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Separation of oligomers of nonlphenylethylene oxide on a porous graphitized carbon column[1]

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Abstract

The retention of nonylphenyl ethylene oxide oligomer surfactants was determined on a porous graphitized carbon (PGC) column using water—methanol mixtures as eluents. Linear correlations were calculated between the logarithm of the capacity factor (k') and the methanol concentration in the eluent. To test the validity of the hypothesis that in the case of homologous series of solutes the intercept and slope values are intercorrelated linear correlation was calculated between the two chromatographic parameters. To elucidate the role of the length of the polar ethylene oxide chain in the retention linear correlations were calculated between the chromatographic parameters and the number of ethylene oxide groups per molecule. Nonylphenyl ethylene oxide oligomers were well separated on the PGC column. Significant linear relationships were found between the corresponding chromatographic parameters indicating that the solutes behave as a homologous series of compounds. The retention of surfactants increased linearly with increasing number of ethylene oxide groups per molecule indicating hydrophilic interactions between the solutes and the surface of PGC support. © 1997 Elsevier Science B.V.

Keywords: Nonionic surfactants; Porous graphitized carbon column

1. Introduction

Nonionic surfactants are composed of a hydrophobic moiety (generally fatty acids, fatty alcohols or alkylphenol derivatives) and of a hydrophilic ethylene oxide chain of various lengths. Due to their favourable physicochemical characteristics nonionic surfactants are extensively used in pharmaceutical [1] and agrochemical formulations [2], in cosmetics [3] and in various biotechnological processes [4]. Nonionic surfactants not only influence the biological efficacy of active ingredients but also show marked biological activity themselves. They enhance the decomposition rate of polychlorinated biphenyls [5] and polycyclic aromatic hydrocarbons [6], promote the removal of phenanthrene from soil [7,8] and that of heavy metals from waste waters [9]. However, nonionic surfactants can also be toxic. Thus, they can cause ocular [10–12] and skin irritancy [13,14] and skin dehydration [15].

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As it has been many time proved that both the character of the hydrophobic moiety and the length of ethylene oxide chain influence the biological efficacy [16–18] many efforts have been devoted for the development of HPLC methods for the separation of surfactants in both direction that is according to the hydrophobic moiety and the length of ethylene oxide chain. Reversed-phase supports such as C18 [19], C8 an C6 [20], and polyethylene-coated silica [21] have been successfully used for the separation of various surfactants according to the character of the hydrophobic moiety. Silica [22], and C1 silica separated well various surfactants according to the length of the ethylene oxide chain [23]. A sensitive thermospray LC/MS method was also developed to detect nonionic surfactants at 2 ppb level [24]. It is generally accepted that for the separation of surfactants in both direction needs two different supports. It has been recently proved that surfactants can be separated in both direction in one run on an alumina support [25,26].

Porous graphitized carbon (PGC) has been developed as a very insoluble and stable HPLC support [27,28]. Its retention characteristics and application have been recently reviewed [29].

The objectives of this work were to study the retention behaviour of nonylphenyl ethylene oxide oligomer surfactants on PGC column, to elucidate the effect of various molecular substructures on the retention and to find the relationship between the retention parameters and solute characteristics.

2. Materials and methods

The PGC column (Shandon Hypercarb 100 × 4.7 mm I.D., particle diameter 7 μm) was purchased from Shandon Scientific (UK). The HPLC system consisted of a Liquopump Model 312 (Labor MIM, Budapest, Hungary) pump, a Cecil CE-212 variable wavelength UV detector (Cecil Instr., Cambridge, UK), a Valco injector (Valco, Houston, TX, USA) with a 20 μl sample loop and a Waters 740 integrator (Water-Millipore, Milford, MA, USA). The flow-rate was 1.0 ml min^{-1} and the detection wavelength was set to 230 nm. Mixtures of methanol–water were used as eluents, methanol concentration ranged from 72.5 to 97.5 vol.% in steps of 2.5 vol.%. The separation of nonionic surfactant according to the character of the hydrophobic moiety was carried out on a C6 column (250 × 4 mm I.D., particle size 5 μm; eluent methanol–water 4:1 v/v; flow-rate 0.5 ml min^{-1}; detection wavelength 230 nm). The columns were not thermostated each determination was run at room temperature. A sample of a commercial nonylphenyl ethylene oxide surfactant containing in average five ethylene oxide groups (n_e) per molecule (Hoechst AG, Frankfurt, Germany) was dissolved in the eluents at a concentration of 0.5 mg ml^{-1}. The retention time of the sample in each eluent was determined with three consecutive determinations. Linear correlation was used to describe the dependence of the $\log k'$ value on the concentration of methanol in the eluent:

