Effect of Temperature upon Viscosity of Micelles in Different Selective Solvents

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Summary: Phenomenon of micellization of block copolymers in nine different selective solvents is studied. For this purpose the viscositv of the micelles in different concentrations and at different (278.16–333.16°K) temperatures is determined. By considering the change of Huggins constant and intrinsic viscosity with the change in temperature, it is concluded that the micelles are more compact at lower temperatures. They expand as the temperature is raised. At higher temperatures the solvent can not hold the molecules together and these micelles change to unimers. One maxima is observed, when the intrinsic viscosity was plotted against temperature. This may be due to the phenomenon stated above.

Introduction

In two earlier papers, we have investigated the micelles behaviour in different selective solvents. These investigations were made by light scattering. Dissymmetry was determined at different temperatures in different selective solvents (1). In this way the change of the size of the micelles with respect to temperature was determined. It was concluded that the micelles at higher temperatures may change to unimers and hence the size is decreased. To find the shape of the micelles before and after micellization and the change of shape during micellization, the dissymmetry was found at different angles in different selective dolvents (2). It was concluded that the shape of the dissolved copolymer changes from coil like to spherical particles, as the micellization takes place. It was also concluded that the compactness of these spherical micelles depends upon the selectivety of the solvent and composition of the selective solvent, in case of binary solvent system.

To explain fully the maxima observed in dissymmetry when it was plotted against temperature (1,3). It is necessary to have some more data at these temperatures, obtained by some other method, function of size and molecular weight. In this respect viscosity is the only property which can be useful. Price and Woods (4,5) performed some experiments by considering graft copolymer in a selective solvent. They obtained two maxima in the intrinsic viscosity when it was plotted against temperature. They assigned these maxima to intermolecular phase separation and intramolecular phase separation. To obtain such type of data for block copolymer in different selective solvents and to check the compactness of the micelles at different temperatures we have found the viscosity of the three block copolymer poly* (styr./butad./styr.) in eight different selective solvents. The selective solvents were prepared by mixing dioxan and alcohols. The viscosity was determined at different temperatures from 278.16–333.16°K. In this way the dependence of viscosity upon concentration in different selective solvents is studied. The dependence of K the Huggins constant(6) and intrinsic viscosity upon temperature is discussed in detail.

Experimental

Three block copolymer poly (styr./butad./stryr.) was used for this investigation. The solvents used were dioxan, mixture of dioxan and one of the following alchohol: (i) methanal, (ii) ethanol, (iii) n-propanol, (iv) iso-propanol, (v) n-butanol, (vi) iso-butanol, (vii) n-amylalcohol and (viii) iso-amylalcohol. The above solvents were selected due to their following properties. (i) They and their mixtures have different viscosity than the solute itself, (ii) These alcohols are miscible with dioxan in a required ratio and form selective

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*Poly (styrene/butadiene/styrene), trade name DST-50.

solvent, which means styrene block will be only soluble in such solvents, (iii) These alcohols have different precipitating power so one can note the effect of this upon other parameters. All the solvents were of analytical grade and distilled before use. The solution preparation and micellization is given elsewhere(1). Five different concentrations were used to measure the viscosity. These solutions were filtered using nitrogen gas pressure, through millipore filters, before making the investigations.

Viscosity Measurement:– Ostwald-Fenske capillary type viscometer was used to find out the viscosity of the solution. To minimize the experimental errors the following measurements were made. i) The positive pressure was applied to fill the viscometer. (ii) Same volumes of the solutions were taken every time, to find the viscosity. (iii) Strict measurements were made to avoid evaporation especialy at high temperatures. (iv) The temperature was kept constant upto the accuracy of ± 0.02°K of the required temperature and the solutions were kept at the required temperature for about 20 minutes before the investigations were made. The flow time was measured upto 0.01 second.

To calculate the reletive viscosity the following (7) equation was used.

$$\eta_r = \ell_i t_i / \ell t \qquad (1)$$

where η_r is the relative viscosity ℓ_i and ℓ are the density of the solution and solvent respectively: t_i and t are the flow times for solution and solvent of a specific volume respectively. As the density of the solution and solvent were same, so there was no use of finding the density of the solvent or solution. By this supposition the equation (1) becomes

$$\eta_r = t_i/t \qquad (2)$$

Reduced viscosity of the solutions was calculated by using the equation given by (7),

$$\text{Reduced viscosity} = \eta_{sp}/c = (\eta_r - 1)/c \qquad (3)$$

where η_{sp} is called specific viscosity and c is the concentration in g/ml.

