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Note

Retention behaviour of alkylene oxides in reversed-phase high-performance liquid chromatography

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Alkylene oxide type non-ionic surfactants are widely used as emulsifiers, wetting agents and detergents. Many procedures for chromatographic analysis of non-ionic surfactants have been reported. For example, the molecular weight distribution of ethylene oxide adducts has been determined^{1–8}, and the determination of polyethylene glycols (PEG)^{9–13} and of homologous alkyl chain distribution¹⁴ in ethylene oxide adducts have been reported. However, there have been few reports on other types of non-ionic surfactants, such as poly(oxypropylene) alkyl ethers, poly(oxypropylene) poly(oxyethylene) alkyl ethers and copolymers of ethylene oxide (EO) and propylene oxide (PO), using high-performance liquid chromatography (HPLC), although their use as surfactants is increasing.

In this study, retention data of non-ionic surfactants in reversed-phase HPLC were collected for a wide range of EO and/or PO adducts. The logarithm of the capacity factor, $\log k'$, was used as an index of retention time, and the retention behaviour of non-ionic surfactants was elucidated in terms of the hydrophilic or hydrophobic properties of the EO or PO chains. The separation of non-ionic surfactants can be predicted from a linear relation between $\log k'$ and the degree of polymerization of EO or PO. It was also possible to estimate the degree of polymerization or alkyl chain length from the $\log k'$ value.

EXPERIMENTAL

Chemicals

Poly(oxyethylene) alkyl ethers (R-EO) were purchased from Kao-Atlas (Tokyo, Japan), and the block copolymers of EO and PO and PPG 4000 (polypropylene glycol) from Asahi Denka (Tokyo, Japan). PEG 4000 (polyethylene glycol) was obtained from Wako (Tokyo, Japan). Poly(oxypropylene) alkyl ethers (R-PO) and poly(oxypropylene) poly(oxyethylene) alkyl ethers (R-PO/EO) were synthesized in our laboratories.

HPLC

Analyses were performed with a liquid chromatograph (TRI Rotar; Jasco, Japan) equipped with variable loop injector (VL-611, Jasco), differential refractom-

eter (SE-11, Shodex) and Hewlett-Packard 7101 BM strip chart recorder. All results were obtained on stainless-steel columns (250 × 4.0 mm I.D.) packed with porous polymer gel (No. 3011; Hitachi, Japan). An acetone-water mixture was used as mobile phase at a flow-rate of 1.0 ml/min.

Sample solutions of *ca.* 10% were prepared in the mobile phase and 10 μ l of each solution were injected into the chromatographic system. The logarithm of the capacity factor, $\log k'$, of each sample was calculated from the chromatogram.

RESULTS AND DISCUSSION

Fig. 1 shows the linear relation between $\log k'$ and n , the degree of polymerization, for C_{12} -EO $_n$. Here, C_{12} -EO $_n$ denotes the adduct between an average of n moles of EO and 1 mole of lauryl alcohol. The $\log k'$ value decreases by 0.2 between $n = 5$ and 12. Thus, the retention time of C_{12} -EO $_5$ is 1.5 times longer than that of C_{12} -EO $_{12}$, the longer EO chain enhancing the hydrophilic property of C_{12} -EO $_{12}$. For the EO adducts of C_{16} and C_{18} alcohols, parallel lines (broken lines in Fig. 1) can be drawn although only two data points are available, because the only difference between C_{12} -EO $_n$ and C_{16} -EO $_n$ or C_{18} -EO $_n$ is in the alkyl chain length. The effect of the EO chain on the retention behaviour will not change for adducts with different alkyl chain lengths. The retention times of the adducts increase in the order C_{12} -EO $_n < C_{16}$ -EO $_n < C_{18}$ -EO $_n$ in accordance with the hydrophobic property of the alkyl chain.

