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AQUEOUS SIZE-EXCLUSION CHROMATOGRAPHY OF MICELLES OF POLY(OXYETHYLENE) METHYL-*n*-ALKYL ETHERS

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SUMMARY

Aqueous size-exclusion chromatography was used to determine hydrodynamic volumes of micelles formed by four series of poly(oxyethylene) methyl-*n*-alkyl ethers, $CH_3(OCH_2CH_2)_mO(CH_2)_nH$, with *m* having number-average values in the range 13–53 and *n* having values in the range 12–21. The surfactants in solution were injected at concentrations far above their critical micelle concentrations in order to avoid complexities due to the micelle–free-chain equilibrium. The hydrodynamic volumes of the micelles were found to increase with increase in *n* at fixed *m* and also with increase in *m* at fixed *n*. The effects of block lengths *m* and *n* on the aggregation numbers of the micelles was roughly estimated by combining their hydrodynamic volumes with measures of their intrinsic viscosities.

INTRODUCTION

In the aqueous size-exclusion chromatography (SEC) of a surfactant the elution may be complicated by the micelle–free-chain equilibrium[1,2]. Nevertheless in a suitable chromatographic system injection of a small volume of surfactant solution at a concentration well above its critical micelle concentration (CMC) into a stream of water can result in the emergence of a micellar peak, and so to a direct determination of micellar elution volume and an estimate of micellar size.

Our previous systematic work in this area[3] was carried out with two series of poly(oxyethylene) methyl-*n*-alkyl ethers, $CH_3(OCH_2CH_2)_mO(CH_2)_nH$, with *m* having number-average values of 27 and 53 and *n* in the range 12–30. The investigation has now been extended to include another two series of poly(oxyethylene) methyl-*n*-alkyl ethers with $m = 13$ and 40 and *n* in the range 12–21. New results for all 4 series allow a more complete assessment of the effect of the oxyethylene chain length on the elution behaviour of these compounds.

EXPERIMENTAL

Materials

Preformed samples of α-methyl, ω-hydroxy-poly(oxyethylene),

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$CH_3(OCH_2CH_2)_mOH$, with number-average values of the oxyethylene chain length m = 13 and 40, were reacted with *n*-alkyl bromides in a modified Williamson reaction to form the required *n*-alkyl ethers, $CH_3(OCH_2CH_2)_mO(CH_2)_nH$. Samples were purified by preparative-scale SEC on Sephadex LH-20 gel. Conversion to *n*-alkyl ether, as determined by infra-red and ^1H NMR spectroscopy and by elemental analysis, was essentially complete. Analytical SEC on Styragel with tetrahydrofuran at 25°C was used to show that the samples had very narrow molecular weight distributions with ratios $M_w/M_n < 1.05$. Details of the methods employed have been given elsewhere[3–5].

The samples are denoted 1-*m*-*n*, *e.g.* the sample $CH_3(OCH_2CH_2)_{13}O(CH_2)_{14}H$ is denoted 1-13-14.

Size-exclusion chromatography

Sepharose 4B gel (Pharmacia), swollen with distilled water plus sodium azide (0.2 g dm^{-3}) as bactericide, was packed into a glass column (bed length 75 cm, internal diameter 2.6 cm, total bed volume 400 cm^3) and maintained at constant temperature of 25 ± 0.2°C by circulating water from a thermostat through a jacket. Compared with the Sepharose column used in earlier work[3] micellar elution volumes were about 5% smaller and free chain elution volumes about 10% smaller. The solvent, distilled water plus sodium azide, was pumped (Metering Pumps, Series II micropump with short-stroke action) through the column at a rate of about 0.4 cm^3 min^{-1}. The flow-rate was checked by timing the collection of a known volume of solvent at frequent intervals, and also by means of a 3-cm^3 symphon, although this latter method was unreliable when surfactants were emerging due to variation in surface tension. Samples in dilute solution (c < 10 g dm^{-3}) were injected into the solvent stream by means of a 1.5-cm^3 loop of a rotary injection valve (Altex Scientific, Model 202.00). A differential refractometer (Waters Assoc., Model 403) connected to a strip-chart recorder was used to detect emerging sample. The void volume of the column (100 ± 5 cm^3) was determined by eluting a dilute solution of Polyox WSR N750 (Union Carbide), a poly(oxyethylene) containing material of high molecular weight.