$$\log k' = \log k'_0 + b \times C \quad (1)$$

where $\log k'$ is the logarithm of capacity factor; $\log k'_0$ is the logarithm of capacity factor; extrapolated to zero methanol concentration in the eluent (intercept, related to the retention capacity of the column); b is the change of $\log k'$ value caused by unit change (1 vol.%) of methanol concentration (slope, related to the specific surface area of solutes in contact with the PGC surface); and C is the methanol concentration in the eluent (vol.%).

To test the validity of the hypothesis that in the case of homologous series of compounds the slope and intercept values of Eq. (1) are intercorrelated [30], linear correlation was calculated between the two retention parameters:

$$\log k'_0 = A_1 + B_1 \times b \quad (2)$$

To increase the reliability of the identification of the main peaks on the chromatograms a graph of $\log k'$ against the tentative number of ethylene oxide groups per molecule was constructed for each eluent composition. The linearity of the graph indicates that any adjacent two main peaks differ from each other in one ethylene oxide group per molecule.

To elucidate the role of the length of the polar ethylene oxide chain in the retention of surfactants on PGC column linear correlations were calculated between the chromatographic parameters calculated with Eq. (1) and the number of ethylene oxide groups per molecule (n_e):

$$\log k'_0 = A_2 + B_2 \times n_e \quad (3)$$

$$b = A_3 + B_3 \times n_e \quad (4)$$

3. Results and discussion

The sample contained many fractions indicating that nonylphenyl ethylene oxide oligomers can be successfully separated on PGC column (Fig. 1). We assume that each main fraction corresponds to an oligomer with a defined number of ethylene oxide group per molecule. As we cannot find pure standards to identify the fractions we supposed that the first fraction contains one, the second fraction two ethylene oxide groups per molecule, etc. The fractions present in lower quantities between the main peaks probably correspond to the surfactants with identical number of ethylene oxide groups per molecule but with different hydrophobic moiety. This supposition was supported by the finding that the sample was inhomogeous

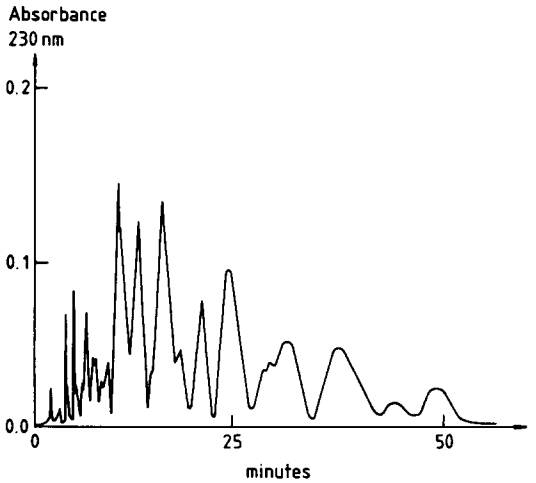

Fig. 1. Chromatogram of nonylphenyl ethylene oxide oligomers on PGC column. Eluent: methanol–water (97.5:2.5 v/v); detection 230 nm; flow-rate 1 ml min^{-1}.

