location is subject to considerable uncertainty'. Unfortunately, he is missing the important point we are making, i.e., we can determine an approximate distribution function, and consequently, compute not only the mean but also other moments from the distribution function as shown in our Tables 2 and 4 of ref. 2. A simple comparison of the numbers given in Tables 2 and 4 (histograms vs. cumulants) will show that the histogram method and the cumulants method are in excellent agreement.

The statement 'Despite the considerable and complex calculations required by the method and its demands on high quality data it offers no advantages over simpler fitting procedures for investigations of the concentration

dependence and indeed turn out to be not as accurate', is incorrect because for a polydisperse polymer solution, it is very difficult to determine the mean linewidth using the standard cumulants method. The force fitting of single exponentials with unjustifiable floating baselines, as Caroline[6] has done, is likely to introduce systematic errors for polydisperse polymer solutions.

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A study of micelles in a base lubricating oil by gel permeation chromatography

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Micellar solutions of two polystyrene–poly(ethylene/propylene) block copolymers in a base HVI lubricating oil were studied by gel permeation chromatography (g.p.c.). The Styragel columns employed in the work were calibrated using polyisobutylene fractions. At 50°C each copolymer solution gave a single sharp peak which was well within the resolution of the columns, indicating that the micelles were able to enter the pores of the Styragel and elute through the columns as stable particles. Analysis of the chromatograms showed that the micelles had narrow size distributions. Light scattering provided a method of determining the weight-average molecular weights and apparent mean-square radii of gyration of the micelles. Molecular weights determined from g.p.c. using the universal calibration procedure were in fair agreement with the light scattering values. Unfortunately g.p.c. experiments attempted over the range 75°–150°C were unsuccessful because the Styragel strongly absorbed the copolymer at these higher temperatures.

Introduction

Since the early 1920s investigations have been made of the reversible aggregation of amphiphiles dissolved in water, the colloidal products of aggregation being termed micelles[1,2]. More recently studies have shown that certain block[3-7] and graft[8,9] copolymers in hydrocarbon solvents that are selectively bad for one of the polymer components can also interact reversibly to form large aggregates. The aggregates are usually globular in shape and consist of a compact swollen core of insoluble polymer blocks surrounded by a protective flexible fringe of soluble blocks. These investigations indicate that association colloids can be formed in the absence of water (or other hydrogen-bonding solvents) and the hydrophobic effect. Consequently the term micelle has been extended to cover any aggregate formed under reversible conditions regardless of the nature of the solvent.

Block copolymers of the type polystyrene–poly(ethylene/propylene), designated SEP, have been found to possess good viscosity index improver properties for lubricating oils. The mechanism by which the

viscometric properties are modfied in such systems is believed to involve the formation of micelles by the block copolymers[10]. In the present work we have investigated the use of gel permeation chromatography (g.p.c.) for characterizing the micellar aggregates formed by two SEP copolymers in a base lubricating oil. The oil is a selectively bad solvent for the polystyrene blocks which form the cores of the micelles. Light scattering and dilute solution viscometry have been used to provide additional characterization data.

Experimental

Materials. The two block copolymers, SEP 1 and SEP 2, were provided by Shell Research Ltd. They had been prepared by hydrogenating the polyisoprene blocks of anionically synthesized polystyrene–polyisoprene block copolymers. Molecular characteristics of the copolymers determined by light scattering and g.p.c. (via the universal calibration procedure) in toluene are given in *Table 1*. Also listed are the percentages by weight of polystyrene in the copolymers as determined by ultra-violet spectroscopy of

Table 1 Light scattering, g.p.c. and u.v. spectroscopy values for SEP 1 and SEP 2 copolymers

Copolymer	Light scattering $\bar{M}_w/10^5$ g mol^{-1}	G.p.c.		U.v. % wt. polystyrene
		$\bar{M}_w/10^5$ g mol^{-1}	$\bar{M}_w/\bar{M}_n$	
SEP 1	1.06 ± 0.11	1.18 ± 0.12	1.14	38.5 ± 3.0
SEP 2	1.68 ± 0.17	1.53 ± 0.12	1.15	34.1 ± 3.0

chloroform solutions.