RESULTS

SEC curves obtained for the samples of the 4 series of ethers (m = 13, 27, 40 and 53) are illustrated in Figs. 1 and 2. The concentration of sample in the injected solution was normally $c_0 \approx 4.5$ g dm^{-3}, but certain samples were injected at the higher concentration of $c_0 \approx 9$ g dm^{-3} in order to detect the emergence of micelles more readily[3].

A calibration curve for the system, determined by means of poly(oxyethylene) standards as described earlier[3], is shown in Fig. 3. The samples 1-*m*-*n* used in this investigation had number-average molecular weights in the range 770 (1-13-12) to 2660 (1-53-21). Considered as if poly(oxyethylene) they should elute in the volume range 320–360 cm^3: see Fig. 3. Consequently narrow peaks appearing before 300 cm^3 can be assigned to micelles. The recorded elution volumes of the micelles are listed in Table I, results obtained for injection at the higher concentration being included where appropriate.

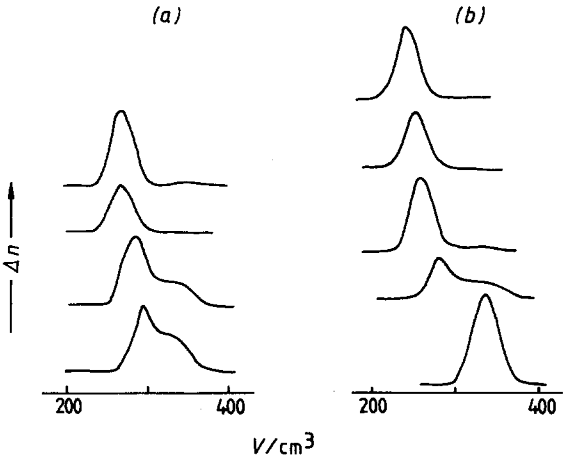

Fig. 1. Size-exclusion chromatography of poly(oxyethylene) methyl-*n*-alkyl ethers in aqueous solution at 25°C. Samples are (a) series 1-13-*n* with, from top to bottom, n = 18, 16, 14 and 12, and (b) series 1-27-*n* with, from top to bottom, n = 21, 18, 16, 14 and 12. Concentration of injected solutions was normally 4–5 g $\mathrm{dm^{-3}}$, but was 9 g $\mathrm{dm^{-3}}$ for samples 1-13-12 and 1-13-14.

DISCUSSION

Within a set of *n*-alkyl ethers of constant oxyethylene chain length the observed variation in elution profile (see Figs. 1 and 2) can be ascribed to the decrease in CMC which accompanies an increase in *n*-alkyl chain length in these compounds[6]. Taking as an example the results for series 1-27-*n* at constant injected concentration (c_0 = 4.5 g $\mathrm{dm^{-3}}$, see Fig. 1b), samples emerge either as free chains (n = 12), or predominantly as micelles (n = 18, 21), or as micelles followed by free chains (n = 14, 16).

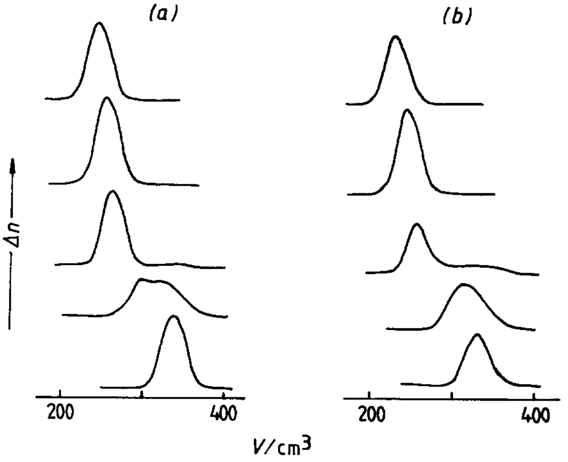

Fig. 2. Size-exclusion chromatography of poly(oxyethylene) methyl-*n*-alkyl ethers in aqueous solution at 25°C. Samples are (a) series 1-40-*n* with, from top to bottom, n = 21, 18, 16, 14 and 12 and (b) series 1-53-*n* with, from top to bottom, n = 21, 18, 16, 14 and 12. Concentration of injected solution was 4–5 $\mathrm{dm^{-3}}$ for all samples.

