The Hydrodynamic Properties of Micelles Formed by Block Copolymers of Isoprene and tert-Butylacrylate in n-Octane

Halil İbrahim ÜNAL[1*]**, Colin PRICE**[2]

[1]*Gazi University, Science and Arts Faculty, Chemistry Department,*
06500 Teknikokullar Ankara-TURKEY
[2]*Manchester University, Chemistry Department, Manchester M13 9PL-ENGLAND*
e-mail: hiunal@gazi.edu.tr

The hydrodynamic properties of micelles formed by 2 block copolymers of isoprene and tert-butylacrylate in n-octane were investigated by dynamic light scattering (DLS) over a range of temperatures and concentrations using both the cumulants and histogram methods. By means of the histogram method it was possible to determine the average hydrodynamic diameters of both micelles and unassociated-chains in the same solution. It was also used to determine the z-average fraction of unassociated-chains at a particular concentration and temperature, and it provided an alternative route when combined with static light scattering (SLS) for determining the thermodynamics of micellisation. The overall-average diffusion coefficient, $\overline{D}_z$, values and the average hydrodynamic diameters, $(\overline{d_h^{-1}})_z^{-1}$, of the 2 block copolymers were determined by means of the cumulants method.

Key Words: Block copolymers, hydrodynamic properties, micellisation.

Introduction

Recently dynamic light scattering (DLS) has been applied to various polymer systems to study a number of properties, such as macromolecular translational and rotational diffusion, particle growth during polymerisation, intermolecular interactions, and intramolecular relaxation[1−11]. The experimental data are normally acquired as an autocorrelation function of scattered light intensity from a laser light-scattering apparatus. The interpretation of the autocorrelation function to obtain molecular parameters is relatively simple if only average values from a sample with a narrow distribution are sought. However, if information about the breadth and shape of a distribution is also required, the interpretation of the intensity autocorrelation to obtain reliable information is a more challenging task; the problem becomes particularly demanding when the distribution is multimodal and the peaks of free-chains and micelles are closely spaced. The ability to determine the fine structure of the distribution becomes an important issue when characterising the size distribution of associated systems.

*Corresponding author

The most widely used methods of distribution analysis are cumulants and histogram methods[12,13]. More recently other methods based on least-squares optimisation have also been used. These include exponential sampling derived from the Laplace transform[14], a subdistribution method[15,16] a non-negatively constrained fit of a modified histogram[17,18], and a method using constrained regularisation[23−26].

In the present contribution, we report an investigation of the hydrodynamic properties of micelles formed by a polyisoprene-poly(tert-butylacrylate) 2 block copolymer in n-octane which is a selectively bad solvent for the poly(tert-butylacrylate) block. The technique which has been used in the investigation is DLS with the cumulants and histogram methods of analysis. We also report thermodynamic parameters of micellisation for the block copolymers calculated from the DLS data.

The average relaxation time, Γ, was related to the average translational diffusion coefficient, $\overline{D}$, for the system[12,23,24] by

$$\Gamma = 2\overline{D}K^2 \tag{1}$$

The scattering vector is

$$K = 4\pi \sin(\theta/2)\lambda \tag{2}$$

where λ is the wavelength of the light source in the medium and θ is the scattering angle. In using Equation (1) it is assumed that contributions to the linewidth from internal modes of motion and rotational motion are negligible. For spherical particles, the radius is related to the diffusion coefficient through the Stokes-Einstein[25] formula

$$\overline{D} = k_B T/6\pi\eta r_h \tag{3}$$

where k_B is the Boltzmann constant, T is the absolute temperature in Kelvin, η is the viscosity and r_h is the hydrodynamic radius of the particles.

Since the contribution of each species to DLS is determined by its intensity of scatter, I, the average diffusion coefficient $\overline{D}$ is given by

$$\overline{D} = \frac{\sum\limits_i I_i D_i}{\sum_i I_i} \tag{4}$$

For high polymers intramolecular interference must be taken into account. Since the intensity of scatter from any species is proportional to $w_i M_i (P\theta)_i$, the average is

$$\overline{D} = \frac{\sum\limits_i w_i M_i (P\theta)_i D_i}{\sum\limits_i w_i M_i (P\theta)_i} \tag{5}$$

where w_i is the weight of particles having molecular weight M_i, diffusion coefficient D_i and intraparticle interference function $(P\theta)_i$.