The copolymers do not aggregate in toluene which is a good solvent for both polystyrene and poly(ethylene/propylene). From the data in *Table 1* the number-average molecular weights of the polystyrene blocks were calculated to be 37 800 for SEP 1 and 47 600 for SEP 2.

The base lubricating oil used in the study was a highly paraffinic HVI oil derived from a light Iranian crude. The viscosity of the oil was 27.68 cSt at 40°C and 4.90 cSt at 100°C.

Light scattering. Measurements were made using a Sofica PGD 40B photogoniometer. Light scattering measurements were made with light of wavelength 546 nm at eleven angles from 30° to 150°. Sealed cells were used for the experiments. The instrument was calibrated using pure benzene together with a secondary glass reference standard.

Solutions were prepared by dissolving the copolymer in the oil (in the absence of air) at 135°–140°C. Frequent agitation of the solutions was required for periods up to 16 hours to ensure that all the copolymer dissolved. Samples of base lubricating oil used in the scattering experiments were subjected to the same heating procedure as the solutions to ensure optical uniformity.

Solutions and neat base oil were filtered several times at 80°C using PTFE Millipore filters of nominal pore size 0.2 μm to remove dust. Tests showed that solution concentrations were not changed by filtration. Refractive index increments were measured as a function of temperature using a Brice-Phoenix differential refractometer.

In the limit of zero angle and at low concentration, the light scattered from a solution of homopolymer, or a copolymer each chain of which has the same chemical composition, is given by[11–13]

$$(Kc/R_\theta)_{\theta=0} = \bar{M}_w^{-1} + 2A_2c + 3A_3c^2 + \ldots \qquad (1)$$

where K is an optical constant for the system in question, c the concentration, R_θ the difference between the Rayleigh ratio of the solution and that of the pure solvent, $\bar{M}_w$ the weight-average molecular weight, and A_2 and A_3 are the second and third virial coefficients. Hence for these cases the weight-average molecular weight may be readily obtained by carrying out a double extrapolation of the data to zero angle and concentration.

$$(Kc/R_\theta)_{\substack{c=0 \\ \theta=0}} = \bar{M}_w^{-1} \qquad (2)$$

In the case of copolymers that are heterogeneous in chemical composition equation (2) yields an apparent molecular weight, the value of which is dependent on the refractive index of the solvent, rather than the true weight-average molecular weight[12,13]. However, the homogeneity of the present copolymers was undoubtedly

sufficient to make this effect unimportant in the analysis of the results. For a solution of a homopolymer in the limit of zero concentration and at sufficiently small angles.

$$(Kc/R_\theta)_{c=0} = \bar{M}_w^{-1}[1 + (16\pi^2/3\lambda^2)\langle \overline{S^2}\rangle_z \sin^2(\theta/2)] \qquad (3)$$

where λ is the wavelength of the incident light in the scattering medium. The z-average root mean-square radius of gyration, $\langle \overline{S^2}\rangle_z$, may be calculated therefore from the limiting slope of the plot $(Kc/R_\theta)_{c=0}$ against $\sin^2(\theta/2)$. For a copolymer, even when the chains are homogeneous in size and chemical composition, the method yields[14] an apparent mean-square radius of gyration, $\langle S^2_*\rangle$.

For spherical micelles

$$\langle S^2_*\rangle = y\langle S^2_A\rangle + (1-y)\langle S^2_B\rangle \qquad (4a)$$

whereas the true mean-square radius of gyration

$$\langle S^2\rangle = W_A\langle S^2_A\rangle + (1-W_A)\langle S^2_B\rangle \qquad (4b)$$

In these equations $\langle S^2_A\rangle$ and $\langle S^2_B\rangle$ Are the mean-square radii of gyration of the components, A and B, about the centre of gravity of the micelle and $y = W_A v_A/v$; W_A is the weight fraction of the A component, and v_A and v are the refractive index increments of the A component and total copolymer respectively. For the two systems studied in the present work we estimate $\langle S^2_*\rangle^{1/2}$ may be up to 20% lower than $\langle \overline{S^2}\rangle_z^{1/2}$.

