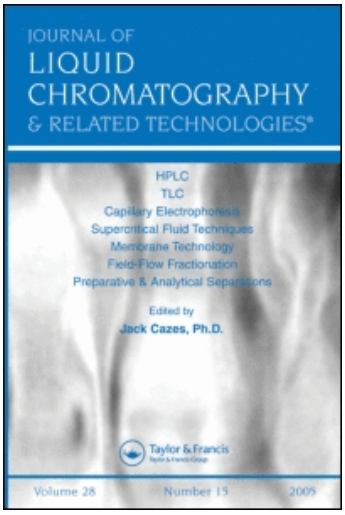

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Németh-Kiss, Veronika(1996) 'Separation of Ethoxylated Tributylphenol Oligomers on Porous Graphitic Carbon Column', Journal of Liquid Chromatography & Related Technologies, 19: 2, 217 — 229

To link to this Article: DOI: 10.1080/10826079608005508

URL: http://dx.doi.org/10.1080/10826079608005508

J. LIQ. CHROM. & REL. TECHNOL., 19(2), 217–229 (1996)

SEPARATION OF ETHOXYLATED TRIBUTYLPHENOL OLIGOMERS ON POROUS GRAPHITIC CARBON COLUMN

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ABSTRACT

Commercial ethoxylated tributylphenol oligomers were separated according to the number of ethylene oxide (EO) units by reverse phase high performance liquid chromatography on porous graphitic carbon column at different eluent concentration (methanol-water). The retention time increased with decreasing methanol concentration of the eluent and increased with the ethylene oxide unit number. Linear correlation was found between $\lg k_0'$ and fraction of EO number. Stepwise regression analysis indicated the appearance of the helical form of the oligomers.

INTRODUCTION

Nonionic surfactants generally consist of a polar chain containing some ethylene oxide (EO) units, and an apolar hydrocarbon moiety.[1,2]

Ethoxylated alkylphenols belonging to nonionic surfactants have been used in a wide variety of commercial products such as detergents,[3,4,5,6] cosmetic preparations,[4] industrial formulations,[4,6] emulsifying agents.[5,6,7]

Commercial polyethoxylated alkylphenols are manufactured by reacting

alkylphenols with an excess of ethylene oxide. Like many condensation and polymerization reactions, the final product is a complex mixture of oligomers in which the number of EO units varies over a considerable range. The distribution of ethylene oxide oligomers in a commercial product often follows the Poisson law. The length of ethylene oxide chain exerts a considerable influence on the physical and chemical properties, and even on the biodegradability in the environment.[5,8,9,10]

Normally, surfactants are discharged with waste water after application. Depending on their structure, they have a more or less toxic effect on aquatic life forms such as fish, daphnia and algae.[11]

Various chromatographic procedures have been developed for the separation of the commercial ethoxylated alkylphenols into their different oligomers.

Thin layer chromatography is of limited applicability in this area because of its poor reproducibility and lack of quantitation.[12,13] Using gas chromatography, only a limited number of oligomers are eluted from the column, even if the volatility of the sample is increased by derivatization.[14,15] High performance liquid chromatography has been shown to be a suitable technique for separating the different oligomers.[16] Most of the investigations that have been done so far, using normal phase HPLC with ultraviolet detection, the applied column types were : Spherosil silica and Kieselguhr diatomaceous earth product. With isocratic elution, the eluent was carbon-tetrachloride and a mixture of carbon-tetrachloride-i-octane in 1:1 ratio,[4] LiChrosorb-NH_2, with the gradient elution, the eluent concentration was changed from 98 % n-hexane, 2 % (1:1 n-hexane-2-propanol) to 30 % n-hexane, 70 % (1:1 n-hexane-2-propanol),[5] LiChrosorb-NH_2, with gradient elution, the eluent was a mixture of isooctane-methylene chloride-methanol and the ratio of the components was changed from 95:5:3 to 60:40:7.5[7]. Alumina, with isocratic elution, the eluent was a mixture of ethyl acetate-n-hexane, where the ethyl acetate concentration was varied from 100 % to 50 %,[18] Zorbax-CN, with gradient elution the eluent concentration was changed from 2 % to 50 % (75:25 2-methoxy-ethanol-isopropanol) in n-hexane,[19] and fluorescence detection on Zorbax-NH_2, Partisil-5PAC, with gradient elution the eluent concentration was changed from 0.1 % acetic-acid in methyl tert.-butyl ether to 0.1 % acetic-acid in acetonitrile-methanol (95:5).[3] LiChrosorb-Si60, gradient elution was used, the eluent was changed from n-hexane to ethanol-tetrahydrofuran-water (60:40:1),[20] only a few researchers used reverse phase HPLC for samples up to 9 or 10 EO units using C_{18} coated silica column; with isocratic elution the eluent was a mixture of methanol-water (60:40) and 0.1 M ammonium acetate in water in the ratio of 8:7,[11] μBondapak-C_{18} and μBondapak-NH_2, gradient elution was used, the concentration of the eluents were changed from 50 % to 85 % p-dioxane in water, from 10 % to 55 % of (55 % tetrahydrofuran in water) in (10 % tetrahydrofuran in water), from 15 % to 100 %

