Association of a three-block copolymer B–A–B in selective solvents for blocks B: spherical micelles

Ondřej Procházka, Zdeněk Tuzar and Pavel Kratochvíl
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia
(Received 5 July 1990; accepted 22 October 1990)

A theoretical model is proposed for micellization of a three-block copolymer B–A–B in solvents selective for outer blocks B. The association number, the micellar dimensions and the Gibbs energy change accompanying micelle formation are expressed in terms of the structural and thermodynamic parameters of a given block copolymer–selective solvent system.

(Keywords: three-block copolymer micelles; theory of micellization; association number; micellar dimensions; Gibbs energy of micellization)

INTRODUCTION

Micellization of block copolymers in solvents selective for one block has been approached theoretically in several studies. Nagarajan and Ganesh[1] review these studies and present a theory of their own, which deals, however, with diblock copolymers only. We therefore decided to modify Nagarajan and Ganesh's theory[1] of micelle formation for the case of a three-block copolymer B–A–B in a solvent selective for the outer blocks B. Since this work is in many respects an extension of Nagarajan and Ganesh's paper[1], their notation is used throughout.

THEORETICAL

Let us consider a three-block copolymer B–A–B with molecular volumes v_A and v_B of the respective blocks. Both blocks B are of the same length and each of the three blocks is assumed to be so long and flexible as to be considered Gaussian. Dissolved in a solvent with molecular volume v_S, the numbers of segments in blocks A and B are defined as $m_A = v_A/v_S$ and $m_B = v_B/v_S$, respectively. Under specific thermodynamic conditions, when the solvent used is good for blocks B and poor for blocks A, copolymer molecules form organized structures, i.e. multimolecular spherical micelles (*Figure 1*), consisting of a dense spherical core with a geometric radius R in a concentric shell of thickness D. The number of copolymer molecules in the micelle, g, is called the association number.

In the model of Nagarajan and Ganesh[1], a greatly simplified but generally accepted concept of a micellar core formed exclusively from blocks A is assumed. In our more realistic model, supported by a number of experimental data[2], the micellar core is partially swollen by the solvent, the average segmental fraction of which is φ_S^C. Accepting Nagarajan and Ganesh's theoretical conclusions about a very narrow distribution in the association number g, we postulate that g is the same for all micelles in a given system. For the volume of micellar core, V^C, the following formula holds true:

$$V^C = (4/3)\pi R^3 = g v_A/(1-\varphi_S^C) \tag{1}$$

The micellar shell contains $2g$ subchains of type B, highly swollen by the solvent. The shell volume, V^{Sh}, can be written, by analogy with equation (1):

$$V^{Sh} = (4/3)\pi[(R+D)^3 - R^3] = 2g v_B/(1-\varphi_S^{Sh}) \tag{2}$$

where φ_S^{Sh} is the average segmental fraction of the solvent in the shell.

Micelles in solution coexist with the molecularly dissolved copolymer (unimer). The unimer $\rightleftharpoons$ micelles equilibrium results from the existence of a minimum of the Gibbs energy, G, in the system:

$$G = N_S\mu_S + N_1\mu_1 + N_g\mu_g \tag{3}$$

where N_i is the number of particles, μ_i is the chemical potential, subscripts S, 1 and g relate to solvent, unimer and micelles with the association number g, respectively.

By differentiating equation (3) according to composition and applying the Gibbs–Duhem equation and the mass

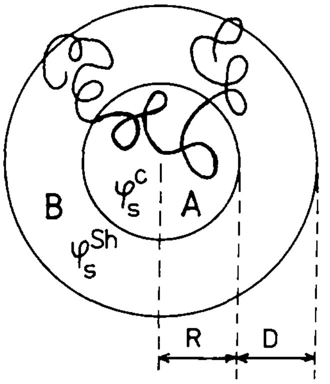

Figure 1 Sketch of a micelle of a three-block copolymer B–A–B in a solvent selective for blocks B. Thick line and thin lines refer to blocks A and B, respectively. φ_S^C and φ_S^{Sh} are the segmental solvent ratios in the core and the shell, respectively