Viscometry. Solution flow times were measured using standard Ubbelohde viscometers. Measurements were made at seven concentrations ranging from 5×10^{-4} to 2×10^{-2} g cm^{-3} and plots of η_{sp}/c and ln η_r/c versus concentration were extrapolated to infinte dilution to obtain the intrinsic viscosity.

Gel permeation chromatography using the base lubricating oil as eluent. The HVI base oil was degassed in a reservoir tank and gravity fed through a filter to an Altex model 110 solvent metering pump. Four stainless steel columns (0.95 cm diameter and 1.22 m long) packed with Styragel of nominal pore size 10^6, 7×10^4–5×10^5, 5×10^3–1×10^4 and 5×10^2–1.5×10^3 Å were used with a flow rate of 0.3 cm^3 min^{-1}. The Styragel columns were enclosed in a pyrex pipe (10 cm diameter and 1.83 m in length) filled with vermiculite. The columns were electrically heated using Nichrome 5 resistance wire which was wound around the pyrex pipe in nine 15.2 cm sections of about 100Ω resistance each. The pyrex pipe was lagged with layers of asbestos tape and a fibre-glass shell. The temperature was controlled with the aid of a time-based proportional Tinicon temperature controller, the probe of which was placed equidistant from the pyrex pipe and the columns. Rheostats provided a means of adjusting any temperature imbalance along the columns. An electronic

thermometer was used to monitor the temperature of the columns at various positions along their length. It was found that the temperature of the columns could be controlled to better than $\pm 1°C$ of the required temperature. The detector was a Waters model R-403 differential refractometer. The latter and all connecting tubes were well lagged to minimize temperature variations. The elution volume was determined using an electronically monitored 3 cm^3 siphon counter.

Gel permeation studies of SEP 1 and SEP 2 in the base lubricating oil were attempted at five temperatures: $50°$, $75°$, $100°$, $120°$ and $150°C$. Solutions were first filtered through a 500 nm Millipore filter unit and then injected in 2 cm^3 aliquots. At $50°C$ the copolymers eluted through the columns without difficulty and gave very reproducible results. At the four higher temperatures, however, no copolymer elution was observed owing to very stong adsorption of the copolymer by the Styragel.

The columns were calibrated at $50°C$ using five polyisobutylene fractions with weight-average molecular weights: 0.189×10^5, 0.51×10^5, 2.29×10^5, 9.3×10^5 and 21.4×10^5 g mol^{-1}. The polyisobutylene fractions had been isolated from Vistanex polyisobutylene at $26°C$ using toluene/methanol as a solvent/non-solvent system. No difficulty was encountered in eluting the polyisobutylene fractions through the Styragel columns at any of the five temperatures covering the range $50°-150°C$.

Results and Discussion

Lightscattering. Measurements were made at seven temperatures from $26°$ to $80°C$. The results are given in *Table 2* and typical plots of $(Kc/R_\theta)_{\theta=0}$ against c for SEP 1 and SEP 2 are shown in *Figure 1*. The results indicate that both polymers form globular micelles in the lubricating oil. The $(Kc/R_\theta)_{\theta=0}$ against c plots are approximately linear and have positive slopes over the dilute solution region studied suggesting that for the range $26°$ to $80°C$ association equilibrium

$$NP_1 \rightleftarrows P_N$$
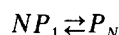
between copolymers in the free-coil form (P_1) and in the micelle form (P_N) is predominantly in favour of micelle formation.

Figure 1 Plots of $(Kc/R_\theta)_{\theta=0}$ against concentration for the polystyrene–poly(ethylene/propylene) block copolymers in the base lubricating oil at $53.8°C$ (a — SEP 1, b — SEP 2)
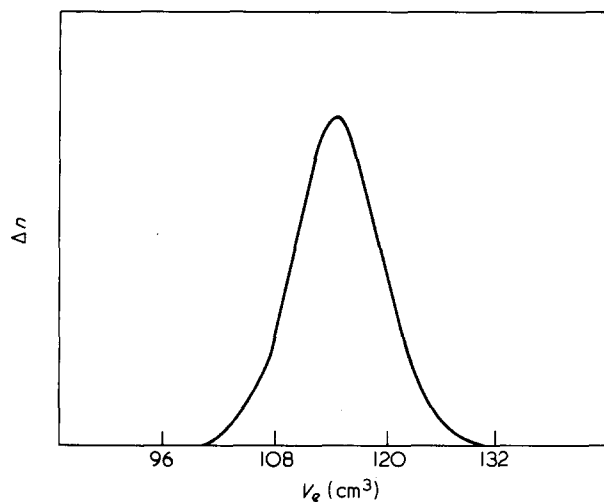
Figure 2 G.p.c. plot of refractive index difference between solution and neat oil (Δn) against elution volume (V_e) for the polystyrene–poly(ethylene/propylene) block copolymer, SEP 1, in the base lubricating oil at $50°C$