hexafluoroisopropanol in water[17]; LiChrospher RP-18, with gradient elution the eluents were acetonitrile-water and methanol-water containing alternatively $NaClO_4$, TFA, $TBAH_2PO_4$ as phase modifiers;[21] Porasil A(60), gradient elution was used, the eluent concentration was changed from ethyl acetate-acetic acid-water (100:32:30) to ethyl acetate.[22]

Isocratic mode with mixed solvent on silica column allows separation of oligomers up to 10 EO units; gradient programming moves the limit up to 15 EO units. For higher EO values (up to 25) a Zorbax-NH_2 column can be used either with isocratic or gradient mode.[10]

Porous graphitic carbon (PGC) is a non-polar adsorbent, which can be used in both the normal and reverse phase modes and is stable across the whole pH range from 0-14. The uniqueness of PGC compared to conventional reverse phase HPLC supports is due to its delocalized band of electrons, available for electronic interactions, especially donor-acceptor (charge transfer) interactions and direct π-electron overlap. It possesses a rigid, planar surface, which is capable of dispersion and charge-transfer interactions.[23,24] The planar surfaces of the PGC Hypercarb-S allows special stereoselectivity.[25] The retention on a carbon phase seems to be determined by how much contact is possible between a solute and carbon surface.[26,27]

The aim of this study was to determine the relationship between the molecular structure of the surfactant and its retention behaviour on porous graphitic carbon column; to separate the different oligomers of polyethoxylated alkylphenol according to the EO number. As the PGC column is available for electronic interactions, and the separation is influenced by the steric effects on its surface, these properties made us suppose that PGC column would be suitable for separating the oligomers of different ethylene oxide units.

EXPERIMENTAL

Measurements were carried out on a porous graphitic carbon (PGC) column – Shandon Hypercarb 100 x 4.6 mm I.D., partical diameter 7 μm (Shandon Scientific Ltd., Cheshire, England). The applied equipment consisted of a Gilson pump 307 (Gilson, Villiers-le-Bel, France), a Valco injector with a 20 μl sample loop (Valco Instruments Co. Inc., Houston, USA), a Biotronik UV detector BT 3030 (Wissenschaaftliche Geräte GmbH, Frankfurt, Germany) and a Hewlett Packard integrator HP 3396A (Hewlett-Packard company, Avondale, USA). The detection wavelength was 220 nm and the flow rate was 1 mL/min.

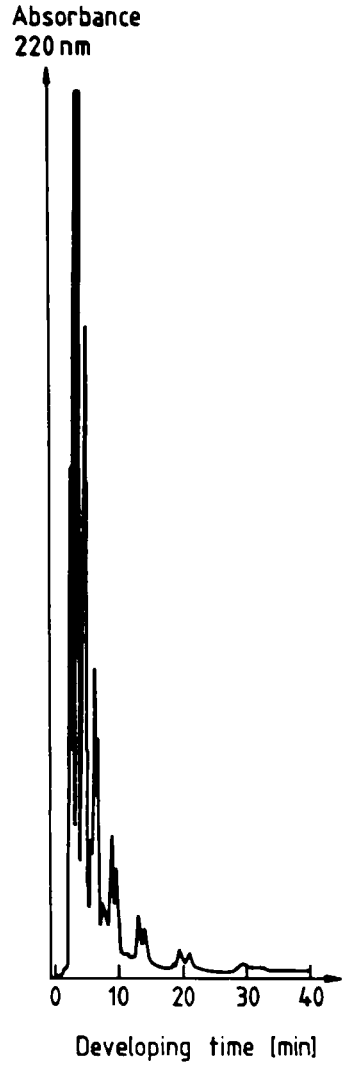

Figure 1. Chromatogram of ethoxylated tributylphenol oligomers with average EO unit number of 4 on a PGC column. Eluent 97.5 % methanol+2.5 % distillated water. Detection wavelength 220 nm. Flow rate 1 mL/min.