For a polydisperse system, in which all the particles are small compared with the wavelength of incident light, the $(P\theta)_i$'s = 1

$$\overline{D} = \frac{\sum\limits_i w_i M_i D_i}{\sum\limits_i w_i M_i} = \frac{\sum\limits_i z_i D_i}{\sum\limits_i z_i} = \overline{D}_z \tag{6}$$

where $\overline{D}_z$ is the z-average diffusion coefficient.

Hence the z-average diffusion coefficient $\overline{D}_z$ may be obtained from the slope of the plot of Γ versus $\mathbf{K}^2$. If the system also contains particles of the order of the wave length of the incident light for which $(P\theta)_i \neq 1$ except $\theta = 0$, it becomes necessary to determine the limiting slope of the plot as K $\to$ 0 to obtain $\overline{D}_z$. From $\overline{D}_z$ for spherical particles, the Stokes-Einstein equation leads to the z-average reciprocal hydrodynamic radius

$$\overline{(r_h^{-1})}_z = \frac{\sum\limits_i (r_h^{-1})_i w_i M_i}{\sum\limits_i w_i M_i} \tag{7}$$

i.e. the average hydrodynamic radius obtained from DLS is: $\overline{(r_h^{-1})}_z^{-1}$.

This technique has already been used for the measurement of the diffusion coefficient of micellar aggregates[26,27] and has enabled the calculation of hydrodynamic dimensions[28].

There is a weighing factor which may be introduced based on some assumptions (about the shape of the particle e.g., random, coil, rod-like) which converts the intensity distribution to the weight distribution or number distribution by dividing the intensity distribution by $d^3 P(\theta)$ or $d^6 P(\theta)$:

$$d_w = g^{(1)} \Gamma / d^3 P(\theta) \tag{8}$$

$$d_n = g^{(1)} \Gamma / d^6 P(\theta) \tag{9}$$

where d_w is the weight distribution, d_n is the number distribution, $g^{(1)}$ is the first order correlation function, d is the hydrodynamic diameter and $P(\theta)$ is the interference factor in the Rayleigh-Gans theory[29].

Experimental

The 2 previously synthesised block copolymers of isoprene and tert-butylacrylate (by sequential anionic polymerisation using tetrahydrofurane as solvent and sec-butyl lithium as primary initiator) were used and coded as COP3 and COP5. Details concerning the method of synthesis, structural characterisation and micellar properties have been described elsewhere[30]. Weight-average molecular masses, $\overline{M}_w$, determined by SLS at 20 °C and 50 °C were: for COP3 468 x 10^5 and 204 x 10^3 g mol^{-1}; and for COP5 128 x 10^5 and 101 x 10^3 g mol^{-1}, respectively. Association numbers calculated were for COP3, 229 and for COP5 126 in n-octane at 20 °C. The number-average molecular masses of polyisoprene blocks of copolymers were 31 x 10^3 and 36 x 10^3 g mol^{-1}respectively (determined by GPC in THF, using polystyrene standards). All the solvents used were Aldrich, analytical grade.

An Otsuka DLS-700 light scattering instrument with a vertically polarised uniphase 5 mW He-Ne laser was used as the light source (λ_o= 632.8 nm) and scattered radiation was detected at $\theta = 45°$ by a Hamamatsu R649S end window photomultiplier. Light from a laser was focused into a glass tube containing a dilute solution of particles. Each of the particles illuminated by the incident laser beam scatters light in all directions. The sample chamber was filled with dibutyl phthlate and the temperature was controlled to $\pm$ 0.02 °C.

Results and Discussion

Dynamic light scattering (DLS) measurements were carried out on solutions of COP3 and COP5 in n-octane, which is a selectively good solvent for polyisoprene block and a selectively bad solvent for poly(tert-butylacrylate) block[30]. The solutions of COP3 were studied at 20, 25, 30 and 50 °C, and those of COP5 were studied at 20, 25 and 30 °C. Measurements were made over a range of concentrations in each case.

DLS results obtained at the different temperatures for COP3 and COP5 in n-octane for solution concentrations of c = 2.26 g dm^{-3} and c = 2.53 g dm^{-3} are given in Tables 1 and 2, respectively. Included in the Tables are the overall-average $\overline{D}_z$ values (determined by the cumulants method) and the average hydrodynamic diameters $\overline{(d_h^{-1})}_z^{-1}$ of the 2 components of the bimodal size distribution (determined by the histogram method with non-negatively constrained least-squares, NNLS fits), which are assumed to be those of micelles and unassociated-chains. The values of $\overline{D}_z$ for COP3 and COP5 are seen to increase linearly with temperature.

Values of the overall-average $\overline{D}_z$ values for the 2 systems at 5 separate concentrations at T = 25 °C are given in Table 3.