Gel permeation chromatography. At $50°C$ each copolymer solution gave a single sharp peak which was well within the resolution of the columns; a chromatogram is shown in *Figure 2*. Solutions having initial concentrations of 0.002 g cm^{-3} and 0.003 g cm^{-3} gave identical results. The low elution volumes listed in

Table 2 Light scattering results for the polystyrene–poly(ethylene/propylene) copolymers in the lubricating oil

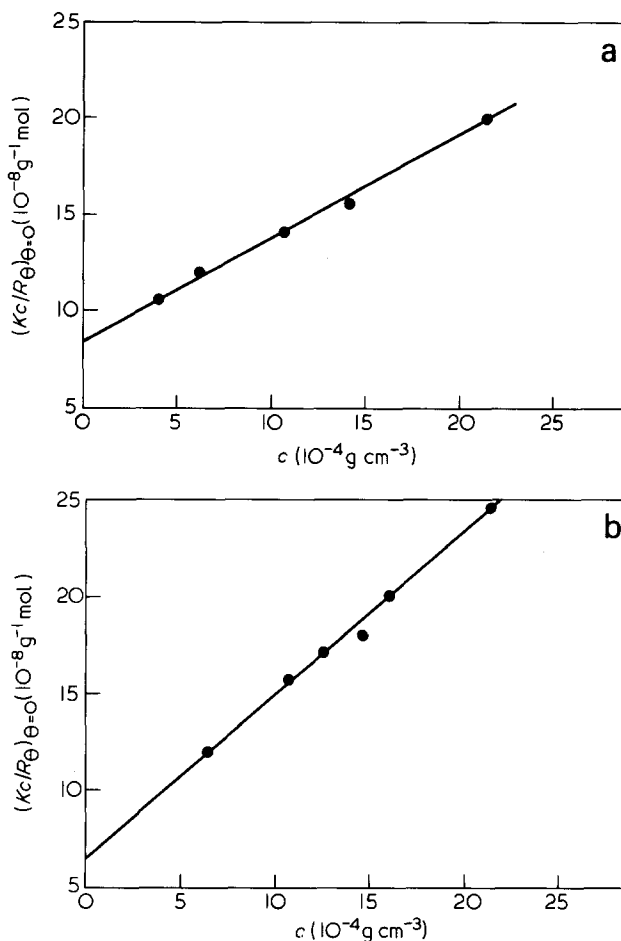| Copolymer	T ($°C$)	$\bar{M}_W$ (10^6 g mol^{-1})	$\langle S_*^2 \rangle^{1/2}$ (nm)	$\dfrac{\bar{M}_W \text{ (micelles)}}{\bar{M}_W \text{ (free-chains)}}$
SEP 1	26.0	14.0 ± 1.1	46	132
SEP 1	36.8	13.3 ± 1.1	46	125
SEP 1	45.6	12.5 ± 1.0	48	118
SEP 1	52.8	11.8 ± 0.9	46	111
SEP 1	61.0	11.7 ± 0.9	47	110
SEP 1	69.7	9.8 ± 0.8	43	92
SEP 1	80.5	9.1 ± 0.7	43	86
SEP 2	26.0	20.0 ± 1.6	50	119
SEP 2	36.8	19.2 ± 1.5	50	114
SEP 2	45.6	18.2 ± 1.5	51	108
SEP 2	52.8	15.4 ± 1.2	55	92
SEP 2	61.0	15.4 ± 1.2	51	92
SEP 2	69.7	15.2 ± 1.2	51	90
SEP 2	80.5	15.0 ± 1.2	52	89