Eluent was water-methanol mixture, the methanol concentration varying between 80 %-97.5 % v/v in steps of 2.5 %, v/v.

Table 1.

The lgk' Values Depending on the Methanol Concentration (v/v %) and the Number of Ethylene Oxide (EO) Units.

Fraction (EO) Number	lgk[1] Methanol Concentration [Volume %] 97.5	95.0	92.5	90.0	87.5	85.0	82.5	80.0
1	-0.24	-0.16	0.01	0.03	0.12	0.21	0.31	0.43
s.d.*	0.003	0.009	0.001	0.033	0.005	0.003	0.011	0.001
2	-0.03	0.06	0.20	0.22	0.42	0.43	0.54	0.68
s.d	0.007	0.007	0.001	0.032	0.006	0.007	0.000	0.003
3	0.09	0.18	0.26	0.34	0.48	0.58	0.69	0.80
s.d.	0.011	0.006	0.000	0.024	0.008	0.009	0.001	0.004
4	0.18	0.29	0.37	0.46	0.60	0.70	0.81	0.93
s.d.	0.014	0.003	0.001	0.015	0.006	0.009	0.007	0.005
5	0.33	0.43	0.52	0.61	0.74	0.84	0.95	1.07
s.d.	0.019	0.003	0.018	0.006	0.005	0.009	0.011	0.004
6	0.50	0.60	0.67	0.78	0.90	1.01	1.12	1.24
s.d.	0.024	0.002	0.001	0.002	0.004	0.010	0.013	0.003
7	0.67	0.76	0.84	0.95	1.07	1.17	1.28	1.41
s.d.	0.028	0.002	0.001	0.007	0.003	0.011	0.014	0.003
8	0.84	0.94	1.01	1.12	1.24	1.34	1.45	1.58
s.d.	0.033	0.003	0.001	0.011	0.003	0.012	0.012	0.003
9	1.02	1.11	1.18	1.30	1.41	1.51	1.63	1.75
s.d.	0.037	0.002	0.002	0.014	0.003	0.012	0.009	0.006
10	1.20	1.29	1.36	1.47	1.58	1.68	1.81	1.94
s.d.	0.042	0.002	0.002	0.014	0.004	0.017	0.011	0.010
11	1.38	1.47	1.53	1.64	1.76	1.87		
s.d.	0.046	0.008	0.000	0.009	0.010	0.010		

*s.d. Standard Deviation

The sample was a commercial ethoxylated tributylphenol oligomer (Hoechst, Frankfurt, Germany). That surfactant was a mixture of ethylene oxide (EO) oligomers, its average number of EO units was 4 per molecule. The hydrophilic moiety (tributylphenol) had isomers depending on the position of butyl groups. The sample was a methanolic solution with 0.1 mg/1 mL methanol concentration. The experiments were carried out at room temperature (22-24 °C), and 3-4 paralell

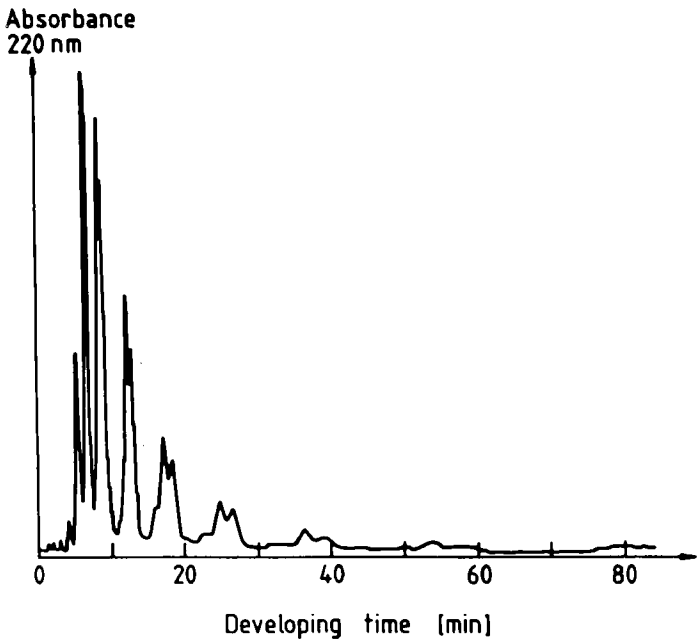

Figure 2. Chromatogram of ethoxylated tributylphenol oligomers with average EO unit number of 4 on a PGC column. Eluent 85 % methanol+15 % distillated water. Detection wavelength 220 nm. Flow rate 1 mL/min.