Table 1. DLS results for COP3 in n-octane (c = 2.26 g dm^{-3}).

T °C	$\overline{D}_z/10^{-12}$ m^2/s	$\overline{(d_h^{-1})}_z^{-1}$ of micelle nm	$\overline{(d_h^{-1})}_z^{-1}$ of free-chain nm	weight % free-chain	Γ 1/s	μ/Γ^2 /10^{-2}	$\frac{d_w}{d_n}$
20	4.2 ± 0.4	184 ± 19	53 ± 4	3.0 ± 0.2	1618	8.6	1.31
25	5.0 ± 0.5	165 ± 14	48 ± 2	4.0 ± 0.2	1974	8.2	1.22
30	5.9 ± 0.9	157 ± 21	39 ± 2	9.0 ± 0.5	2304	12.0	1.08
50	28.0 ± 1.7	-	32 ± 2	100	181	29.0	1.05

Table 2. DLS results for COP5 in n-octane (c = 2.53 g dm^{-3}).

T °C	$\overline{D}_z/10^{-12}$ m^2/s	$\overline{(d_h^{-1})}_z^{-1}$ of micelle nm	$\overline{(d_h^{-1})}_z^{-1}$ of free-chain nm	weight % free-chain	Γ 1/s	μ/Γ^2 /10^{-2}	$\frac{d_w}{d_n}$
20	5.1 ± 0.2	152 ± 7	-	0.0	1968	1.0	1.01
25	5.9 ± 0.9	143 ± 19	7 ± 1	8.0 ± 1.1	2244	1.4	1.00
30	6.9 ± 1.0	136 ± 19	11 ± 1	14.0 ± 1.3	2659	1.7	1.05

In Table 1 and 2: μ/Γ^2 is the deviation from linearity, and d_w/d_n is the average polydispersity.

Table 3. Results showing the changes of the z-average diffusion coefficient with concentration for COP3 and COP5 in n-Octane at 25 °C.

COP3		COP5	
c g dm^{-3}	$\overline{D}_z/10^{-12}$ m^2 s^{-1}	c g dm^{-3}	$\overline{D}_z/10^{-12}$ m^2 s^{-1}
1.50	5.5 ± 0.6	1.50	6.1 ± 0.9
1.75	5.3 ± 0.5	1.76	6.0 ± 0.9
2.00	5.1 ± 0.5	2.06	6.0 ± 0.9
2.26	5.0 ± 0.5	2.22	5.9 ± 0.9
2.53	4.9 ± 0.5	2.53	5.8 ± 0.9

