Micellization of a polystyrene-*block*-poly(ethylene/propylene) block copolymer in ketones

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The concentration and temperature dependences on micelle formation by a polystyrene-*block*-poly(ethylene/propylene) copolymer in several ketones (methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, dipropyl ketone, 5-methyl-2-hexanone and 5-methyl-3-heptanone) are studied by laser light scattering and viscometry. No micelles were detected in solutions of 5-methyl-3-heptanone. The standard Gibbs energy, ΔG°, the standard enthalpy, ΔH°, and the standard entropy, ΔS°, of micellization were estimated from the dependence of the critical micelle temperature on concentration. The values of ΔG°, ΔH° and ΔS° were negative for all ketones studied. ΔG° and ΔH° depend on the polar character of the ketone. The weight average molar mass, second virial coefficient and apparent radius of gyration have been calculated from the standard Zimm plots obtained. Huggins and Kraemer equations have been employed to determine the limiting viscosity number of the micelles. The micelles formed in ketone solutions show larger association numbers and densities than those formed in n-alkane solutions.

(Keywords: micelle; polystyrene-*block*-poly(ethylene/propylene); ketone; structure; thermodynamics)

INTRODUCTION

Block copolymers form micelles when they are in solutions of selective solvents which are thermodynamically good solvents for one block and precipitants for the other. The micelles formed have a relatively compact core of insoluble blocks and a highly swollen shell of soluble blocks[1,2]. At concentrations above the so-called critical micelle concentration, *CMC*, all copolymer chains added to the solution aggregate to form block copolymer micelles. Thus, the *CMC* is defined as the concentration at which the experimental method used can just detect the presence of micelles in the system when the concentration is increased at constant temperature.

Chromatographic analysis[3] and electron micrographs[4,5] of the micellar particles isolated from dilute copolymer solutions show micelles that are generally spherical and have a narrow size distribution, and this justifies the use of the close association model[6].

A thermodynamic study of micelle formation can be carried out from the temperature dependence of the *CMC*. It is assumed in the analysis that micellization is a single-stage equilibrium between unassociated copolymer molecules and micelles with an association number, m:

$$mA_1 \rightleftarrows A_m \tag{1}$$

It is also assumed that m is independent of temperature and that the copolymer solution can be considered as ideally dilute except for intramicelle interactions between copolymer molecules.

For micelles having a narrow size distribution, the standard Gibbs energy of micellization per mole of copolymer chain is given by:

$$\Delta G^\circ \simeq RT\ln(CMC) - RTm^{-1}\ln([A_m]) \tag{2}$$

For copolymer systems with a high enough m and a low micelle concentration, the second term of the above equation is very small and so:

$$\Delta G^\circ \simeq RT\ln(CMC) \tag{3}$$

If m is independent of temperature, it follows from the above equation and the Gibbs–Helmholtz equation:

$$\Delta H^\circ \simeq R\frac{\mathrm{d}\ln(CMC)}{\mathrm{d}T^{-1}} \tag{4}$$

This equation allows one to estimate the contribution of the enthalpy term to ΔG°, and the standard entropy of micellization, ΔS°, can be determined from both.

Block copolymer micelles have certain features in common with micelles of low molar mass surfactant, but the thermodynamic factors responsible for association in both cases are quite different. A positive ΔS° is the thermodynamic factor mainly responsible for micelle formation for conventional surfactants. The ΔH° can be positive or negative depending on the system but, in any

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case, remains generally small[7]. In contrast, for block copolymers in organic solvents, ΔH° is solely responsible for micelle formation[8–12]. The entropy is negative and, therefore, unfavourable to micelle formation, as would be expected from simple statistical arguments.

The factors that influence the micellization process and the structural parameters of the micelles include composition[9,13], structure[14] and molar mass[15] of the copolymer, interactions between the copolymer blocks and the solvent[13,16,17], copolymer concentration[16,17], temperature[16,17] and the methods of preparation[18].

