Determination of Size and Shape of the Micelles by Dissymmetry Method in Different Selective Solvents

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Introduction

Block and graft copolymers in selective solvents [1] form spherical micelles. Their core consists of insoluble blocks and the shell is formed by solvated blocks. The results obtained by different techniques show that the block copolymer micellize in the same way as soap or surfactants, by the route of so called "closed association" [2].

To know the exact mechanism of micellization, it is necessary to study them in different conditions, for example using different concentrations of copolymer, different selective solvents and at different temperatures. For this purpose a few scientists [3,4] have studied in two different selective solvents and at three different temperatures. They concluded [4] that the molecular weight and size of the micelles depend on selective solvent and temperature of the system. In our last communication [5] the size of the micelles for different concentrations and temperatures was determined. The conclusions drawn were, that the mechanism and structure in all the selective solvents is same and is very much dependent on the selective solvent, composition and temperature.

In the present work a new equation is proposed. By this equation the radius of gyration of the micelles is determined. The shape of the micelles is also determined by comparing the results obtained by two different techniques.

Theoretical

The dissymmetry of a particle is given [6] as

$$Z_d \text{ (dissymmetry)} = I_\Theta / I_{(180-\Theta)} = P_\Theta / P_{(180-\Theta)} = R_\Theta / R_{(180-\Theta)} \quad \ldots\ldots\ldots(1)$$

where I,P,R, are the scattered intensity, scattering function and Rayleigh ratio respectively, measured at respective angle P_Θ for coil-like molecules is given [7] as

$$P_\Theta = 2/u^2(e^{-u} - 1 + u) \quad \ldots\ldots\ldots(2)$$

where

$$u = (4\pi/\lambda')^2 \, [Rg]^2 \sin^2\Theta/2 \quad \ldots\ldots(3)$$

For spherical particles P_Θ is given [8] as

$$P_\Theta = [3/x^3(\sin^2 x - x \cos x)]^2 \quad \ldots\ldots\ldots(4)$$

and

$$x^2 = 5/3(\pi^2 4/\lambda'^2) \, [Rg]^2 \, \text{Sin}^2\Theta/2 \quad \ldots(5)$$

Rg, Θ and λ' are the radius of gyration, angle at which the measurements are made and wave length of incident light in medium respectively. From the equations (1,2 and 3) the dissymmetry

Table: Values of radius of gyration in A^{0} units, in different solvents as determined by different methods.

Solvent used	[Rg]calculated by Zimm plots method+	[Rg]calculated by using equation (6)	[Rg]calcul. by using equation (7)
Dioxane	1220	1224	1581
Dioxane/methanol	990	774	1000
Dioxane/ethanol	840	648	836
Dioxane/n-propanol	980	765	987
Dioxane/iso-propanol	870	671	866
Dioxane/allyl alcohol	1100	866	1118
Dioxane/n-butanol	809	642	829
Dioxane/iso-butanol	590	490	632
Dioxane/tert-butanol	333	274	353
Dioxane/n-amyl alcohol	1070	866	1118
Dioxane/iso-amylalcohol	1750	1396	1802

+These results are taken from [5].

for coil-like particles is given [9] as

$$Z_{d(coil)} = 1 + 1/3\ (4\pi/\lambda')^2\ [Rg]^2\ \cos\theta \ldots (6)$$

Similarly from equations (1,4 and 5), dissymmetry for spherical particles is given as

$$Z_{d(Spheres)} = 1 + 1/5\ (4\pi/\lambda')^2 [Rg]^2\ \cos\theta \ldots (7)$$

These are straight line equations and slopes of these provide the [Rg] values for coil-like and spherical particles. To make use of these equations, it is necessary to assume the shape of the molecules as coil-like or spherical. Determining the [Rg] values in this way and by any other method like Zimm plot [5], the shape of the molecules can be confirmed. Moreover equation (7) has the same limitations as equation (6) and are explained some where else [9,10].

Experimental

The copolymer, poly (styrene/ butadiene/styrene) was micellized in ten different selective solvents (mixture of dioxane and alcohols) [5]. The dissymmetry of every sample, varying the concentration from 0.2 to 1.0% of copolymer and at different angles ie 45°, 55°,65°,75° and 90° with respect to incident light, were measured. For this purpose Brice Phoenix Light Scattering Photometer was employed. The clarification of the solution was made as before [5]. The temperature was kept constant at 25°C $\pm$ 0.02° through out the measurements.

Results and Discussion

The dissymmetries for zero concentration and for every angle were determined by extrapolation method. [Rg] values determined from these Z_d values and using equations (6,7) and Zimm Plots [5] are reported in the table. The results show that the equation (7) provide accurate and reliable results with in experimental error (in case of spherical molecules). Moreover the copolymers behave coil-like in dioxane and spherical in all the selective solvents. The differences in the values of [Rg] calculated by Zimm plots and by equation (7) shows the extant of swelling of the micelles in that selective solvent. In this way it can be concluded that the micelles are more compact in the selective solvents having stronger precipitant and vice versa. The dependence of Z_d upon Cos is shown in fig 1.

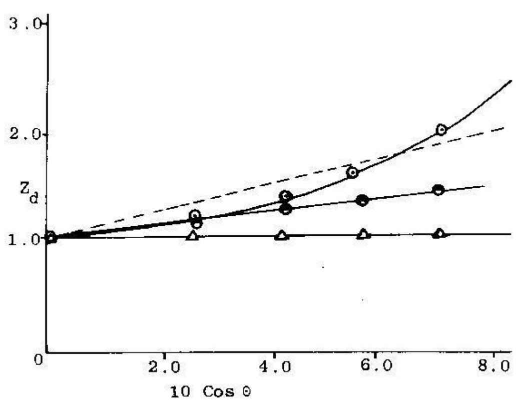

Fig.1: Dependence of dissymmetry upon Cos θ of (○) 0.8% of copolymer in dioxane/n-amyl alcohol, (Δ) in dioxane/iso-propanol and (●) 0.2% of copolymer in dioxane/ethanol

This dependence varies as the selective solvent is changed. This may be due to the change in inter - and intramolecular interactions. Which are responsible for the compactness of micelles in case of selective solvents having stronger precipitants. On the other hand the [Rg] values decreases

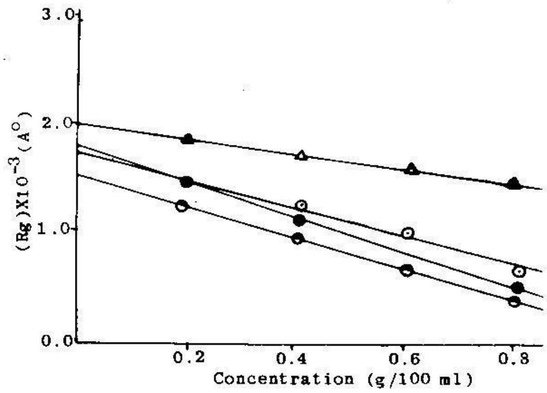

Fig.2: Radius of gyration as a function of copolymer concentration using (○) dioxane, (◒) dioxane/methanol, (●) dioxane/n-propanol and (Δ) dioxane/allyl alcohol as a solvents.

as the concentration of copolymer increases (fig. 2). This decrease is due to decrease in solvation power of the solvent. From the above given results and such type of dependence of different parameters upon each other, it can be concluded that i) The micelles change their shape from coil-like to spherical. ii) The micelles are more compact in case of selective solvent having stronger precipitant (iii) . The equation (7) proposed by us gives accurate results, with in experimental error and one can find in this way the shape of the particles.

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