The histograms of scattering intensity versus species diameter determined at different temperatures are given in Figure 1a-d for COP3 and Figure 2a-c for COP5. The results indicate that both the unassociated-chains and the larger micellar particles had moderately narrow size distributions. The proportion of light scattered by unassociated-chains relative to micelles increased markedly as the temperature was increased, mainly due to the influence of temperature on the micelle–unassociated-chain equilibrium. It was observed that as the temperature increased the micelle/free-chain equilibrium shifted in favour of the free-chains. Relaxation time distributions of the type investigated can provide an enlightening means of obtaining semi-quantitative insights into the inter-relationships between the different components of complex systems. This approach has been used widely in polymeric systems[31−37]. Caution is necessary, however. The presence of noise on the correlograms (as well as dust in the solutions) can lead to spurious peaks. In addition, it is not possible to apportion the total scattering between the individual components. However, when peaks are well separated, as in Figures 1a-c and 2b,c the overall trends in the data become systematic and the sizes of components match those expected from the structures of the free-chain and micelle.
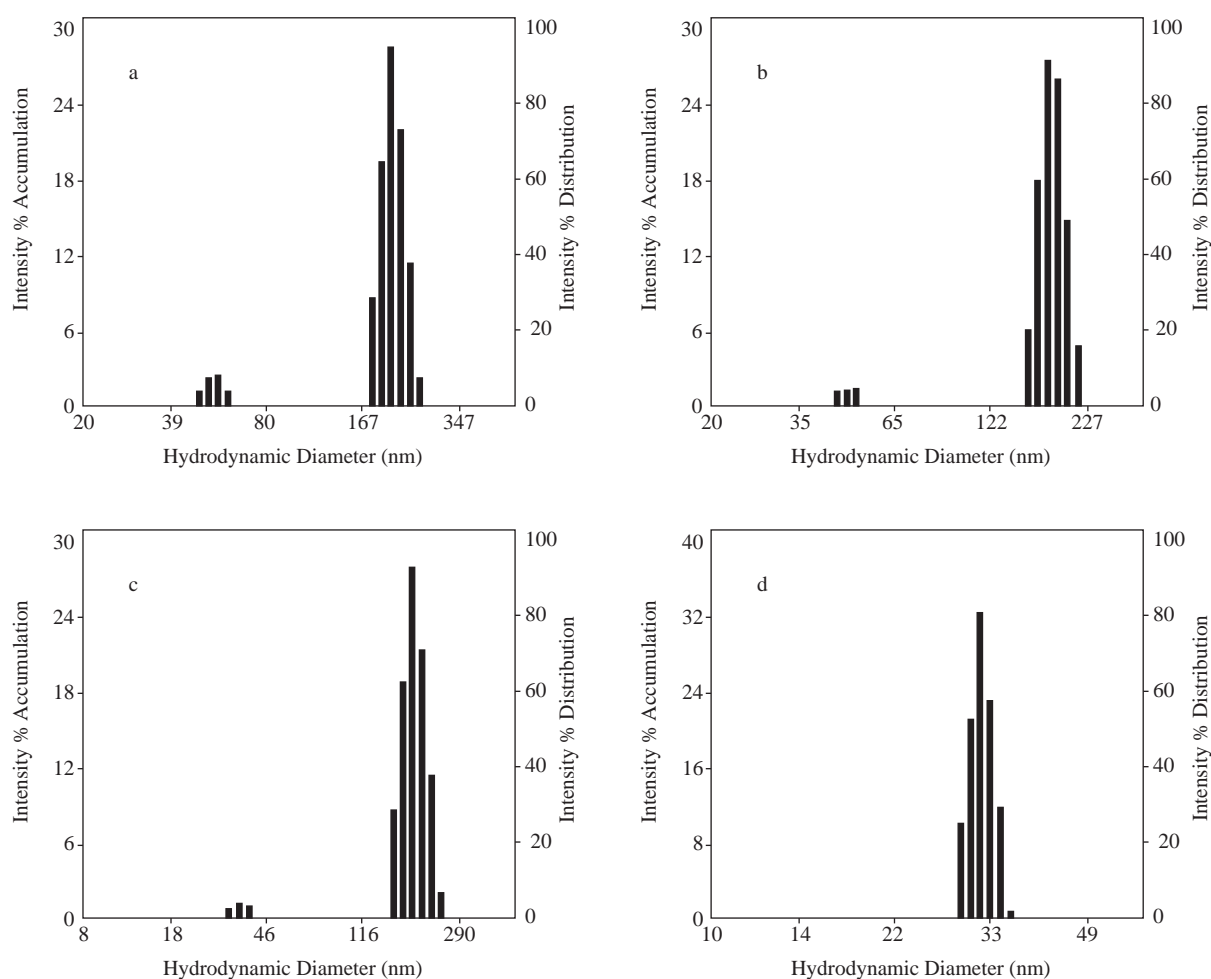