The aim of the present study was to analyse the thermodynamics of micellization and micellar structure as a function of the interactions between the block copolymer and the solvent. The investigation was carried out on a polystyrene-*block*-poly(ethylene/propylene) copolymer in different ketones: methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, dipropyl ketone, 5-methyl-2-hexanone and 5-methyl-3-heptanone. These liquids are good solvents for the polystyrene block and poor solvents for the poly(ethylene/propylene) block.

Light scattering was used to determine the temperature dependence on the *CMC* for the different ketones. Also this technique was employed to characterize the weight average molar mass, M_w, the second virial coefficient, A_2, and the apparent radius of gyration, $R_{G,app}$, of the micelles. Viscometry was used as a complementary technique. The hydrodynamic radius, R_h, of the micelles has been calculated from the values of the limiting viscosity number, $[\eta]$, and M_w.

EXPERIMENTAL

The polystyrene-*block*-poly(ethylene/propylene) copolymer sample, designated SEP2, was a commercial copolymer (Shell). It was prepared by hydrogenating the polyisoprene block of an anionically synthesized polystyrene-*block*-polyisoprene copolymer. The M_w of SEP2 determined by laser light scattering in tetrahydrofuran (THF) and chloroform, at 25°C, was 1.05×10^5 g mol^{-1}. The difference in the molar mass in both solvents was smaller than the experimental error. As both solvents have different refractive index values, this copolymer can be considered to have a homogeneous chemical composition. The ratio of the weight average to number average molar mass of SEP2 was 1.08, and was determined by size exclusion chromatography, at 25°C, using chloroform as solvent and a standard polystyrene calibration. U.v. spectroscopy of SEP2 in THF showed that the copolymer contained 35 ± 3 wt% polystyrene.

All the ketones employed (analytical purity grade) were used without further purification. Solutions were prepared by dissolving the copolymer in the ketones at high temperatures (70–100°C). In order to clarify copolymer solutions for the laser light scattering measurements, they were filtered at room temperature directly into the scattering cells, which were sealed.

Light scattering measurements were carried out using a modified FICA 42000 equipped with an He–Ne laser (Spectra-Physics, model 105) which emits vertically polarized light (632.8 nm, 5 mW).

Investigations of the thermodynamics of micellization of block copolymers in organic solvents[19] have shown that it is far better experimentally to find the critical micelle temperature, *CMT*, by carrying out measurements in which the concentration is kept constant and the scattered light intensity monitored over a range of temperatures than to determine the *CMC* by keeping the temperature constant and varying the concentration. The *CMT* of a solution at a given concentration is the temperature at which the formation of micelles can just be detected experimentally. Therefore, for block copolymers in organic solvents it has been shown that, within experimental error:

$$\frac{\mathrm{d}\ln(CMC)}{\mathrm{d}T^{-1}}=\frac{\mathrm{d}\ln(c)}{\mathrm{d}(CMT)^{-1}} \tag{5}$$

Thus, equation (4) becomes

$$\Delta H^\circ \simeq R\frac{\mathrm{d}\ln(c)}{(CMT)^{-1}} \tag{6}$$

To establish *CMT*s, measurements of light scattered intensity were carried out at a series of temperatures within the range of 25–90°C at three scattering angles (45, 90 and 135°).

Solution concentrations were recalculated at the *CMT*s. As used polymer solutions are diluted, we have assumed that the solutions have the same thermal expansion coefficient as that of the pure solvent.

To obtain classical Zimm plots, light scattering measurements were taken at 10 angles between 37.5° and 150° for each solution at 25°C. The photogoniodiffusometer was calibrated[20] with pure benzene taking the Rayleigh ratio at 25°C as 12.55×10^{-6} cm^{-1}.