measurements were made. Retention time of 1 % $NaNO_3$ solution was consider as dead time.

Linear correlations were calculated between the logarithm of the capacity factors and the concentration of the methanol in the eluent :

$$\lg k' = \lg k'_0 + b \cdot C \qquad (1)$$

where k` is the actual capacity factor of an ethoxylated tributylphenol oligomer at a given methanol concentration in the eluent, $k_o$` is the theoretical capacity factor of an ethoxylated tributylphenol oligomer at 0 % (v/v) methanol (100 % (v/v) distillated water) concentration, b is the change in the logarithm of capacity factor caused by a 1 % (v/v) change in methanol concentration in the eluent (related to the surface area of the solute in contact with the stationary phase), C is the concentration (v/v %) of methanol in the eluent.

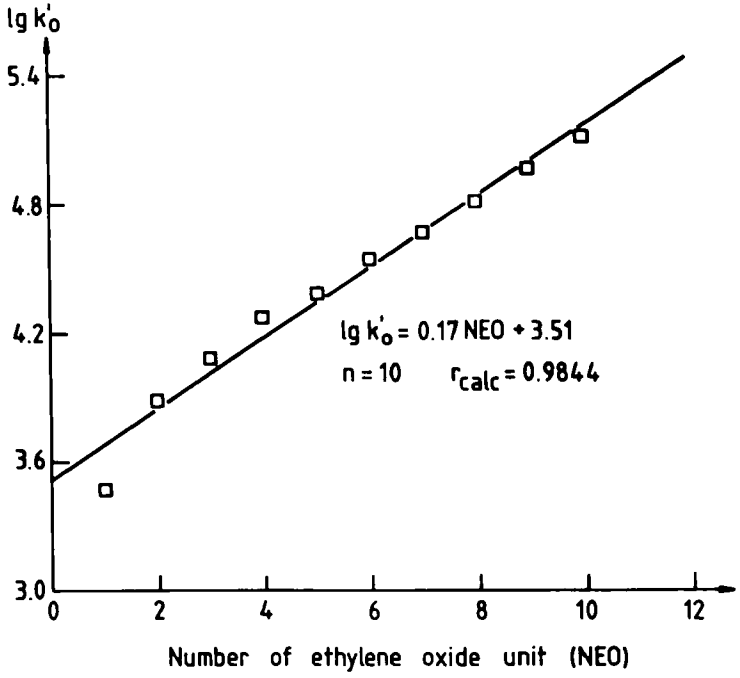

Figure 3. Relationship between the variable lgk_o' and the number of ethylene oxide units (NEO).

To determine the dependence of the retention on the number of ethylene oxide units per molecule and on the eluent concentration, five stepwise regression analysis were calculated. Linear correlation was calculated between lgk_0' and the number of ethylene oxide units (NEO) :

$$lgk_0' = BNEO + C \quad (2)$$

and between lgk_0' and lgNEO :

$$lgk_0' = BlgNEO + C \quad (3)$$

Logarithmic and quadratic correlations were also applied between the contact surface area (b) and lgk_0' :

$$b = A(lgk_0')^2 + Blgk_0' + C \quad (4)$$

between the contact surface area (b) and the number of ethylene oxide units (NEO) :

$$b=ANEO^2+BNEO+C \quad (5)$$

and between b and lgNEO :

$$b=AlgNEO^2+BlgNEO+C \quad (6)$$

Table 2

Relationship Between the Number of Ethylene Oxide (EO) Units, lgk_0' and b Values