Figure 1. Histogram of the hydrodynamic diameter of COP3 at (a) 20 °C, (b) 25 °C (c) 30 °C (d) 50 °C.
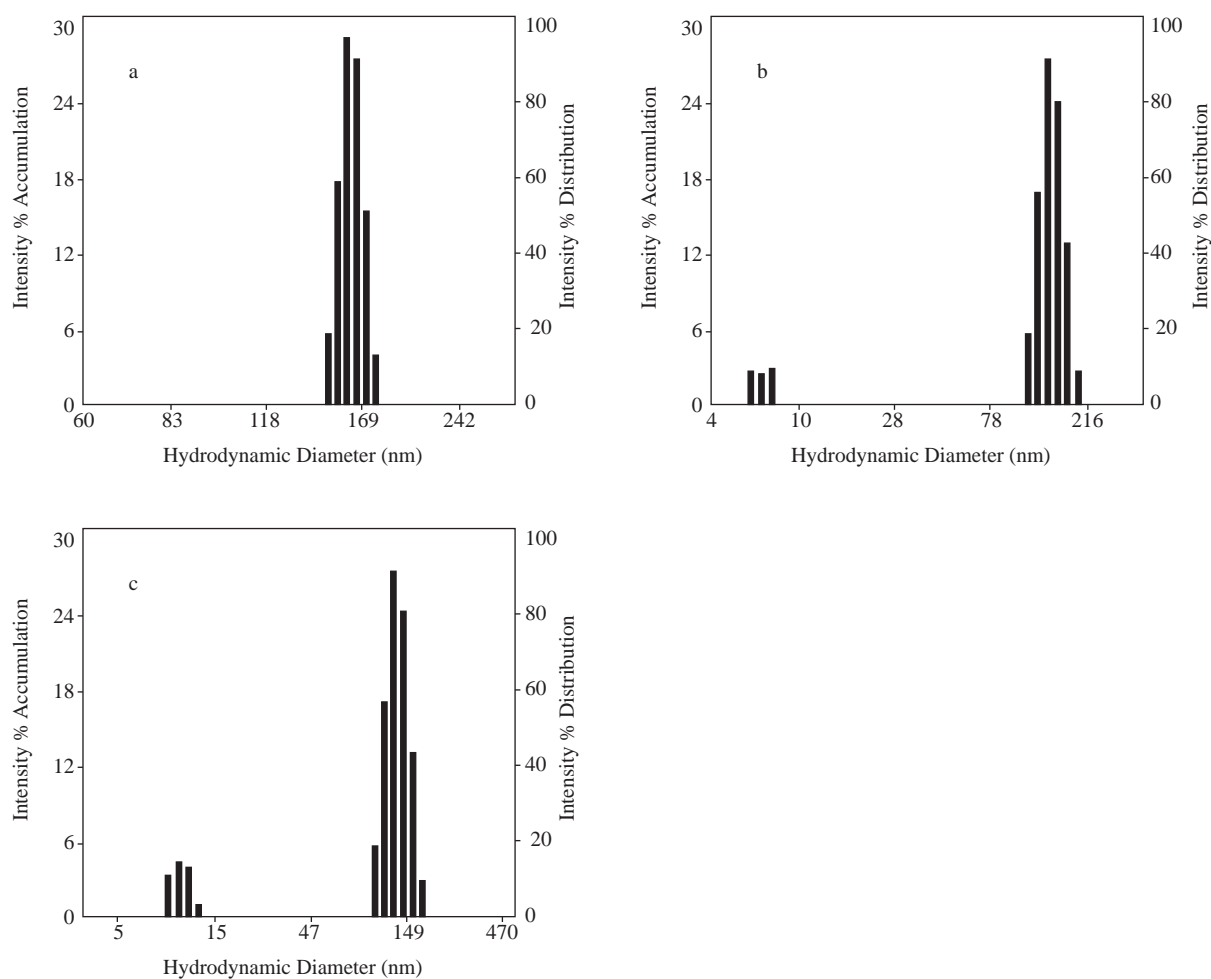
Figure 2. Histogram of the hydrodynamic diameter of COP5 at (a) 20 °C, (b) 25 °C (c) 30 °C.

Variations in the average dimensions of the micelles with temperature were within the experimental uncertainty of the measurements. Surprisingly, the hydrodynamic diameters of the unassociated-chains of COP3 showed a systematic decrease on raising the temperature. The origin of the effect is not clear and needs further investigation. One possibility is that at the lower temperatures the observed peaks contain contributions from dimeric or even trimeric species in the solution. The presence of such species has been predicted theoretically for the case of polystyrene-*block*-polyisoprene copolymers[38]. It should be noted, however, that in the case of COP5 the average dimensions of the unassociated-chain peak increased with temperature, as might have been expected, although in this case results could only be recorded for 2 temperatures. At 20 °C n-octane is a selectively good solvent for polyisoprene block and a selectively bad solvent for poly(tert-butylacrylate) block and the copolymer form micelles. As the temperature increases, n-octane becomes a good solvent for poly(tert-butylacrylate) block as well. These data are in accordance with the histograms presented in Figures 1 and 2 and change of % free-chain with temperature tabulated in Tables 1 and 2.

In the case of COP3 at 20 °C, there was approximately 3 % by weight of free-chains in micellar solution and this steadily increased with increasing temperature up to 100 % at 50 °C (Table 1). This indicated that there were no micellar particles in the solution at this temperature. This is also in very good agreement with the results obtained from the thermodynamics of micellisation work which is presented in detail in

the literature[39,40]. In the case of COP5 (Table 2) no free-chain was observed at 20 °C which indicated 100 % micellar solution, but only approximately 8 % free-chain at 25 °C and 14 % free-chain at 30 °C were observed. No free or micellar particle could be observed at 50 °C due to instrumental limitations.

Determination of Standard Gibbs Energies of Micellisation

Standard Gibbs energies of micellisation for COP3 and COP5 in n-octane were determined from the DLS data using the relationship:

$$\Delta G_m^{o\rho} = -RT \ln \frac{(\rho_m)^{1/m}}{\rho_1} \tag{10}$$

where ρ_m $(= n_m/V)$ is the molar concentration of micelles in moles dm^{-3}, ρ_1 is the molar concentration of free-chains in moles dm^{-3}, and m is the association number.