The light scattered by a dilute polymer solution may be expressed as[21]:

$$\frac{Kc}{\Delta R(\theta)}=\frac{1}{M_w}\left[1+\frac{16\pi^2 n_0^2 R_G^2}{3\lambda_0^2}\sin^2(\theta/2)+\cdots\right]+2A_2c+\cdots \tag{7}$$

where c is the polymer concentration, K an optical constant, $\Delta R(\theta)$ the difference between the Rayleigh ratio of the solution and that of the pure solvent, R_G^2 the mean square radius of gyration, n_0 the solvent refractive index and λ_0 the wavelength in vacuum.

The refractive index increments, $\mathrm{d}n/\mathrm{d}c$, of the copolymer solutions were measured at 632.8 nm using a Brice-Phoenix differential refractometer, previously calibrated with solutions of highly purified NaCl, using a He–Ne laser (Spectra-Physics, model 156) with a power of 1 mW as light source.

The viscosity measurements were made in a Lauda automatic Ubbelohde viscometer (model Viscoboy 2), which was placed in a thermostatically controlled bath, with a precision of ±0.01°C. The viscometer was calibrated using several standard solvents. Kinetic energy corrections were carried out by means of the equation:

$$\eta=A\rho t-\frac{B\rho}{t} \tag{8}$$

where ρ is the density of the liquid, t the efflux time and A and B are the calibration constants ($A=1.016\times10^{-4}$ cm^2 s^{-2} and $B=4.3\times10^{-3}$ cm^2). The viscosity measurements were carried out within the polymer concentration range $2\times10^{-3}\leqslant c\leqslant 6\times10^{-3}$ g cm^{-3}. The basic solution was diluted directly in the viscometer. The data were evaluated according to the equations of Huggins[22] and Kraemer[23]:

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c \qquad (9)$$

$$\frac{\ln \eta_r}{c} = [\eta] - k_1'[\eta]^2 c \qquad (10)$$

where c is the polymer concentration, η_{sp} the specific viscosity, η_r the viscosity ratio and k_1 and k_1' are the Huggins and Kraemer coefficients, respectively.

RESULTS AND DISCUSSION

Relationships between concentration and *CMT* for the copolymer SEP2 in diethyl ketone, dipropyl ketone, methyl isobutyl ketone and 5-methyl-2-hexanone were determined. It was not possible to determine this relationship for methyl ethyl ketone and methyl propyl ketone because the *CMTs* were higher than the maximum temperature that our experimental set-up could reach. To find lower *CMTs* we must employ solutions of such low concentrations that the light scattering technique cannot be used to study them. Considering that the *CMT* corresponding to a solution with a concentration of 3×10^{-6} g cm^{-3} is >85°C, the *CMC* at 85°C is lower than this concentration. So, $\Delta G°$ corresponding to the block copolymer SEP2 in methyl ethyl ketone and methyl propyl ketone at this temperature is < -51 kJ mol^{-1}.

No micelles were detected at 25°C in a 5-methyl-3-heptanone solution with a concentration of 7×10^{-3} g cm^{-3}. Solutions with higher concentrations were not studied because going into the range of semidilute and concentrated solutions, periodic structure[24] or macroaggregates can be formed.

Light scattering intensities measured at observation angles of 45, 90 and 135°, are plotted against temperature for a methyl isobutyl ketone solution with a concentration of 1.2×10^{-4} g cm^{-3} in *Figure 1*. The shape of the curve is due to the influence of temperature on the equilibrium between micelles and free chains. At low temperatures the equilibrium is overwhelmingly in favour of micelle formation whereas at the upper end of the temperature range studied only free chains exist in the solution. On lowering the temperature from these values, a sharp increase in the scattered intensity is observed due to the appearance of micelles. Similar curves have been found when increasing and decreasing the temperature for all the systems studied, supporting the closed association model that is applied to these systems. The temperature at which the presence of micelles can just be detected in the solutions was considered as the *CMT*.

In a similar way, *CMTs* were determined for other solutions of the copolymer in methyl isobutyl ketone covering a range of concentrations, and also for solutions of the copolymer in the other ketones. All the plots were similar to the one shown in *Figure 1*.

