STUDY OF SEDIMENTATION VELOCITY OF BLOCK COPOLYMER MICELLES

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Dedicated to Professor Václav Horák on the occasion of his 70th birthday.

No anomalies were observed during the measurement of sedimentation coefficients of block copolymer micelles formed by copolymers of styrene and methacrylic acid in a mixed solvent; 80 vol.% of dioxane and 20 vol.% water. The shapes of the sedimenting boundaries suggest that the size heterogeneity of the micelles is small. Linear relations between $1/s$ and c were obtained. The value of the hydrodynamic coefficient κ was between 2 and 4 in a good agreement with the value 2.75 or 2.86 that was obtained by combining Burgers' or Fixman's values of the coefficient of the concentration dependence k_s^V for hard spheres with Einstein's value of $[\eta]$ for spheres.

Sedimentation velocity experiments may provide many valuable insights into the nature and behavior of macromolecules and other particles. In this study we are reporting on sedimentation velocity of block copolymer micelles formed by diblock and triblock copolymers of styrene and methacrylic acid. These micelles are an object of a broad research in our laboratory. The synthesis of copolymers and evaluation of their molecular properties have been described elsewhere[1]. All our copolymer samples formed micellar solutions when dissolved in a mixture of 80 vol.% of dioxane and 20 vol.% of water (80D/20W). In these systems, the polystyrene blocks are segregated in the micellar cores that are presumably swollen by dioxane. The methacrylic acid blocks form much looser shells surrounding these cores.

In this preliminary study we are trying to answer two questions about the utility of sedimentation velocity experiments: 1. How polydisperse are the micelles? 2. Does the concentration dependence of sedimentation coefficients display anomalies connected

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with the polyelectrolyte nature of the methacrylic acid or are the polyelectrolyte effects absent in our mixed solvent?

EXPERIMENTAL

Micellar solutions were prepared by direct dissolution of dry samples in the 80D/20W solvent. Typically, the stock solution was diluted to yield four or five samples with different concentrations.

Sedimentation velocity measurements at 25 °C were performed using the Beckmann model E ultracentrifuge, with electronic speed control and Schlieren optics. The samples were loaded into Kel–F double sector cells with sapphire windows. The rotor speed was 52,000 r.p.m. The sedimentation coefficients were evaluated in a routine way.

Intrinsic viscosities were measured using Ubbelohde type viscometer with a photoelectric registration of flow times. The temperatures were controlled within 25 ± 0.01 °C.

RESULTS AND DISCUSSION

The shape of sedimentation boundaries is governed by diffusion of the solute, by polydispersity of the sedimentation coefficients, and by concentration effects in the cell (self-sharpening of the boundary). For our experiments, the shape of the boundary did not change appreciably with the change of concentration (Fig. 1). Hence we feel that the self-sharpening phenomena were moderate at worst and that the shape of the peak reflects mainly the sedimentation–diffusion processes. In all experiments, the boundary was unimodal, slightly sharper on the trailing side. The velocity of the leading edge was always less than twice the velocity of the peak maximum. Considering the fact that the hydrodynamic dimensions of micelles obtained by quasielastic light scattering (QELS) are comparable with typical dimensions of macromolecular coils, we feel that our boundary shapes reveal only moderate polydispersity of the micelles. We have not observed any indication of a slow unimer boundary for any of our samples.

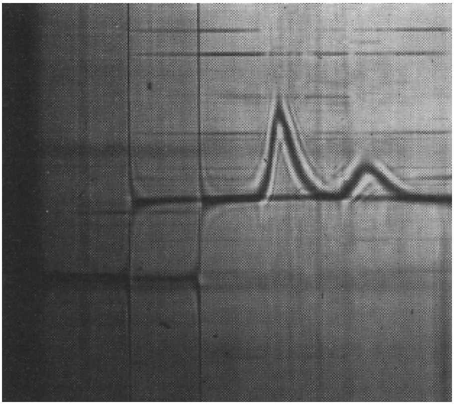

FIG. 1

Sedimentation velocity experiment. Diblock copolymer micelles SA-5 in 80D/20W solvent. Double sector cell: shorter column (right peak) c = 1.53 mg/ml; longer column (left peak) c = 3.06 mg/ml. 52,000 r.p.m., after 20 min

The concentration dependence of the sedimentation coefficients for all samples can be expressed by the standard relation:

$$1/s = (1/s_0)(1 + k_s c)\,, \qquad (1)$$

where s and s_0 are the sedimentation coefficients at finite and vanishing concentration, respectively; c is the micelle concentration and k_s is a characteristic coefficient of the concentration dependence (Figs 2 and 3).