Fraction (EO) Number	lgk_0'	$-b\cdot10^2$	$s_b\cdot10^3$	r_{calc}
1	3.46	3.86	1.47	0.9942
2	3.89	4.06	1.52	0.9944
3	4.07	4.13	1.04	0.9975
4	4.29	4.25	0.94	0.9980
5	4.38	4.19	1.08	0.9974
6	4.54	4.18	1.19	0.9968
7	4.67	4.14	1.31	0.9960
8	4.82	4.11	1.45	0.9951
9	4.96	4.07	1.58	0.9940
10	5.12	4.05	1.72	0.9929
11	4.99	3.72	2.77	0.9838

k_0' = theoretical capacity factor of an ethoxylated tributylphenol oligomer at 0% (v/v) methanol (100 % (v/v) distilled water); b = change in the logarithm of capacity factor caused by a 1% (v/v) change in methanol concentration in the eluent; s_b = standard deviation of b value; r_{calc} = correlation coefficient.

because we supposed, that the oligomers would have special retention behaviour, and on the other hand coiling helically of oligomers was likely to appear causing extreme retention behaviour, and the quadratic correlation was suitable to describe that shape.

Even a structure analysis was also calculated by computer (Alchemy software) on the ethoxylated tributylphenol oligomer at all EO unit numbers from 1 to 11. It seemed to be suitable to determine the probability of coiling helically of the molecule. The software calculated the structure of the lowest energy in all case of the different EO units.

RESULTS AND DISCUSSION

Eleven fractions of ethoxylated tributylphenol were detected on the PGC column. Each of the fractions was supposed to belong to one EO number. The peaks were symmetric. The fractions were separated well. (see Figures 1., 2.)

As it was expected the number of ethylene oxide units effected on the retention behaviour. Higher retention time belonged to longer polyethylene oxide chain.

Each of the mentioned fractions is supposed to belong to one EO number. The equation (1) was suitable to describe the results. The Table 1. contains the lgk' values calculated by the equation (1) depending on the methanol concentration (v/v %) and the EO number. The correlation between the logarithm of actual capacity factor (lgk') and the concentration of methanol (C) was significant. The lgk' values are increasing by decreasing the methanol concentration and increasing the EO number as it was expected.

The relationship between the fraction of EO number and lgk_0' values was significant. The results of the linear correlation based on the equation (1) are collected in Table 2.. It can be seen in Table 2., that extreme retention behaviour started at the EO unit number of 4. After that fraction the properties of the oligomers became opposite ones. Before that point the b value increased with lgk_o' and NEO, but after it b decreased with them. Here presumably the helical form of the EO chain appeared and that event had a prominent effect on the electronic interactions between the stationary phase and the solute. The stepwise regression analysis between lgk_o'-NEO (2) — the lgk_o'-NEO correlation (2) as a linear one wasn't so significant, but the lgk_o'-lgNEO (3) gave a better correlation coefficient for the linear correlation — proved, that one fraction belongs to one EO number. (see Figure 3.) Quadratic correlation was found between b and lgk_o', and between b and NEO, which proved, that a helical form of oligomers appeared and the change

in the retention behaviour was at the EO number of 4. (see Figure 4., 5.) In addition to the b-lgNEO parabolic correlation was more significant, than the b-NEO. Results of the stepwise analysis are summarized in the Table 3. (the general forms of the equations (2,3,4,5,6) see above in the section "**EXPERIMENTAL**"). The significant level of variables was 99.9 %, except in the case of b-NEO, where it was 99 % (based on F value). The significant level of correlation was 99.9 % in every case (based on t – Student – value).

Table 3

Results of Stepwise Analysis on b, lgk_0' and the Number of Ethylene Oxide Units (NEO) (General Form : $Y=AX^2+BX+C$).

Parameter	Equation Number				
	2	**3**	**4**	**5**	**6**
A	–	–	-0.36	-0.01	-0.92
s_A	–	–	0.125	0.004	0.205
B	0.17	1.58	3.16	0.14	1.13
s_B	0.004	0.022	0.978	0.044	0.207
C	3.51	3.38	-2.81	3.79	3.84
s_C	0.049	0.059	1.968	0.184	0.135
r	0.9844	0.9869	0.9614	0.8927	0.9648
n	10	10	10	10	10
$F_{99.9\%}$	21.69	21.69	23.70	23.70	23.70
F_{calc}	250.86	300.25	42.73	13.74*	47.17

* = that correlation was significant at the level of 99 %, as $F_{99\%} = 9.78$.
A, B, C = coefficients of the equations; s_A, s_B, s_C = standard deviations of coefficients; r = correlation coefficient; n = number of samples; $F_{99.9\%}$ = F value belonging to the 99.9% significance level; F_{calc} = calculated F value.

