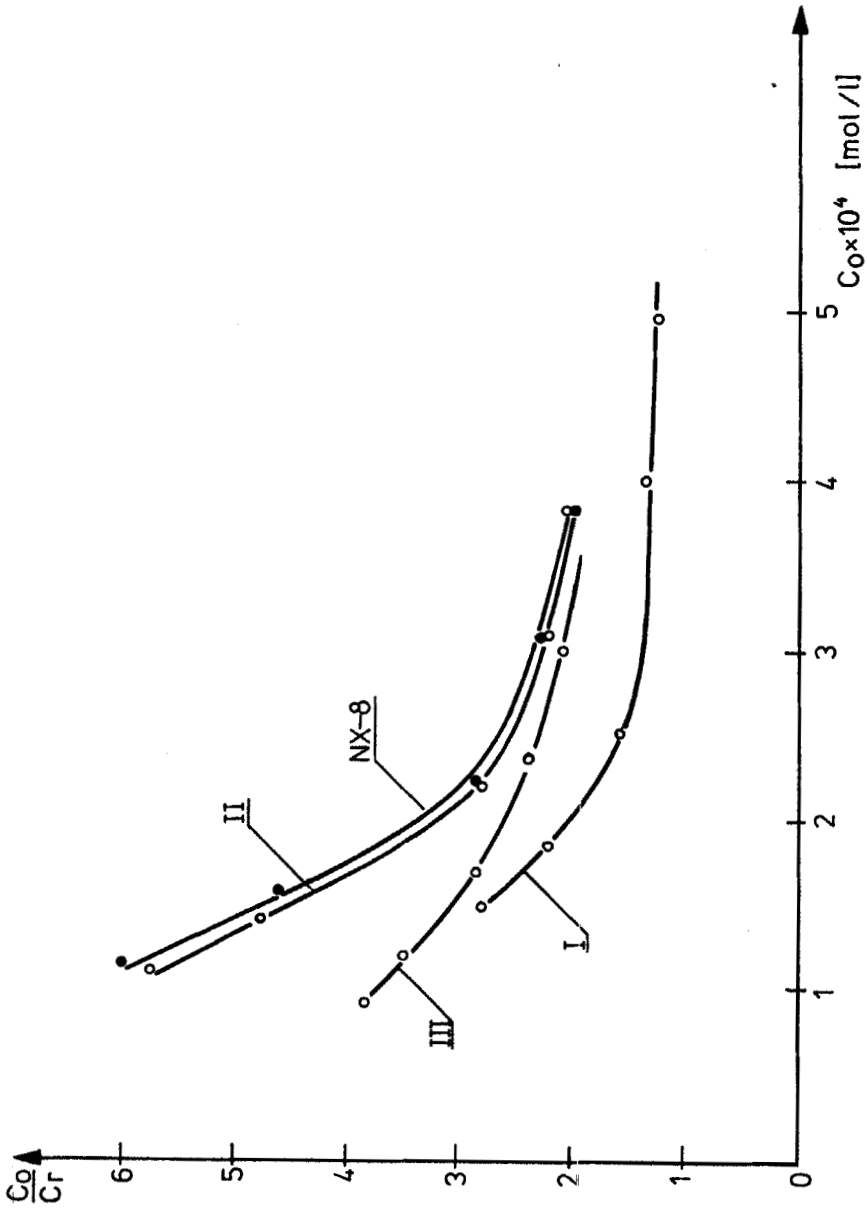


FIG. 2. Decontamination factor dependence on detergent concentration in solution with Rokaphenol NX-8 and its Fractions I, II, and III.