Results and discussion

The reduced viscosity of block copolymer in dioxan and its dependence upon concentration at different temperatures show that the slope of the plots of reduced viscosity against concentration increases as the temperature increases, which means that the extent of interactions increases as the temperature increases. This increase is due to increase in solvation power of the solvent. The intrinsic viscosity calculated at different temperatures is plotted against temperature and is shown in fig. 1. From this figure it is clear that the intrinsic viscosity decreases as the temperature increases. This decrease in viscosity is perhaps due to stretching(8) of the polymers which takes place at high temperature, and it is due to thermal properties of the polymer and solvent used.

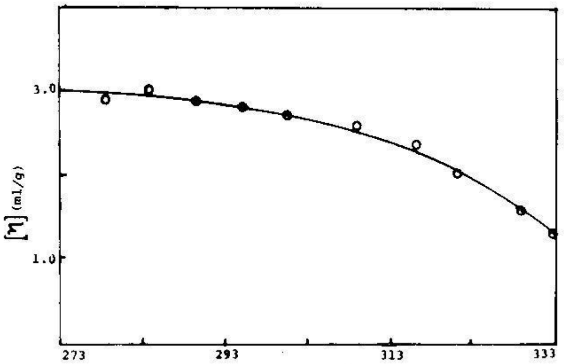

Fig. 1: Dependence of intrinsic viscosity [η] upon temperature in dioxan solvent.

The viscosity of the miceller system in different selective solvents and at different temperatures is determined. The values of the reduced viscosity were plotted against concentration for every selective solvent and for every temperature, but here only for one solvent and for a few temperatures is plotted and shown in figure 2. From these plots we concluded that the slope of these plots increases as the temperature increases. This increase is also due to the change of nature and extent of interactions, that is the solvation power of the solvent changes. Due to this effect the interactions between copolymer molecules in between themselves, the interaction between solvent species and the interaction between copolymer molecules and solvent species change with the change in temperature. Though the increase in slopes was observed for every selective solvent but the extent of increase was different for different solvents. In some cases we also obtained some negative slopes. These may be due to more interactions inbetween the copolymer, copolymer species than copolymer and solvent

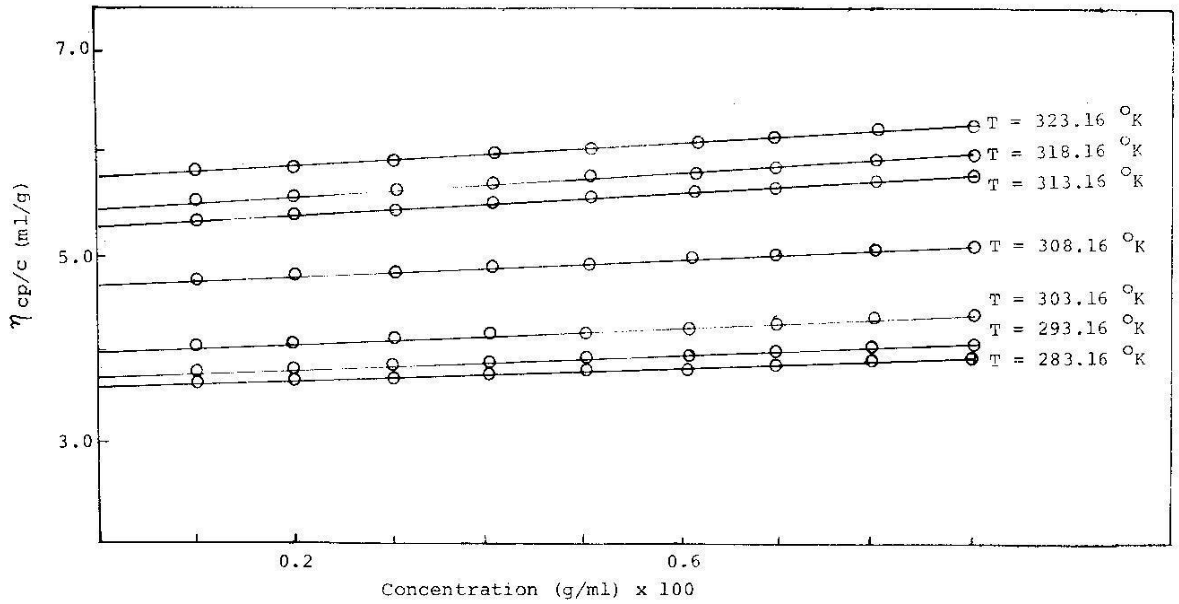

Fig. 2: Dependence of reduced viscosity of micelles at different temperatures and in dioxan/ethanol solvent upon concentration of copolymer.

molecules (9). This explanation is supported by the observations that, when we had a strong precipitant in selective solvent, then by increasing the quantity of alcohol in solvent the slopes became negative.