Plots of $\ln c$ against $(CMT)^{-1}$, which are equivalent to plots of $\ln CMC$ as a function of T^{-1}, for the different ketones are shown in *Figure 2*. All these plots were linear within experimental error over the dilute solution range studied.

The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ have been calculated from the experimental data by means of equations (3) and (6) and are shown in *Table 1*. The values listed are per mole of copolymer chain. The standard states for micelles and chains[25] are states with ideally dilute solution behaviour and a concentration of 1 mol dm^{-3}. The $\Delta G°$ shows negative values for the four ketones, as expected. The $\Delta S°$ is also negative in all the ketones and, therefore, unfavourable to the micellization

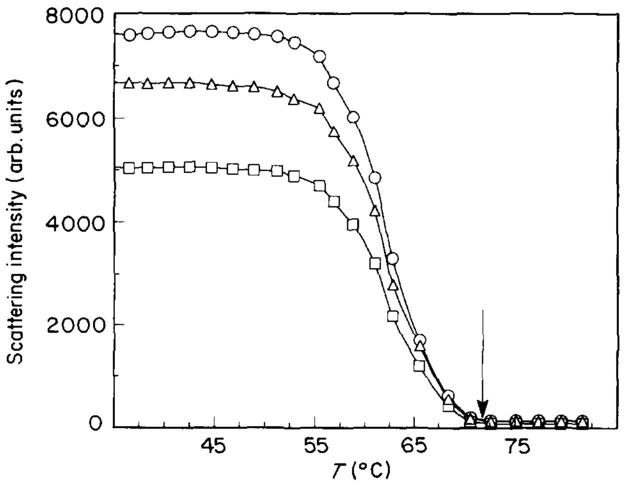

Figure 1 Plot of scattering intensity against temperature for a solution of the SEP2 copolymer in methyl isobutyl ketone ($c = 1.2 \times 10^{-4}$ g cm^{-3}). The scattered angles are 45 (○), 90 (□) and 135° (△). The arrow indicates the *CMT*

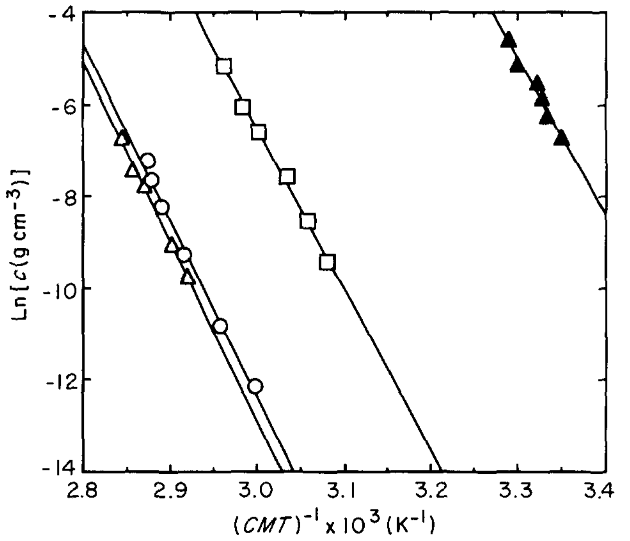

Figure 2 Plots of the logarithm of the solution concentration as a function of the reciprocal of the *CMT* for the copolymer SEP2 in different ketones: methyl isobutyl ketone (△), diethyl ketone (○), 5-methyl-2-hexanone (□) and dipropyl ketone (▲)

Table 1 Thermodynamic data for the micellization of the copolymer SEP2 in different ketones at 25°C

Solvent[a]	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})	$\Delta G°_{25°C}$ (kJ mol^{-1})	$CMC_{25°C}$ (g cm^{-3})
EEK	−318	−0.813	−75.5	5.5×10^{-12}
MIBK	−323	−0.825	−77.6	2.6×10^{-12}
MIAK	−292	−0.783	−58.5	5.7×10^{-9}
PPK	−284	−0.856	−28.6	1.0×10^{-3}

[a] EEK, diethyl ketone; MIBK, methyl isobutyl ketone; MIAK, 5-methyl-2-hexanone; PPK, dipropyl ketone

process. The thermodynamic behaviour underlying micelle formation by polystyrene-*block*-poly(ethylene/propylene) copolymer in ketones is different from that observed for micromolecular surfactants in aqueous media[7], where entropy is largely responsible for micelle formation. The negative values of the ΔS° can be explained by simple statistical arguments. The fact that the copolymer chains are less swollen in the micelles than as free chains leads to a loss in combinatorial entropy.