The peak areas observed for micelles, I_m, and free-chains, I_1, in the DLS experiments are proportional to $w_m M_m (P\theta)_m$ and $w_1 M_1 (P\theta)_1$ in ideally dilute solution, where w_m is the weight of micelles of molar mass M_m and particle scattering factor $(P\theta)_m$, and w_1 is the weight of free-chains of molar mass M_1 and particle scattering factor $(P\theta)_1$.

The fractions of the total scattering in DLS due to micelles, I_m', and free-chains, I_1', at c=0 (or a good approximation. at low concentration) are therefore given by

$$I_m' = \frac{I_m}{(I_1 + I_m)} = \frac{w_m M_m (P_\theta)_m}{w_1 M_1 (P_\theta)_1 + w_m M_m (P_\theta)_m} \tag{11}$$

and

$$I_m' = \frac{I_m}{(I_1 + I_m)} = \frac{w_1 M_1 (P_\theta)_1}{w_1 M_1 (P_\theta)_1 + w_m M_m (P_\theta)_m} \tag{12}$$

The weight fractions of micelles, $\overline{W}_m$, and free-chains, $\overline{W}_l$, can be determined from

$$\overline{W}_m = \frac{\frac{I_m}{(M_m)(P_\theta)_m}}{\frac{I_1}{(M_1)(P_\theta)_1} + \frac{I_m}{(M_m)(P_\theta)_m}} \tag{13}$$

and

$$\overline{W}_1 = \frac{\frac{I_1}{(M_1)(P_\theta)_1}}{\frac{I_1}{(M_1)(P_\theta)_1} + \frac{I_m}{(M_m)(P_\theta)_m}} \tag{14}$$

In applying Equations (13) and (14) in the present study, the values of I_1 and I_m were taken from DLS and the values of $M_1(P\theta)_1$ and $M_m(P\theta)_m$ from static light scattering (SLS) (see Table 4); the SLS values were established in regions which predominantly either favoured micelles or free-chains and they were assumed to be independent of temperature. The values of ρ_1 and ρ_m required for use with Equation (10) were obtained from $\rho_1 = \overline{W}_1 c/M_1(P_\theta)_1$ and $\rho_m = \overline{W}_m c/M_m(P_\theta)_m$. The values of $\overline{W}_1$ and $\overline{W}_m$ determined from DLS are given in Table 5; the values of M_1 and M_m (noting $M_m/M_1 = m$) were obtained from SLS and c (in g dm^{-3}) was the total weight concentration of polymer in the solution.

Table 4. Results obtained from SLS for COP3 and COP5 in n-octane at $\theta = 45°$.

Sample	c g dm^{-3}	$M_1(P_\theta)_1/10^5$ *(freechain)* g mol^{-1}	$M_m(P_\theta)_{m}/10^6$ *(micelle)* g mol^{-1}
COP3	2.26	1.85	16.0
COP5	2.53	1.00	7.8

Table 5. Summary of DLS data used for the calculation of the standard Gibbs energies of micellisation for COP3 and COP5 in n-octane solution at c = 2.26 g dm^{-3} and c = 2.53 g dm^{-3}, respectively.

T °C	COP3		COP5	
	$\overline{W}_1$	$\overline{W}_m$	$\overline{W}_1$	$\overline{W}_m$
20	0.030	0.97	-	1.00
25	0.040	0.96	0.08	0.91
30	0.090	0.91	0.14	0.86
50	1.00	-	1.00	-

The values of $\Delta G_m^{o\rho}$ for COP3 and COP5 in n-octane determined using Equation (10) are recorded in Table 6, and also given for comparison are values of the standard Gibbs energies of micellisation determined from SLS by the critical micelle concentration, (c.m.c), and critical micelle temperature, (c.m.T), methods[30].

Table 6. Standard Gibbs energies of micellisation for COP3 and COP5 obtained from SLS and DLS at different temperatures in n-octane solution.