If we consider the Huggins$^{(6)}$ equation,

$$\eta_{sp}/c = [\eta] + K'[\eta]^2 \ c \qquad (4)$$

then the slopes of the plots of reduced viscosity versus concentration are equal to K'$[\eta]^2$ and the intercept is equal to $[\eta]$ the intrinsic viscosity, here K' is called the Huggins constant and is a function of size shape and interactions between different species in the solution. The intrinsic viscosity is also function of size of the particles and molecular weight. From this equation we calculated K′ and intrinsic viscosity at different temperatures. These values of K′ decrease as the temperature increases. The change of K′ with the change in temperature also varies from solvent to solvent, used for micellization and decreases more rapidly as the temperature is increased, in case of alcohols which are weak precipitants and used in selective solvents. The intrinsic viscosity found in this way is plotted against temperature for every selective solvent in figures 3,4. From these figures it is clear, that the intrinsic viscosity is constant upto some temperature then increases very rapidly with the increase in temperature, ultimately it approaches or tries to approach maximum value. The increase in intrinsic viscosity with respect to temperature is different for different selective solvents and the maximum is also at different temperatures. This maxima can be shifted to

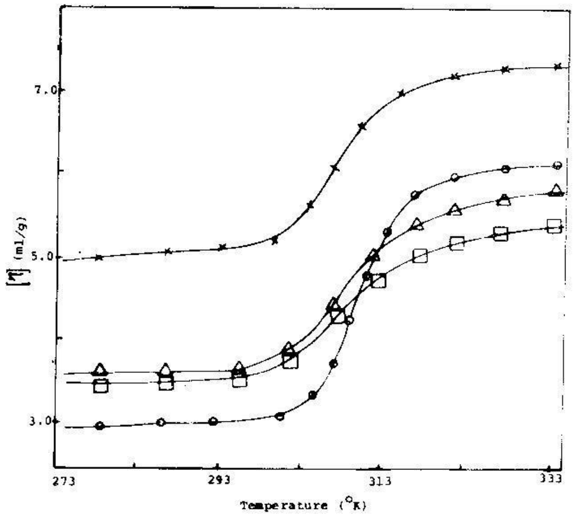

Fig. 3: Dependence of intrinsic viscosity of micelles upon temperature in the solvents (○) dioxan/methanol, (△) dioxan/ethanol,(X) n-propanol and (□) dioxan/iso-propanol.

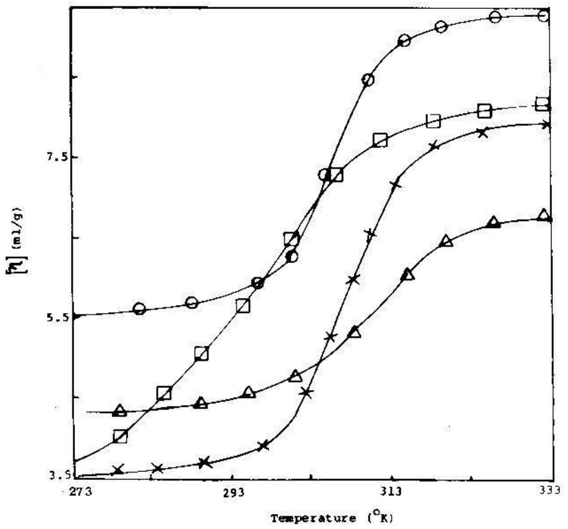

Fig. 4: Dependence of intrinsic viscosity of micelles upon temperature in the solvensts (○) dioxan/n-butanol, (△) dioxan/iso-butanol, (X) dioxan/n-amylalcohol and (□) dioxan/iso-amylalcohol.

higher or lower temperature in a particular solvent by adding more or less quantity of precipitant in the solvent. This change also effects the initial molecular weight and size of the micelles. From the dependence of K′ and intrinsic viscosity upon temperature, it can be concluded that the micelles are compact at lower temperature and expand as the temperature is increased more the selective solvent remains no more as selective but it also dissolves the butadiene block. Due to the above phenomenon the micelles change to unimers as they are already in equilibrium with the unimers(10). We think that if the temperature of such system is increased more than this, the viscosity of the system should decrease. In some cases we obtained such results but these were not so reliable to quote or conclude some thing.

Conclusion

From the results discussed above and the data already available in the literature, whether it was obtained by light scattering measurements or by viscometry, it can be concluded that the micelles properties like molecular weight, size, binding forces of micelles are dependent upon selective solvent composition, concentration of the block copolymer, and temperature of the system. The micelles go on expanding as the temperature increases and ultimately they are converted to unimers. This is due to the increase in solvation power of the solvent. Therefore it can be stated that the effect of increasing the temperature is reciprocal of the addition of precipitant in the copolymer solution.

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