Table 3 G.p.c. and dilute solution viscometry results for the block copolymers in the base lubricating oil at 50°C

Copolymer	Elution volume of micelle peak (cm³)	[η] (cm³ g⁻¹)	M_{pk} (10⁷ g mol⁻¹)
SEP 1	114.4	88.0	1.0 ± 0.3
SEP 2	112.2	140.0	1.2 ± 0.4

Table 3 indicate the eluting species were micelles and not free chains. The micelles were able to enter the pores of the Styragel and elute through the columns as stable species. A similar observation has been reported by our laboratory for micelles formed from a polyisoprene–polystyrene block copolymer in N,N-dimethylacetamide[4].

Comparison of the chromatograms obtained for the micelles with those for the polyisobutylene fractions using the analytical method of Hamilec and Ray[15,16] showed the micelles formed by both copolymers had very narrow size distributions ($\bar{M}_w/\bar{M}_n \leqslant 1.05$). For the SEP 1 micelles in the base lubricating oil a similar conclusion concerning the size distribution was drawn earlier from an electron-microscopy investigation[10].

The elution of many homopolymers and copolymers in g.p.c. has been shown[17] to be governed by a molecular property proportional to the product of intrinsic viscosity, [η], and molecular weight, M. When discussed in terms of the concept of the equivalent hydrodynamic sphere this implies that separation in g.p.c. is governed by the equivalent hydrodynamic volume V_η since within this framework $[\eta]M = 2.5\ V_\eta N_A$.

More recently it was found that the universal calibration method provided a satisfactory procedure for characterizing spherical microgel particles of highly crosslinked poly(styrene/divinyl benzene)[18,19]. When applied to micelles formed from a polyisoprene–polystyrene block copolymer in DMA, however, the method surprisingly gave a value for the molecular weight which was a factor of two too high[4]. For the micellar systems studied in the present work the universal calibration method was found to give molecular weights in fair agreement with the light scattering values. The results from g.p.c. are recorded in *Table 3*. Unfortunately the limits of error attached to the g.p.c. values are quite large and so agreement in this case does not provide a sensitive test of the calibration procedure.

Amphiphilic micelles in aqueous solution are believed to form and break up very rapidly. For such systems transient methods such as pressure-jump and temperature-jump methods give values for the relaxation time ranging from 10^{-5} to 10^{-2} s, while steady-state methods such as ultrasonic adsorption, n.m.r. and e.s.r. give values below 10^{-5} s.[20,21] Muller[22] has argued that the transient methods follow the slow overall breakdown of micelles whilst steady-state methods follow fast individual steps in the dynamic equilibrium. Although many aspects of the mechanism need further study, it is clear that amphiphilic micelles are able to break down very rapidly to form free surfactant molecules.

For our polymeric micelles the situation must be quite different. The micelles took approximately five and a half hours to pass through the gel yet they still eluted as a single sharp peak. This result suggests that at 50°C the rate of dissociation of micelles to free-chains must be extremely slow. It also suggests that at 50°C the polystyrene cores of the micelles are well shielded by the outer fringe of soluble poly(ethylene/propylene) blocks. Since the gel was composed of a styrene/divinylbenzene polymer it contained units that would be expected to strongly adsorb polystyrene blocks in the presence of the base oil. A small amount of polymer was generally lost in the columns during the elution process but essentially at 50°C adsorption was not a significant problem. From 75° to 150°C, however, the situation was very different. In this range adsorption prevented any copolymer material from being eluted through the columns. This problem could have arisen because the protective fringe of soluble blocks may have become less effective as a barrier and/or the relaxation time for the micelle/free-chain transition may have become shorter than the time-scale of the experiment. If the latter effect was involved the very small concentration of free-chains in dynamic equilibrium with the micelles would have been continuously drawn off by adsorption as the system passed through the columns.

It should be emphasized that whilst polymer adsorption prevented successful measurements being made on micelles at 75°C or above, at 50°C the g.p.c. chromatograms were completely reproducible. In future studies we hope to use the g.p.c. technique we have reported here for analysing micellar V.I. improvers which have been subjected to shear and thermal degradation processes. We are also investigating the possibility of using a different gel system so that some measurements can be made at higher temperatures.

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