The ΔH° also shows negative values for the four ketones. These negative values result from the exothermic energy interchange which accompanies the replacement of poly(ethylene/propylene) segment/ketone interactions by poly(ethylene/propylene) segment/poly(ethylene/propylene) segment and ketone/ketone interactions in the formation of the micelle cores. According to the experimental results, ΔH° is solely responsible for micelle formation in the systems studied.

We can observe in *Table 1* that the thermodynamic magnitudes depend on the structure of the ketone. Two factors influence the thermodynamics: the carbon number of the ketone and the position of the ketone group in the solvent molecules. The ΔG° becomes more negative as the carbon number decreases and the ketone group is located at a more asymmetrical position on the structure. So, methyl ethyl ketone, having four carbon atoms, will show a lower ΔG°. Methyl propyl ketone shows a lower ΔG° than diethyl ketone though both have the same carbon number, because the ketone group is at the molecule centre for the diethyl ketone. The same behaviour is shown by the 5-methyl-2-hexanone and the dipropyl ketone. 5-Methyl-3-heptanone having eight carbon atoms does not show a micellization process. The ΔH° shows a similar behaviour whereas ΔS° hardly depends on the ketone type. In conclusion, the solvent selectivity of the ketones increases with the polar character of the solvent molecule.

On the other hand, if the ΔH° values obtained are compared to the values found by Quintana *et al.*[10] for a similar SEP copolymer dissolved in n-alkanes, the former values are about twice as large as the latter ones. This difference is explained by taking into account the relative length of both blocks in the copolymer. The poly(ethylene/propylene) block is approximately twice the length of the polystyrene block. The former blocks form the micelle core in the ketone solutions whereas they form the micelle shell in the n-alkane solutions. Therefore, the number of core block segment/solvent interactions replaced by core block segment/core block segment and solvent/solvent interactions through the micellization process is larger in those micelle solutions.

A Zimm plot obtained at 25°C for the system SEP2/diethyl ketone is shown in *Figure 3*. As can be seen, the concentration and observation angle dependences of $Kc/\Delta R$ are linear as expected for the experimental concentration range (1×10^{-3}–5×10^{-3} g cm^{-3}). These concentrations are very much higher than the *CMC* (*Table 1*). The M_w determined from the double extrapolation to zero angle and concentration, can be considered as the micelle molar mass, since the copolymer is chemically homogeneous and under these experimental conditions micelle formation is overwhelmingly favoured. However, the radii of gyration obtained from the angle dependences of $Kc/\Delta R$ at zero concentration are only apparent, due to the core/shell structure of the micelles and the different refractive indices of both blocks. Polystyrene blocks have a larger refractive index increment than the poly(ethylene/propylene) blocks and therefore the experimental radii of gyration are higher than the true ones.

Similar Zimm plots have been found for other ketones. The M_w, $R_{G,app}$ and A_2 values obtained from these are shown in *Table 2*.

No micelle structural parameters have been obtained for SEP2 in dipropyl ketone because the *CMC* at 25°C is 1.0×10^{-3} g cm^{-3}. In this system, the free chain/micelle equilibrium does not favour overwhelmingly micelle formation and there exists an important unimer contribution to M_w, which depends on copolymer concentration. Consequently, a sharp increase in $1/M_{w,app}$ is observed at lower copolymer concentrations (*Figure 4*).