Table I presents the s_0 and k_s values together with intrinsic viscosities $[\eta]$ and molecular weights of copolymers M_W, their polydispersities M_W/M_n, and molar fraction of the styrene units x_{ps}. The latter data were obtained by NMR and gel permeation chromatography[1].

For the hydrodynamic calculation, it is convenient to express the concentration as volume fraction ϕ that is related to mass per volume concentration c as:

$$\phi = c\upsilon\,, \qquad (2)$$

where υ is the swollen solute specific volume. The latter is different from the usual specific volume of the solute $\bar{v}$. It is also convenient to utilize a modified parameter k_s^v defined as:

$$k_s^v = k_s/\upsilon\,. \qquad (3)$$

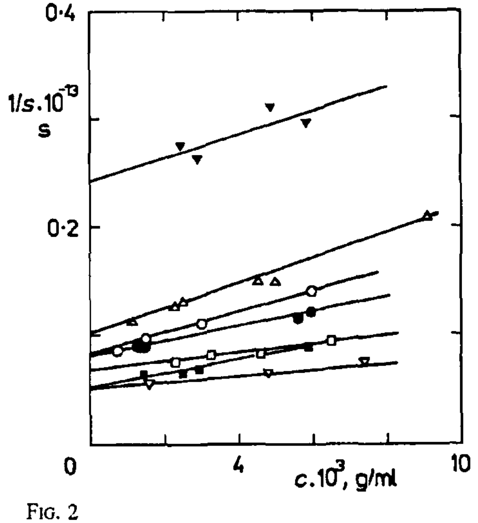

FIG. 2

The concentration dependence of sedimentation coefficients of diblock copolymer micelles in 80D/20W solvent. ● SA-1; ○ SA-2; ▽ SA-5; ▼ SA-9; □ SA-10; ■ N4SA-2; △ N1SA-4

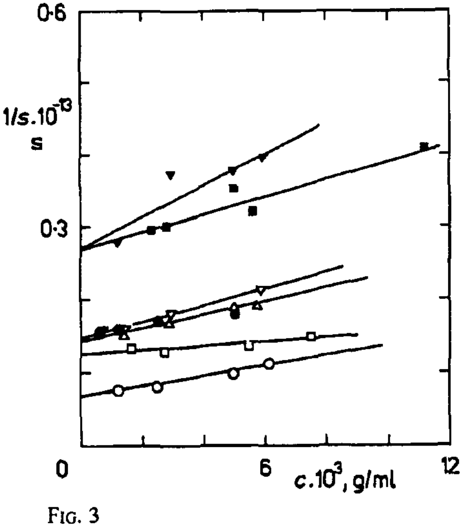

FIG. 3

The concentration dependence of sedimentation coefficients of triblock copolymer micelles in 80D/20W solvent. ○ ASA-3; ● ASA-5; ▽ ASA-6; □ ASA-7; △ ASA-8; ■ ASA-9; ▼ ASA-10

Burgers[2] analyzed the hydrodynamics of a suspension of noninteracting hard spheres. Using the perturbation method, he derived that $k_s^v = 6.875$. Pyun and Fixman[3] extending his calculation to include the higher terms, obtained $k_s^v = 7.157$.

The coefficient k_s is often related to the intrinsic viscosity $[\eta]$ as:

$$k_s = \kappa\,[\eta]\,, \tag{4}$$

where κ is a dimensionless parameter. Its value depends on both thermodynamic and hydrodynamic properties of the particles[4].

According to Einstein, for noninteracting hard spheres (swollen or not), $[\eta]$ may be expressed as:

$$[\eta] = 2.5\,\upsilon\,. \tag{5}$$

TABLE I

Some basic properties of diblock and triblock copolymers[a] and hydrodynamic properties of diblock and triblock copolymer micelles in 80D/20W solutions