T °C	COP3			COP5		
	$(1)\Delta G_m^{o\rho}{}_{(SLS)}$ kJ mol^{-1}	$(2)\Delta G_m^{o\rho}{}_{(SLS)}$ kJ mol^{-1}	$\Delta G_m^{o\rho}{}_{(DLS)}$ kJ mol^{-1}	$(1)\Delta G_m^{o\rho}{}_{(SLS)}$ kJ mol^{-1}	$(2)\Delta G_m^{o\rho}{}_{(SLS)}$ kJ mol^{-1}	$\Delta G_m^{o\rho}{}_{(DoLS)}$ kJ mol^{-1}
20	-35 ± 1	-37 ± 1	-35.7 ± 12	-34 ± 1	-38 ± 1	-
25	-	-36 ± 1	-35.0 ± 12	-	-35 ± 1	-33 ± 11
30	-	-34 ± 1	-34.0 ± 11	-	-34 ± 1	-32 ± 11

(1) Based on c.m.c from the plot of $(Kc/R_\theta)_{\theta=0}$ vs c

(2) Based on c.m.c from the plot of lnc vs (c.m.t)$^{-1}$

Standard Gibbs energies of the 2 systems at different temperatures were also calculated and showed a slight change with temperature. These are also given in Table 6 for the 2 systems. For COP3 and COP5 from the changes of the $\Delta G_m^{o\rho}$ with temperature, standard enthalpies of the micellisation $\Delta H_m^{o\rho}$ were found to be -91 ± 5 kJ mol^{-1} and -83 ± 5 kJ mol^{-1} and the entropy contributions to the micellisation, $-T\Delta S_m^{o\rho}$, were found to be 56 ± 13 kJ mol^{-1} and 48 ± 12 kJ mol^{-1}; respectively. There is seen to be fair agreement between the values obtained from the various methods. This outcome is significant since it serves to validate the use of the c.m.c and c.m.T methods which have been used extensively in recent years to investigate the thermodynamics of micellisation of block copolymers[30,39−45].

The DLS results confirm that, for the block copolymers of isoprene and t-butylacrylate in n-octane, it is the enthalpy contribution to the Gibbs energy which is the driving force behind micelle formation. As could be predicted from statistical arguments, the entropy contribution is unfavourable to micelle formation. This behaviour is in accord with results obtained from SLS[30] and in general with earlier studies of micellisation in organic solvents[39]. The behaviour is quite different from that observed for the association of amphiphilic

block copolymers and other surfactants in aqueous media, for which a favourable entropy change is largely responsible for micelle formation[41].

Conclusion

When the micelle/free-chain equilibrium overwhelmingly favours micelle formation, the micelles can be treated effectively as large macromolecules. This greatly simplifies the interpretation of the results obtained from viscometry, static and dynamic light scattering studies. It was observed that for the system studied in this work, free-chains and micelles coexist in proportions that depend sensitively on temperature and concentration. As the temperature is increased, the equliibrium shifts in favour of unassociated-chains. We may conclude that dynamic light scattering can be used to determine the weight fraction of unassociated-chains at a particular concentration and temperature and that it provides an attractive route when combined with static light scattering to that of c.m.T (or c.m.c) measurements for determining the thermodynamics functions of micellisation.

Acknowledgement

References

1. B. Chu, E. Gülari and E. Gülari, **Phys. Scr.** (Sweden), **19**, 476 (1979).

2. A.M. Jamieson and M.E. McDonnell, **Probing Polymer Structures**, Am. Chem. Soc. Adv. Chem. Ser.No. 174, p. 163, American Chemical Society, Washington, DC., 1979.