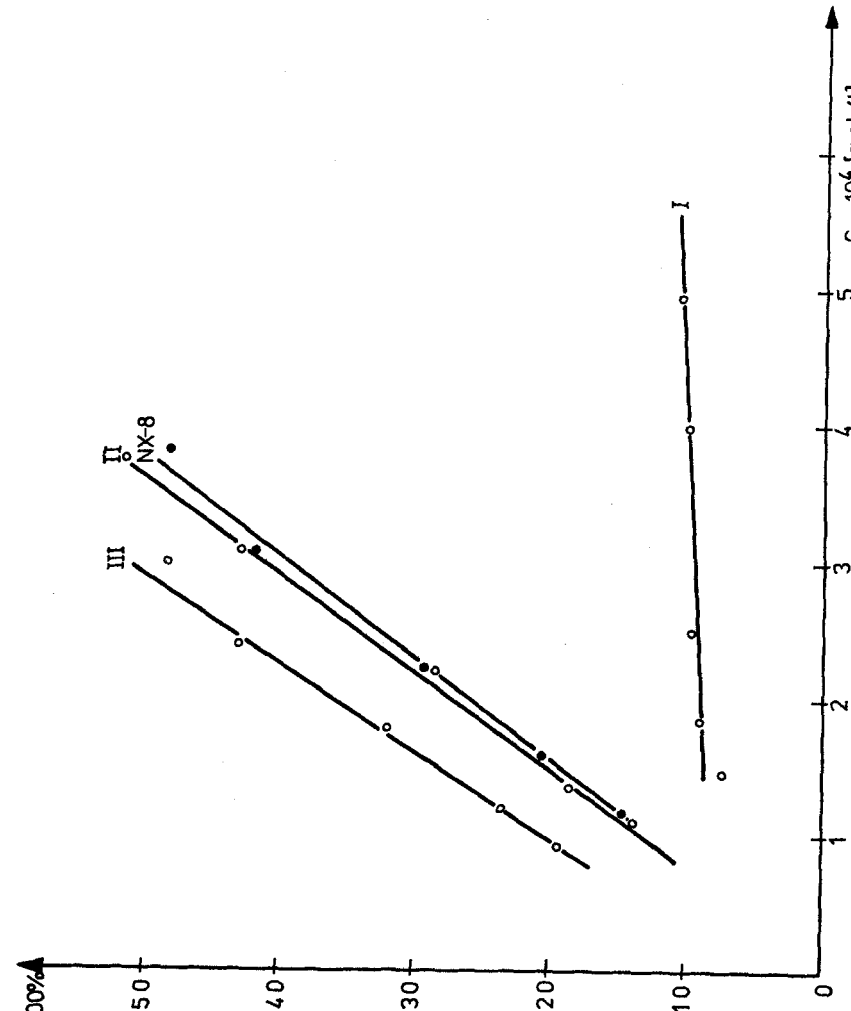


FIG. 3. The dependence of water removal with the foam on the detergent concentration in solution with Rokaphenol NX-8 and its Fractions I, II, and III.

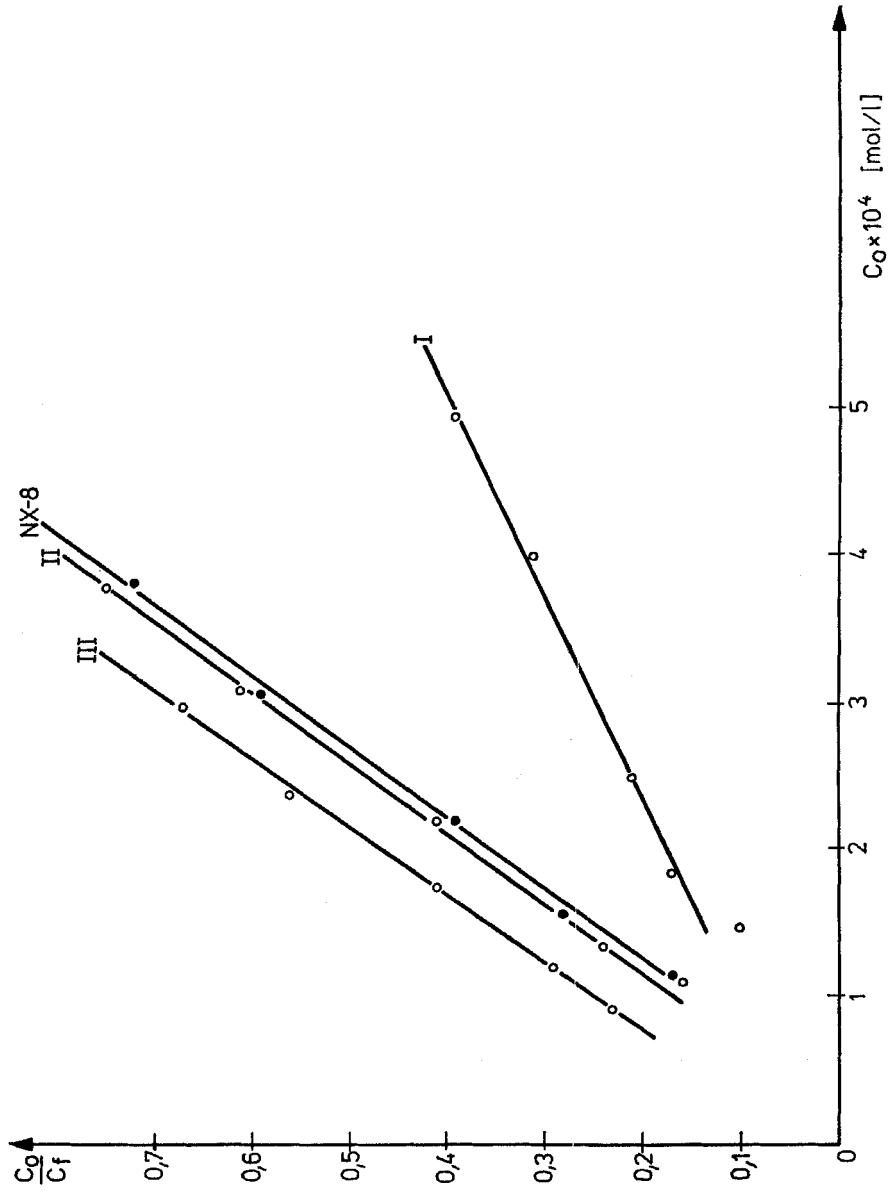


FIG. 4. Foam enrichment factor dependence on detergent concentration in solution with Rokaphenol NX-8 and its Fractions I, II, and III.