Sample	M_w . 10^{-3}	$M_{w,s}$[b] . 10^{-3}	M_w/M_n	PS mole %		$[\eta]$ ml g^{-1}	k_H[c]	$s_0 \cdot 10^{13}$ s^{-1}	k_s ml g^{-1}	κ
				NMR	GPC					
				Diblock						
SA-1	50.4	24.4	1.09	56	56	19.14	1.00	12.4	80.0	4.18
SA-2	84.8	24.4	1.15	36	36	43.67	0.68	12.6	128.0	2.93
SA-4	34.3	24.8	1.06	80	78	9.37	1.26	–	–	–
SA-5	44.0	27.8	1.05	73	70	13.58	1.31	20.1	66.1	4.87
SA-9	25.4	10.8	1.07	53	50	15.27	2.14	4.1	43.8	2.87
SA-10	57.8	30.1	1.10	60	60	15.11	3.68	15.0	59.6	3.94
N4SA-2	60.4	21.3	1.08	45	43	24.12	1.61	10.1	118.7	4.92
N1SA-4	67.2	34.0	1.07	59	58	–	–	18.9	113.6	–
				Triblock						
ASA-3	81.4	45.0	1.09	61	63	19.57	1.17	15.44	109.1	5.57
ASA-4	97.6	55.9	1.09	63	65	21.58	1.49	–	–	–
ASA-5	42.0	33.0	1.09	76	83	11.59	0.68	6.55	35.9	3.10
ASA-6	61.5	33.0	1.19	52	61	28.75	1.11	6.86	76.2	2.65
ASA-7	56.7	38.3	1.08	71	74	10.98	1.32	8.05	21.5	1.96
ASA-8	81.8	38.3	1.13	51	55	28.62	0.68	7.21	69.5	2.43
ASA-9	35.2	22.5	1.12	68	71	9.63	2.07	3.83	49.2	5.11
ASA-10	45.4	22.5	1.11	55	57	16.48	2.09	3.69	82.1	4.98

[a] From ref.[1]; [b] Molecular weight of styrene block; [c] Huggins viscometric constant.

Hence

$$\kappa = k_s^v / 2.5. \quad (6)$$

The Burgers value of κ is 2.75, the Pyun and Fixman value is 2.86.

For polymer solutions, the theory of κ is based on the model of a random coil. Several theoretical treatments, each employing a slightly different model were reported. For polymers in good solvents, Van Holde and Wales[5] predicted κ equal to 1.66 and observed an average of 1.60 for many polymers. Newman and Eirich[6] also found κ = 1.4 to 1.6 for four polystyrene fractions in three solvents.

In 1962, Yamakawa[7] proposed a theory concerning κ on the basis of Kirkwood–Riseman approach. According to his model, κ is given by:

$$\kappa = 1.65\,\omega(x)\,\log(1 + 5.73\,x), \quad (7)$$

where

$$x = z / \alpha^3 .$$

Here $\omega(x)$ is a function of x; z is the volume exclusion parameter and α is the expansion factor. The theory predicts that k_s vanishes at θ condition where $x = 0$.

Pyun and Fixman[3] used the perturbation method also for polymer coils. They obtained

$$\kappa = Q_1\,((7.16 - k_0) + M A_2 Q_2 / [\eta] + \ldots), \quad (8)$$

where $Q_1 = N\,(\Phi^{1/3}/p)^{-3} / 1.62\,.\,10^4\,\pi^2 = 0.24$ is a constant; Q_2 is another constant; A_2 is the second virial coefficient and k_0 is a constant in between 4.0 and 5.0 for most polymer solutions. This theory predicts that at θ condition where A_2 vanishes, the random polymer coil has κ value between 0.52 to 0.76.

Thus, for the spherical particles, the combination of Burgers or Pyun and Fixman's theory with Einstein's theory yields κ = 2.75 or 2.86; while for random coil models, κ according to various theories is between zero and 1.66.

Our experimental values while covering a broad range, are definitely much larger than the coil values, but resonably comparable to the values of the spherical model. This is a very plausible result. Copolymer micelles are known to have a spherical shape and the swelling of the micelles is probably moderate even at the outside shell boundary (compare the low values of intrinsic viscosity). Such moderately swollen particles should behave hydrodynamically like compact spheres.

The differences of κ values among our samples are probable partly due to experimental errors, but the effect of the nonideality (which is not considered in any of the sphere-based theories) may also contribute.

In our future research we are planning to measure the density increments of micelles in order to be able to evaluate the buoyancy term $(1 - \bar{v}\rho)$ where ρ is the density of the solvent. However, the density increment and the apparent volume $\bar{v}$ are functions of both the composition of the copolymer and of the preferential adsorption in the mixed solvent. We are still developing techniques for this measurements. Once the buoyancy factor is known, we can utilize the sedimentation coefficients together with the diffusion coefficients obtained from QELS to obtain the Svedberg molecular weights.

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