For the system SEP2/5-methyl-3-heptanone the *CMC* is higher than the experimental concentrations and no micelles are detected. A Zimm plot which corresponds to the unassociated copolymer is found.

As can be seen in *Table 2*, the *m* values are close to 400 chains per micelle. These values are very much higher than those found by Quintana *et al.*[16] for a similar SEP

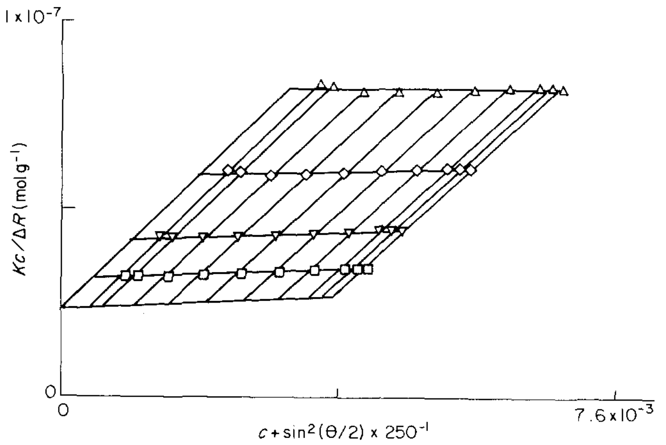

Figure 3 Zimm plot for micellar solutions of SEP2 in diethyl ketone at 25°C

Table 2 Structural parameters of the micelles formed by SEP2 in different ketones at 25°C

Solvent[a]	$[\eta]$ (cm^3 g^{-1})	R_h (nm)	$R_{G,app}$ (nm)	$A_2\times10^6$ (mol cm^3 g^{-2})	$M_w\times10^{-6}$ (g mol^{-1})	*m*
MEK	12.5	45.5	22.1	4.2	47.6	453
MPK	15.0	35.1	17.4	3.1	18.2	173
MIBK	14.0	45.4	22.4	6.8	42.2	402
EEK	17.7	49.4	25.7	9.6	43.0	409
MIAK	16.2	48.1	34.9	7.8	43.5	414

[a] MEK, methyl ethyl ketone; MPK, methyl propyl ketone; EEK, diethyl ketone; MIBK, methyl isobutyl ketone; MIAK, 5-methyl-2-hexanone; PPK, dipropyl ketone

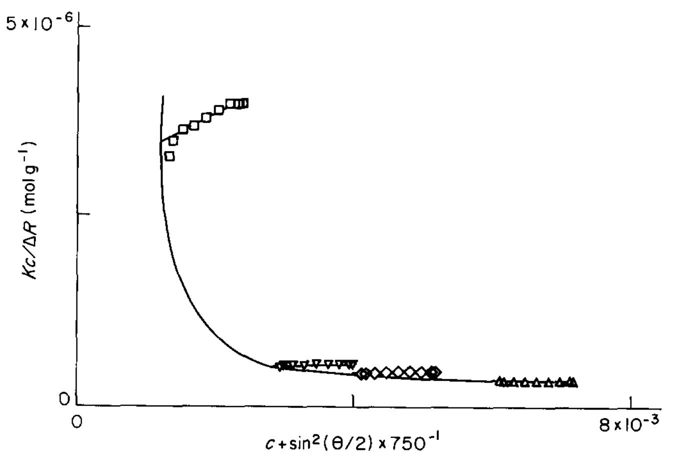

Figure 4 Zimm plot for solutions of SEP2 in dipropyl ketone at 25°C

copolymer solved in n-alkanes. The strong difference found between both types of solvent can be attributed to the location of the larger copolymer block in the micelle structure. The micelles formed in ketones have a core of poly(ethylene/propylene) segments, whereas the micelles formed in n-alkanes have a core of polystyrene segments. As the polystyrene block is shorter, the micelles with a polystyrene shell need a higher m in order to become stable.