3. R. Pecora, **Macromo. Chem. Suppl.**, **2**, 73 (1979).

4. V.A. Bloomfield, **Ann. Rev. Biophys. Bioeng.**, **10**, 421 (1981).

5. W. Buchard, **Light Scattering from Polymers, Adv. Polym. Sci.**, **48**, p.1, Springer, New York, 1983.

6. G.D. Patterson, **Light Scattering from Polymers, Adv. Polym. Sci.**, **48**, p.125, Springer, New York, 1983.

7. K.S. Schmitz, **An Introduction to Dynamic Light Scattering by Macromolecules**, Academic Press, New York, 1993.

8. K. Sotiriou, A. Nannou, G. Velis and S. Pispas, **Macromolecules**, **35**, 4106 (2002).

9. J. Wu, E.M. Pearce, T.K. Kwei, A.A. Lefebvre and N.P. Balsara, **Macromolecules**, **35**, 1791 (2002).

10. M. Wang, G.Z. Zhang, D.Y. Chen, M. Jiang and S.Y. Liu, **Macromolecules**, **34**, 7172 (2001).

11. R. Saito, Y. Akiyama, M. Tanaka and K. Ishizu, **Colloid Surff. A-Physicochem. Eng. Asp.**, **153**, 305 (1999).

12. D.E. Koppel, **J. Chem. Phys.**, **54**, 4814 (1972).

13. E. Gülari, E. Gülari, Y. Tsunashima and B. Chu, **J. Chem. Phys.**, **70 (8)**, 3965 (1979).

14. N. Ostrowsky, D. Sornette, P. Parker, and E.R. Pike, **Opt. Acta.**,**28**, 1059 (1981).

15. C.Y. Cha and K.W. Min, **J. Polym. Sci. Polym. Phys. Ed.**, **19**, 1471 (1981).

16. C.Y. Cha and K.W. Min, **J. Polym. Sci. Polym. Phys. Ed.**, **22**, (1984).

17. B.E. Danheke, **Measurement of Suspended Particles by Quasi-Elastic Light Scattering.**, John Wiley and Sons, New York, 1983.

18. E.F. Grabowski and I.D. Morrison, In **Measurement of Suspended Particles by Quasi-Elastic Light Scattering.**, Ed. B.E. Danheke, p. 199John Wiley and Sons, New York, 1983.

19. S.W. Provencher, J. Hendrix, L. De Maeyer and N. Paulussen, **J. Chem. Phys.**, **69**, 4273 (1978).

20. S.W. Provencher, **Macromol. Chem.**, **180**, 247 (1979).

21. S.W. Provencher, **Comput. Phys. Commun.**, **27**, 213 (1982).

22. S.W. Provencher, **Comput. Phys. Commun.**, **27**, 229 (1982).

23. B.J. Berne and R. Pecora, **Dynamic Light Scattering with Applications to Chemistry, Biology and Physics**, Wiley-Interscience, New York, 1976.

24. W.B. Russel and A.B. Glendinning, **J. Chem. Phys.**, **74**, 948 (1981).

25. G. Stokes. **Mathematical and Physical Papers**, vol. **2**, p. 10, vol. **3**, p. 56, Cambridge University Press, 1880.

26. T.P. Lally, **Ph.D Thesis**, University of Manchester (1974).

27. D. Woods, **PhD Thesis**, University of Manchester (1973).

28. C. Price, J.D. McAdam, T.P. Lally and D. Woods, **Polymer**, **12**, 228 (1974).

29. S.A.M. Al-Chalabi and A.R. Jones, **J. Physics. D. Appl. Phys.**, **28**, 1304 (1995).

30. H.I. Ünal, C. Price, P.M. Budd and R.H. Mobbs, **Eur. Polym. J.**, **30(9)**, 1037, (1994).

31. W. Brown and T. Nicolai, **Colloid. Polym. Sci.**, **268**, 977 (1990).

32. T. Nicolai, W. Brown, R.M. Johnsen and P. Stepanek, **Macromolecules**, **23**, 1165 (1990).

33. W. Brown and S. Hvidt, **J. Phys. Chem.**, **96**, 6038 (1992).

34. Z.K. Zhou, B. Chu and D.G. Peiffer, **Macromolecules**, **26**, 1876 (1993).

35. E.J. Amis, D.F. Hodgson and W.J. Wu, **J. Polym. Sci. Pt. B-Polym. Phys.**, **31**, 2049 (1993).

36. V.J. Nagpal, R.M. Davis, Q. Liu, J. Facinelli and J.S. Riffle., **Langmuir**, **10**, 4434 (1994).

37. E.M. Pearce, T.K. Kwei, H.S. Jeon, P.K. Kesani and N.P. Balsara, **Macromolecules, 28**, 1972 (1995).

38. X-F. Yuan, A.J. Masters and C. Price, **Macromolecules**, **25**, 6876 (1992).

39. C. Price, E.K.M. Chan and R.B. Stubbersfield, **Eur. Polym. J.**, **21**, 355 (1985).

40. M. Pitsikalis, J. Woodward, J.W. Mays and N. Hadjichristidis, **Macromolecules**, **30**, 5384 (1997).

41. J.M. Corkill, J.F. Goodman and J.R. Tate, **Trans. Faraday Soc.**, **60**, 996 (1964).

42. C. Price, E.K.M. Chan, G. Pilcher and R.B. Stubbersfield, **Eur. Polym. J.**, **21**, 627 (1985).

43. C. Price, **Pure Appl. Chem.**, **55**, 1563 (1983).

44. R.A. Brown, A.J. Masters, C. Price and X.F. Yuan, In **Comprehensive Polymer Science.**, Eds. G. Allen, J.C. Bevington, C. Booth and C. Price, Vol. 2, Chap. 6, Pergamon Press, Oxford, 1989.

45. J.R. Quintana, M.D. Janez and I. Katime, **Polymer**, **39**, 2111 (1998).