CONCLUSIONS

In general it may be stated that better foaming, i.e., a higher decontamination factor (C_0/C_r) and a lower foam enrichment factor (C_0/C_f) is attained for nonylphenols adducts with a higher content of oxyethylene groups. This is due to a higher affinity to water of compounds with longer polyether chains, i.e., less carrying of the particles of the compound by the gas is connected with inferior foaming. Schönfeldt (*19*) reports that the surface tension of solutions of oxyethylene nonylphenol adducts is lower the lower the content of oxyethylene groups in the particle. Thus adducts with a longer polyether chain have a higher affinity to water. This may be an explanation of the obtained results.

Figure 5, which shows the dependence of the decontamination factor on the logarithm of the detergent molecular weight, indicates that the foaming effect at a certain molecular weight would not be dependent upon the concentration of the detergent in the solution, if a straight-line curve is assumed for the $C_0/C_r = f(\log M)$ function beyond the experimental points. It follows from Fig. 5 that the above-mentioned weight is ~9550. The decontamination factor value, which is also a limiting value for

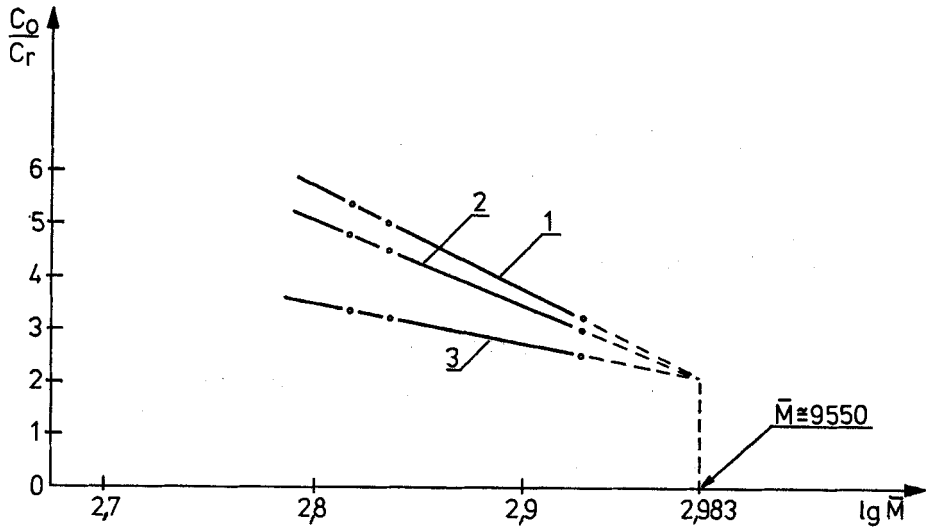


FIG. 5. Decontamination factor dependence on logarithm of the mean molecular weight of the fraction. Detergent concentration in mole/liter: (1) 1.3×10^{-4}, (2) 1.5×10^{-4}, and (3) 2.0×10^{-4}.

compounds with other weights, would amount to about 2.2. That value is close to the limiting value C_0/C_r which follows from Fig. 2, where the value is 2.0.

According to Schönfeldt (*19*), the foaming properties of ethoxylated nonylphenols are dependent upon the number of oxyethylene groups. The foaming power of nonylphenol adducts decreases with an increase in their concentration. It is known that the foaming effect is closely related to the durability of the foam. Compounds which give solutions with higher foam stability foam better.

It follows from the above work that ethylene oxide adducts which contain a lower number of oxyethylene groups and have a higher foam stability, really foam better.

When the content of oxyethylene groups (less than seven) is so low that the solubility of the compound in water becomes poorer, the effect of foaming is also much poorer.

SYMBOLS

$\overline{M}$	mean molecular weight of fraction
h_1	height of the liquid phase
h_c	height of the column
V_g	gas flow rate
V_0	feeding solution flow rate
C_0	detergent concentration in the feeding solution
C_r	detergent concentration in the raffinate
C_f	detergent concentration in the collapsed foam
C_0/C_r	decontamination factor
C_0/C_f	foam enrichment factor
$(V_f/V_0)100\%$	water removal with the foam

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