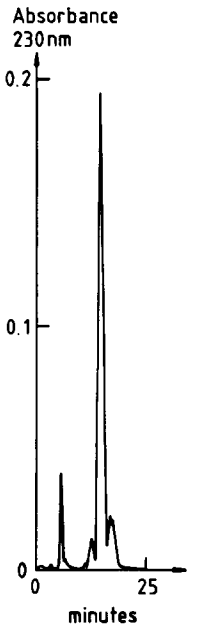

Fig. 2. Chromatogram of nonylphenyl ethylene oxide oligomers on C6 column. Eluent: methanol–water (4:1 v/v); detection 230 nm; flow-rate 0.5 ml min^{-1}.

under reversed-phase conditions proving the presence of different hydrophobic compounds. As surfactants with longer alkyl chain are stronger retained and surfactants with different length of ethylene oxide chain are not separated under reversed-phase chromatographic conditions we assume that the main peak represents all the nonylphenyl ethylene oxide oligomers, the peaks eluted before and after the main peak correspond to octylphenyl and decylphenyl ethylene oxide oligomers (Fig. 2). These results indicate that both the number of ethylene oxide groups and the character of hydrophobic moiety influence the retention on PGC column, that means that nonylphenyl ethylene oxide surfactants can separate in one run both according to the number of ethylene oxide groups and the character of hydrophobic moiety. The parameters of Eq. (1) are compiled in Table 1. The linear correlations between the logarithm of the capacity factor and the methanol concentration in the eluent were significant for each fraction. The retention of surfactants increased with increasing length of the

hydrophilic ethylene oxide chain. The affinity of the ethylene oxide groups for solvent and stationary phase are about the same under reversed-phase conditions, but with PGC the affinity of graphite for the ethylene oxide groups is greater than the affinity of the solvent, in accord with much other evidence regarding retention by graphite [31,32].

The coefficient of correlation of the graphs $\log k'$ against n_e varied between 0.9837 and 0.9901 indicating that the main peaks really represent oligomer fraction differing in one ethylene oxide group per molecule.

A significant linear correlation was found between the slope and intercept values of Eq. (1):

$$\log k'_0 = -0.39 - 127.46 \times b$$

$$r_{calc} = 0.9895 \quad r_{99.9\%} = 0.8471 \qquad (5)$$

The strong correlation indicates that from the chromatographic point of view the nonylphenyl ethylene oxide oligomer surfactants behave as a homologoues series of compounds. This finding supports our previous conclusions that the retention of surfactants is mainly governed by the length of the polar ethylene oxide chain (identical in character in each oligomer) and the nature of the hydrophobic moiety has a secondary influence on retention.

Table 1
parameters of linear correlations between the capacity factor of nonylphenyl ethylene oxide oligomers and the concentration of methanol in the eluent (C)

No of fraction	$\log k' = \log k'_0 + b \times C$			
	$\log k'_0$	$-b \times 10^2$	$s_b \times 10^3$	r_{calc}
1	1.75	1.86	0.26	0.9998
2	2.06	1.94	0.18	0.9998
3	2.37	2.06	0.51	0.9988
4	3.00	2.61	1.00	0.9985
5	3.90	3.48	2.18	0.9923
6	4.00	3.47	1.72	0.9963
7	4.41	3.89	2.06	0.9972
8	4.59	3.46	3.89	0.9876
9	5.08	4.46	0.01	0.9996
10	4.50	3.67	5.68	0.9769
11	4.89	3.96	2.83	0.9949

The number of fractions is probably identical with the number of ethylene oxide groups per molecule.

Good linear correlations were found between the parameters of Eq. (1) and the number of ethylene oxide groups per molecule (n_e):

$$\log k'_0 = 1.66 + 0.33 \times n_e$$

$$r_{calc} = 0.9449 \quad r_{99.9\%} = 0.8471 \qquad (6)$$

$$b = 1.66 + 0.33 \times n_e$$

$$r_{calc} = 0.8962 \quad r_{99.9\%} = 0.8471 \qquad (7)$$

The highly significant dependence of both the retention capacity and specific contact surface of surfactants with the PGC support on the number of ethylene oxide groups proves again the decisive role of hydrophilic interactions in the retention behaviour. This finding indicates that the PGC column has different retention characteristics from those of traditional reversed-phase supports, although the eluents used are typical reversed-phase eluents.

It can be concluded from the data that PGC support is specially suitable for the separation of nonylphenyl ethylene oxide oligomer surfactants, separating the compounds both according to the length of the polar ethylene oxide chain and that of the hydrophobic alkyl chain.

Acknowledgements

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