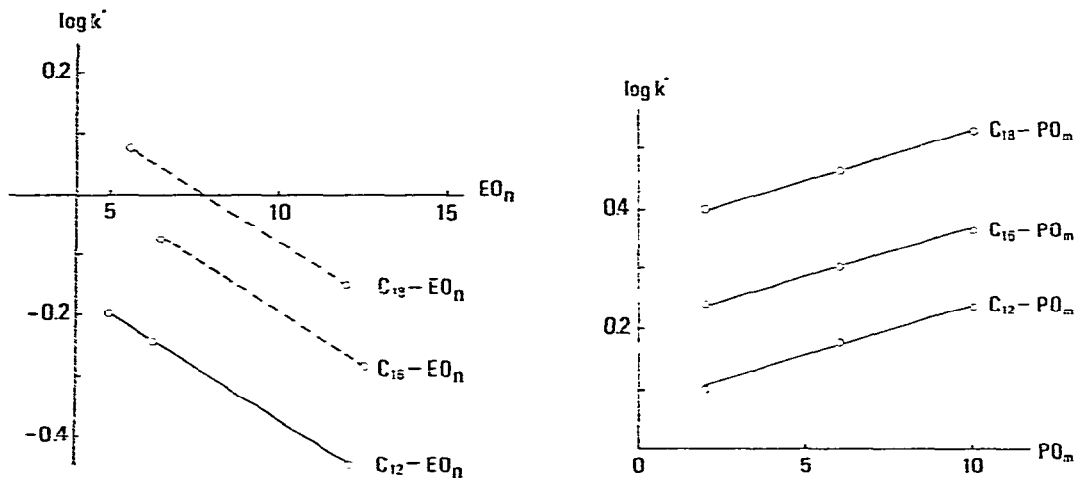


Fig. 1. Relations between $\log k'$ and the degree of polymerization of EO for (R-EO $_n$).

Fig. 2. Relation between $\log k'$ and the degree of polymerization of PO for (R-PO $_m$).

Fig. 2 shows a similar relation between $\log k'$ and the degree of polymerization of PO in R-PO. Although the relation is linear, the slope is positive due to the hydrophobic property of the PO chain.

Fig. 3 shows a linear relation between $\log k'$ and n of EO/PO adducts of lauryl alcohol. Again, C_{12} -PO $_m$ EO $_n$ denotes an adduct between an average of m moles of PO, n moles of EO and 1 mole of lauryl alcohol. The linear relation holds only for certain values of m . In Fig. 3, the data for $m = 0, 3, 5$ and 10 are shown. Although

there are only two points each for $m = 3$ and 5, we assume linear relations (broken lines) because linear relations are found for $m = 0$ and 10 and the effect of the EO chain on the retention behaviour of $C_{12}\text{-PO}_m\text{EO}_n$ will not change for constant values of m . The straight lines of negative slope are similar to those in Fig. 1. The elution of $C_{12}\text{-PO}_m\text{EO}_5$ is delayed by the hydrophobic PO chain, and $C_{12}\text{-EO}_5$ is eluted first, followed by $C_{12}\text{-PO}_3\text{EO}_5$ and $C_{12}\text{-PO}_{10}\text{EO}_5$. The retention times of $C_{12}\text{-PO}_{10}\text{EO}_n$ increase in the order $C_{12}\text{-PO}_{10}\text{EO}_{1.5} < C_{12}\text{-PO}_{10}\text{EO}_{10} < C_{12}\text{-PO}_{10}\text{EO}_5$.

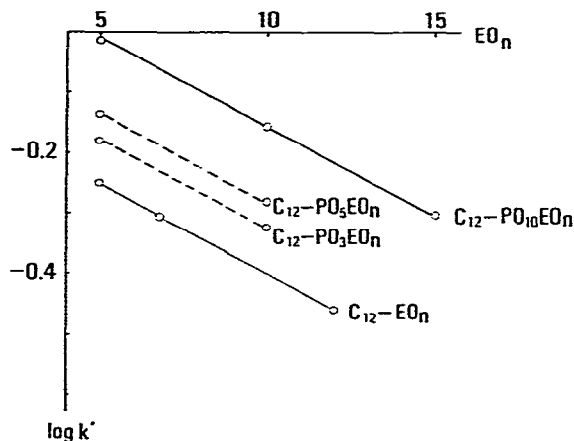


Fig. 3. Relation between $\log k'$ and the degree of polymerization of EO for $(R\text{-PO}_m\text{EO}_n)$.

The elution pattern of block copolymers of PO and EO is similar to that of EO/PO adducts of alcohols (Fig. 3) although these copolymers have no alkyl chain. Fig. 4 shows chromatograms of copolymers with PEG and polypropylene glycols (PPG). The weight percentages of the EO chain (EO %) in the copolymer are 100 (a), 80 (b), 50 (c) and 0 (d), respectively. The retention time of the copolymer increases and the shape of its peak becomes broader as the EO % decreases from 80 to 40, *i.e.*, a copolymer of small EO % has an elution behaviour like PPG, while a copolymer of large EO % behaves like PEG.