The similarity between the M_w found for almost all the studied ketones agrees with the non-dependence of $\Delta S°$ on the type of ketone. A similar m of the micelles will lead to a similar degree of order. The low value of M_w found for the methyl propyl ketone should agree with an increase in $\Delta S°$. However it has been impossible to determine this value experimentally.

The A_2 values were determined from the concentration dependence of $Kc/\Delta R$ at zero angle and for concentrations between 1×10^{-3} g cm^{-3} and 5×10^{-3} g cm^{-3}. Assuming a segregated model with no contact between polystyrene and poly(ethylene/propylene) segments, A_2 is a weighted average of the values for the two blocks. For all ketones, A_2 shows small and positive values according to other reported systems[16,26]. These positive values can be explained by taking into account that the solvent is rejected from the micelle core leading to less unfavourable contacts between the poly(ethylene/propylene) segment and the ketone molecules. The shell of solvated polystyrene segments will hinder long range poly(ethylene/propylene) segment/poly(ethylene/propylene) segment interactions.

Although the radii of gyration obtained are apparent, they can provide qualitative information. The values shown in *Table 2* are very similar to those found by Quintana *et al.*[10] for a similar SEP copolymer in n-alkanes. However, the micelles in the ketones show M_w values between five and seven times larger than in the n-alkanes, i.e. the micelles formed in ketone solutions have a higher density than those formed in n-alkane solutions. The results suggest that, though the micelles have similar total dimensions, the micelles formed in ketone solutions have a bigger core. This fact can be explained by taking into account that these micelles have higher m values and that the poly(ethylene/propylene) blocks which form the micelle cores are the longest of both copolymer blocks.

On comparing the $R_{G,app}$ for the different ketones, similar values just above 200 Å are observed except in two cases. Methyl propyl ketone shows a lower value according to the low M_w that the micelles have in these solutions. The micelles formed in 5-methyl-2-hexanone have a larger $R_{G,app}$ coincident with a higher *CMC* (*Table 1*). This fact suggests that the micelles formed in this solvent should be more solvated since the 5-methyl-2-hexanone is less selective.

In order to obtain complementary information about the micelle structure, viscometry measurements were carried out. The experimental dependences of the reduced viscosity η_{sp}/c (Huggins equation) and of the logarithm of the viscosity number $\ln\eta_r/c$ (Kraemer equation) on the concentration were always linear within the concentration range studied (*Figure 5*), except for dipropyl ketone. There exists a large percentage of free chains in the solutions of this ketone due to the high *CMC* (1.0×10^{-3} g cm^{-3}). The free chain contribution leads to a curvature in the experimental dependences of η_{sp}/c and of $\ln\eta_r/c$ on the concentration (*Figure 6*), in a similar way to the corresponding Zimm plot.

Extrapolations to zero concentration according to the equations of Huggins and Kraemer lead to the same