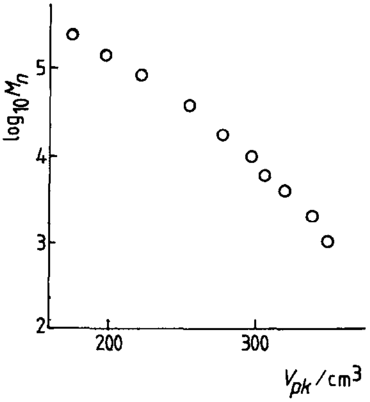

Fig. 3. Logarithm of number-average molecular weight (M_n) *versus* SEC peak elution volume (V_{pk}) for poly(oxyethylene) calibration standards at 25°C.

As discussed elsewhere[3] behaviour of this type reflects the rapid equilibration of free chains and micelles during their elution, as is evident from the satisfactory semi-quantitative description of the experimental results by means of Coll's theory[1,3]. However it has been concluded[3] that the peak elution volumes obtained for micelles are largely unaffected by the dissociation-association process.

Hydrodynamic volume

The peak elution volumes (V_{pk}) listed in Table I vary regularly with *n*-alkyl chain length (*n*) and also oxyethylene chain length (*m*). A semi-quantitative treatment

TABLE I

ELUTION VOLUMES OF MICELLES OF POLY(OXYETHYLENE) METHYL-*n*-ALKYL ETHERS IN WATER

c_0 = approximate concentration of solution injected. V_{pk} = elution volume at peak maximum.

Sample	c_0 ($g\ dm^{-3}$)	V_{pk} (cm^3)	$10^{-5}[\eta]M$ ($cm^3\ mol^{-1}$)
1-13-12	9.0	297	1.7
1-13-14	9.0	287	3.1
1-13-16	4.5	273	7.3
1-13-18	4.5	268	9.6
1-27-14	4.5	280	4.9
1-27-16	4.5	265	11.5
1-27-18	4.5	256	19
1-27-21	4.5	248	28
1-40-14	9.0	276	7.2
1-40-16	4.5	259	16
1-40-18	4.5	250	25
1-40-21	4.5	239	42
1-53-16	4.5	257	18
1-53-18	4.5	246	31
1-53-21	4.5	233	54

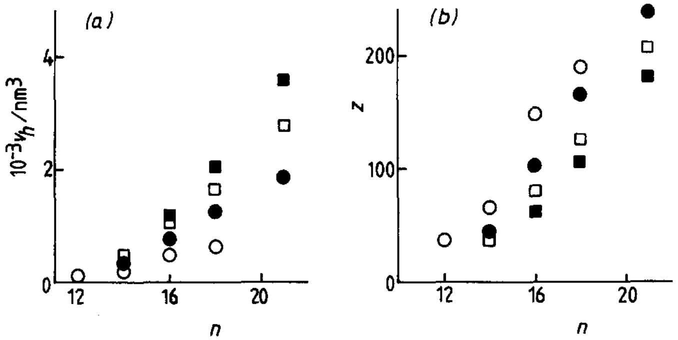

Fig. 4. (a) Hydrodynamic volume (v_h) and (b) aggregation number (z) *versus* *n*-alkyl chain length (n) for micelles of poly(oxyethylene) methyl-*n*-alkyl ethers of series (○) 1-13-*n*. (●) 1-27-*n*, (□) 1-40-*n* and (■) 1-53-*n*.

of this effect can be based on the "universal" calibration concept[7], whereby V_{pk} is determined by the hydrodynamic volume of the solute, *i.e.* by the product of intrinsic viscosity and molar mass, $[\eta]M$. The poly(oxyethylene) standards conform to the Mark-Houwink equation, and the form[8] $[\eta]/(cm^3\ g^{-1}) = 0.0125\ M^{0.78}$ serves to define approximate intrinsic viscosities at 25°C. A calibration curve of $\log_{10}[\eta]M$ *versus* V_{pk} served to determine the values of $[\eta]M$ for the micelles (from their observed values of V_{pk}) which are included in Table I. Values of the hydrodynamic volumes of the micelles, $v_h = [\eta]M/2.5\ N_0$ where N_0 is Avogadro's constant, are plotted against *n*-alkyl chain length (n) and oxyethylene chain length (m) in Figs. 4a and 5a respectively.