The chromatographic separation of non-ionic surfactants can be predicted from the elution data described above. Practically, a complete chromatographic separation is possible if the difference in $\log k'$ values is greater than 0.5. For instance, the separation of R-EO and R-PO can easily be performed because, as shown in Fig. 1 and 2, the difference in $\log k'$ is large in most cases. Fig. 5a shows the separation of $C_{12}\text{-EO}_{12}$ and $C_{12}\text{-PO}_{10}$. In this example, the difference in $\log k'$ is 0.69 and the resolution is calculated from the chromatogram to be 96%. As shown in Figs. 1 and 3, the values of R-PO/EO are close to those of R-EO and a complete separation of these types of non-ionic surfactants not be achieved. The separation of $C_{12}\text{-PO}_m\text{EO}_n$ and $C_{18}\text{-PO}_m$ was achieved fairly easily.

The separation of block copolymers from other non-ionic surfactants was investigated. The separation of PEG and R-EO has already been reported⁹⁻¹³. The block copolymers should behave like PEG when the weight percentage of EO in the molecule is very large. As expected, the behaviour of the copolymer was similar to PEG, but its peak is broader and the retention time is slightly longer than that of

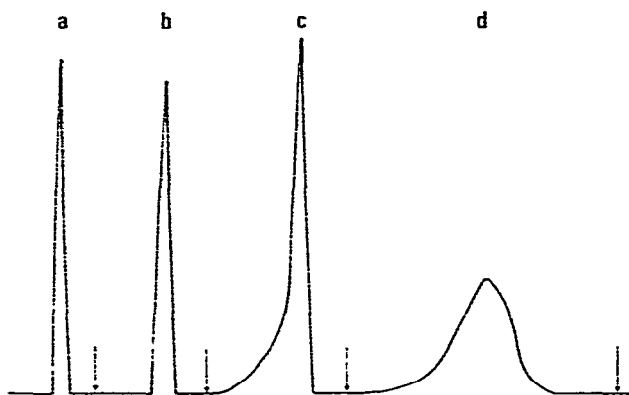


Fig. 4. Typical chromatogram of PEG, the block copolymer, and PPG. a. PEG 4000; b. copolymer (EO%, = 80); c. copolymer (EO%, = 50); d. PPG 4000.

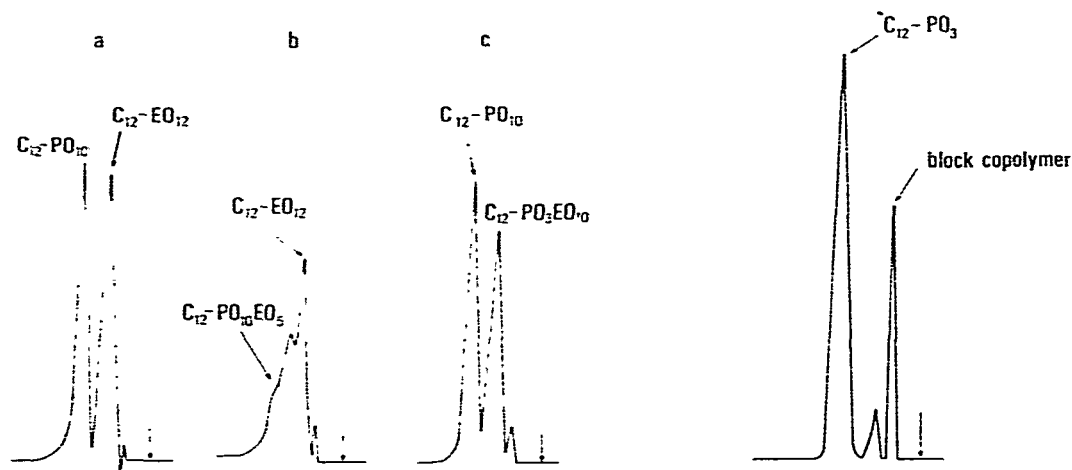


Fig. 5. Separation of alkylene oxide type non-ionic surfactants. a. C_{12} -EO₁₂, C_{12} -PO₁₀; b. C_{12} -EO₁₂, C_{12} -PO₁₀EO₅; c. C_{12} -PO₃EO₁₀, C_{12} -PO₁₀.

Fig. 6. Separation of C_{12} -PO₃ and the block copolymer (EO%, = 80).

PEG. Fig. 6 shows the separation of the block copolymer and C_{12} -PO₃. The small peak between the peaks of the block copolymer and C_{12} -PO₃ is PPG, a by-product.

As described above, the relation between $\log k'$ and the degree of polymerization of EO or PO adducts is found to be linear. This relation is useful not only for the prediction of chromatographic separation but also for the estimation of the degree of polymerization and of the alkyl chain length of alkylene oxide type non-ionic surfactants.

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