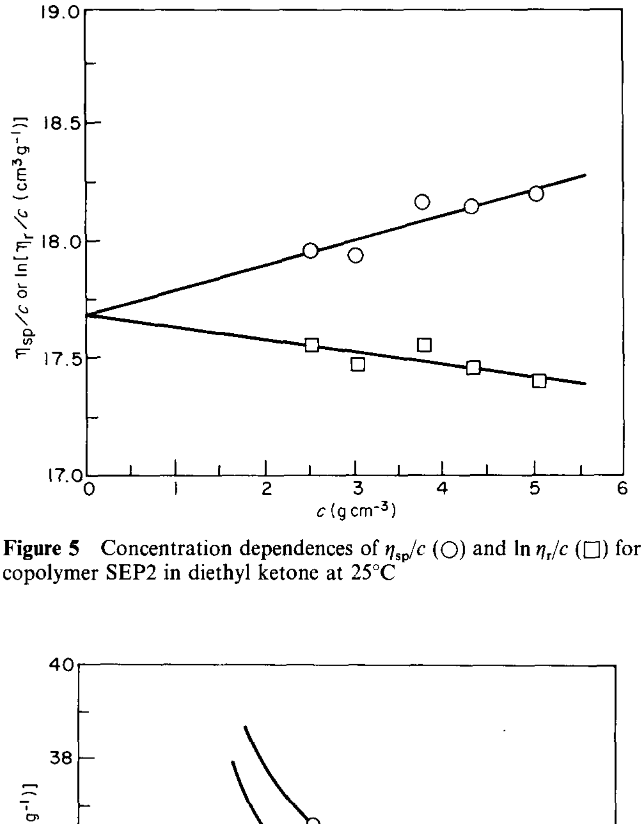

Figure 5 Concentration dependences of η_{sp}/c (○) and $\ln\eta_r/c$ (□) for copolymer SEP2 in diethyl ketone at 25°C

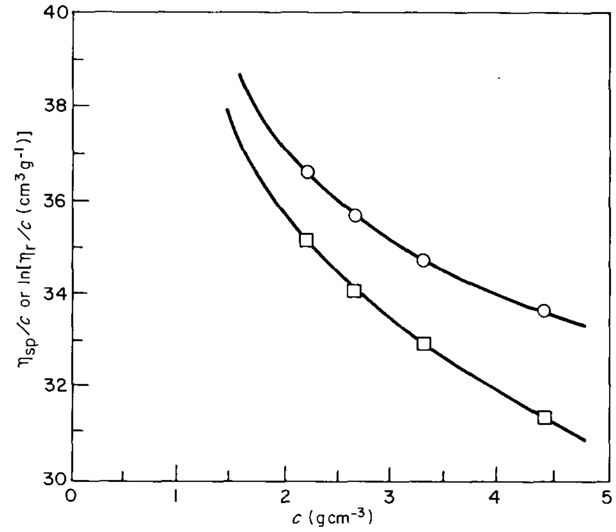

Figure 6 Concentration dependences of η_{sp}/c (○) and $\ln\eta_r/c$ (□) for copolymer SEP2 in dipropyl ketone at 25°C

values of $[\eta]$ (see *Table 2*). The values of the Huggins coefficient corresponding to all ketones were always <0.5.

The $[\eta]$ value found for solutions of 5-methyl-3-heptanone corresponds to the unassociated copolymer. The values obtained for the other ketones can be considered as those corresponding to the micelles since, under the experimental conditions, micelle formation is overwhelmingly favoured.

If the model of the hydrodynamically equivalent sphere is applied to the spherical micelles, $[\eta]$ can be expressed by the Einstein equation:

$$[\eta]=\frac{10\pi N_A}{3}\frac{R_h^3}{M} \qquad (11)$$

where M is the molar mass of the micelles and N_A is Avogadro's number. According to the above equation, $[\eta]$ is inversely proportional to the density of the micelles. Although $[\eta]$ is a viscosity average and the molar mass determined by light scattering is a weight average, both averages can be considered as similar. The spherical micelles have a narrow size distribution, as size exclusion chromatography measurements[3], sedimentation analysis[27] and electron micrographs of micelles isolated from diluted copolymer solutions[5,9] have shown.

The $[\eta]$ values of the micelles, obtained for the different ketones, are very similar and close to 15 $cm^3\,g^{-1}$. These values are very much lower than that obtained for 5-methyl-3-heptanone (53 $cm^3\,g^{-1}$); the higher value corresponds to the unassociated copolymer. This fact gives a qualitative idea of the high compactness of the micelles. Also, the $[\eta]$ values obtained for the micelles formed in ketone solutions are lower than those obtained for n-alkane solutions (65–95 $cm^3\,g^{-1}$)[16]. These results confirm the larger densities of micelles formed in ketone solutions, as suggested by the light scattering measurements.

Table 2 gives the R_h values calculated by means of equation (11). As can be seen, only the methyl propyl ketone shows a R_h value quite different and lower than the other ketones. This result is not surprising since the micelles formed in solutions of this ketone show a lower m. On the other hand, 5-methyl-2-hexanone does not show a higher R_h than the other ketones (cf. $R_{G,app}$ values).

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