Aggregation number

Values of $[\eta]$ at 25°C for micelles of the Texafor series of poly(oxyethylene) hexadecyl monoethers have been reported by El Eini *et al.*[9]. These values were adapted for micelles of our samples of series 1-*m*-16 as follows:

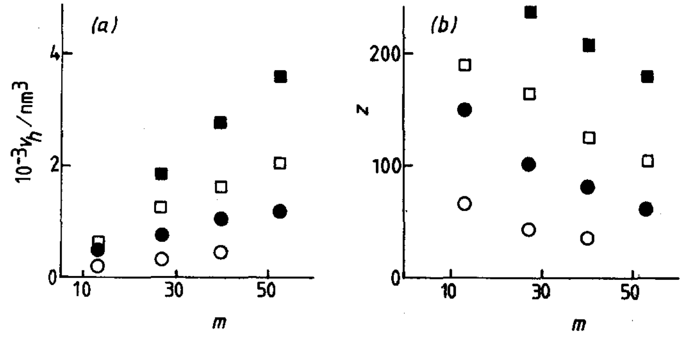

Fig. 5. (a) Hydrodynamic volume (v_h) and (b) aggregation number (z) *versus* oxyethylene chain length (m) for micelles of poly(oxyethylene) methyl-*n*-alkyl ethers of series (○) 1-*m*-14, (●) 1-*m*-16, (□) 1-*m*-18 and (■) 1-*m*-21.

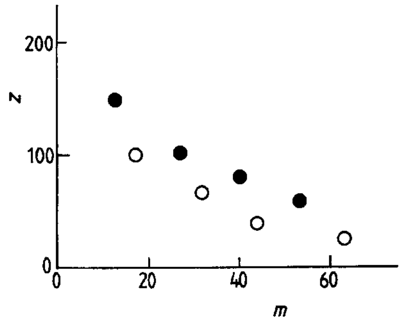

Fig. 6. Aggregation number (z) *versus* oxythylene chain length (m) for micelles of poly(oxyethylene) methyl-n-alkyl ethers of series 1-m-16. (○) Light scattering (ref. 9); (●) size-exclusion chromatography and intrinsic viscosity (this work).

m	13	27	40	53
$[\eta]/(\text{cm}^3\ \text{g}^{-1})$	5.9	7.8	9.7	11.2

Values of M, calculated from $[\eta]M$ (Table I) with values of $[\eta]$ as above, serve to define the molecular weights of the micelles and hence their aggregation numbers $z = M/M_0$, where M_0 is the molecular weight of the surfactant (equal to its formula weight). Values of z for the micelles of series 1-m-16 obtained in this way are plotted against their poly(oxyethylene) chain lengths (m) in Fig. 6. As indicated in that figure, the decrease in z with increase in m is similar in form to that found for the Texafor series by light scattering[9], although, as expected considering the experimental and theoretical difficulties in defining $[\eta]$ for an associating system, the quantitative agreement is not so good. A decrease in aggregation number with increase in poly(oxyethylene) chain length is generally found for comparable poly(oxyethylene) n-alkyl monoethers[10,11] and methyl-n-alkyl ethers[12].

The intrinsic viscosities of the micelles of the other samples cannot be so readily assessed. Our determinations of $[\eta]$ for the micelles of series 1-27-n (n = 14–21) and 1-53-n (n = 16–21) show little variation with n within an experimental scatter of $\pm 2\ \text{cm}^3\ \text{g}^{-1}$, and average values for a given series (*i.e.* given m) correlate satisfactorily with the values for the hexadecyl ethers listed above. Taking $[\eta]$ to be constant for the micelles of samples with the same oxyethylene chain length allows the values set out above to be used for other samples with the same m. The values of z obtained in this way vary with n-alkyl chain length (n) and oxyethylene chain length (m) as shown in Figs. 4b and 5b respectively. An increase in z with increase in n at constant m is in keeping with other results[13].

CONCLUSIONS

The hydrodynamic volumes of surfactant micelles can be determined by means of size-exclusion chromatography. In applying the method it is important to inject the surfactant in solution at a concentration far above its critical micelle concentration, so as to avoid complications arising from the micelle–free-chain equilibrium.

The peak elution volume in a suitably calibrated SEC system provides a direct measure of the hydrodynamic size of a micelle which is not influenced by the hydrodynamic properties of the free chains or by the characteristics of the association process provided that equilibration of micelles and free chains is rapid.

The hydrodynamic volumes of micelles of poly(oxyethylene) methyl-*n*-alkyl ethers, $CH_3(OCH_2CH_2)_mO(CH_2)_nH$, increase with increase in n when m is held constant and with increase in m when n is held constant.

The effects of block length m and n on the aggregation numbers (z) of the micelles can be roughly estimated by combining their measured hydrodynamic volumes with measures of their intrinsic viscosities. The trends in z so obtained are in agreement with those reported in the literature[10–13].

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