Structure analysis was calculated by computer (Alchemy software). As the software couldn't consider the effects of the environment, the result wasn't suitable for representing the events of the experiments, but it was determined, that without any environmental effects the molecule doesn't tend to coil helically, so the reason for coiling must be the environment — the methanol and the water in the eluent, the possibility of coiling changes with the methanol concentration.

It can be concluded from our data, that the retention time of ethoxylated

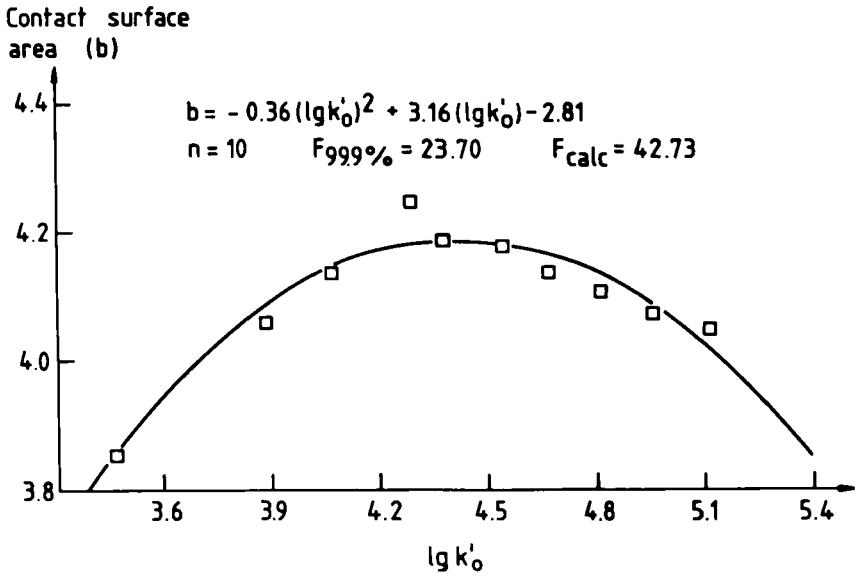

Figure 4. Relationship between the contact surface area (b) and lgk_o'

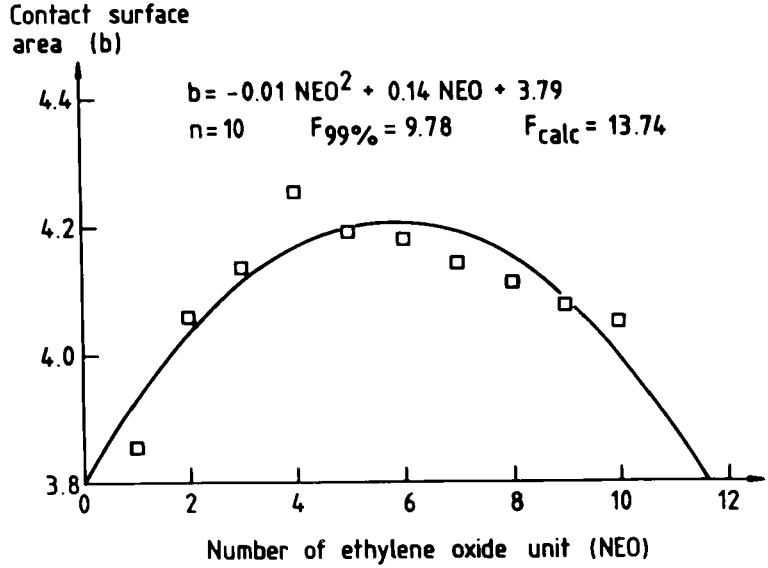

Figure 5. Relationship between the contact surface area (b) and the number of oxylated units (NEO).

tributylphenol oligomer on PGC column increased with decreasing methanol concentration of the eluent and increased with the ethylene oxide unit number. That means it managed to separate well the ethoxylated tributylphenol oligomers. The regression analysis indicated the appearance of the helical form of the oligomers. The same conclusion can be established by observing of lgk_0' and b values in Table 2. It was also proved, that coiling helically started at the EO unit of 4.

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Recieved June 8, 1995
Accepted June 23, 1995
Manuscript 3903