0032-3861/91/163038-07

balance ($dN_S=0$, $dN_1+g\,dN_g=0$), we get the condition of equilibrium:

$$\mu_g/g=\mu_1 \tag{4}$$

Our expressions for the chemical potentials of unimer and micelles are based on the Flory–Huggins equation[3]:

$$\mu_1=(\mu_1^0)+kT\left[\ln\phi_1+1-m\frac{N_S+N_1+N_g}{N_S+mN_1+mgN_g}\right]+kT(1-\phi)^2m\chi_S \tag{5}$$

$$\mu_g=(\mu_g^0)+kT\left[\ln\phi_g+1-mg\frac{N_S+N_1+N_g}{N_S+mN_1+mgN_g}\right]+kT(1-\phi)^2mg\chi_S \tag{6}$$

where ϕ_1 and ϕ_g are segmental fractions of unimer and micelles, respectively, in solution:

$$\phi_1=\frac{mN_1}{N_S+mN_1+mgN_g}$$

$$\phi_g=\frac{mgN_g}{N_S+mN_1+mgN_g} \tag{7}$$

$\Phi=\Phi_1+\Phi_g$, $m=m_A+2m_B$. μ_1^0 and μ_g^0 are the standard chemical potentials of unimer and micelles, respectively, and the standard states correspond to infinite dilution.

From the equilibrium condition (4), equation (8) follows:

$$\phi_g=\phi_1\exp[g-1]\exp[-(\mu_g^0-g\mu_1^0)/kT] \tag{8}$$

For the association number of micelles, g, the condition of the minimum of the free energy per molecule is:

$$\frac{\partial(\Delta\mu_g^0/kT)}{\partial g}=0 \tag{9}$$

where $\Delta\mu_g^0=\mu_g^0/g-\mu_1^0$. The other equilibrium characteristics of micelle, i.e. R and D, can be obtained similarly:

$$\frac{\partial(\Delta\mu_g^0/kT)}{\partial R}=0,\qquad \frac{\partial(\Delta\mu_g^0/kT)}{\partial D}=0 \tag{10}$$

Gibbs energy of micellization

The relation $\Delta\mu_g^0=\mu_g^0/g-\mu_1^0$ in equation (9), representing the change in the Gibbs energy of one copolymer molecule, when transferred from the unimer state into a micelle at infinite dilution, can be divided into several contributions[1]:

$$\Delta\mu_g^0=(\Delta\mu_g^0)_{A,dil}+(\Delta\mu_g^0)_{A,def}+(\Delta\mu_g^0)_{B,dil}+(\Delta\mu_g^0)_{B,def}+(\Delta\mu_g^0)_{loc}+(\Delta\mu_g^0)_{int} \tag{11}$$

Let us consider four separate events in the process of micelle formation.

1. The middle block A, exposed to a poor solvent in the unimer state, is transferred into the micellar core. This is accompanied by changes in the local concentration of segments A and a deformation of block A. These changes are represented by the first two terms in equation (11), i.e. $(\Delta\mu_g^0)_{A,dil}$ and $(\Delta\mu_g^0)_{A,def}$.
2. The solvated outer blocks B in the unimer state are transferred to a micellar shell, highly swollen by the good solvent. As in the case of block A, in this case changes in the local segment concentration and deformation contribute also to a change in the Gibbs energy ($(\Delta\mu_g^0)_{B,dil}$, $(\Delta\mu_g^0)_{B,def}$).
3. The localization of the block A/block B joint into the interface is represented by the pure entropic contribution $(\Delta\mu_g^0)_{loc}$.
4. The generation of the core/shell interface is described by the last term, $(\Delta\mu_g^0)_{int}$.

Change in dilution of block A. In the unimer state, this block assumes a collapsed, globule-like conformation. The globule of radius R_A^u contains the segmental solvent ratio φ_S^u. Nagarajan and Ganesh[1], following de Gennes' argument[4], estimate the expansion of a polymer chain in poor solvent, assuming that the globule is in equilibrium with ambient solvent, and that the external osmotic pressure Π inside the globule is expressed in terms of the Flory–Huggins equation[1]:

$$\frac{\Pi}{\mathscr{R}T}=\frac{1}{V_S}\left[\ln\varphi_S^u+\left(1-\frac{1}{m_A}\right)(1-\varphi_S^u)+\chi_{AS}(1-\varphi_S^u)^2\right]=0 \tag{12}$$

where V_S is the molar volume of solvent.

By solving equation (12) we get the segmental ratio of solvent in the globule of block A in the unimer state and its volume V_A^u $(=(4/3)\pi(R_A^u)^3)$:

$$V_A^u=v_A(1-\varphi_S^u) \tag{13}$$

In the micellar state the blocks A are in the micellar cores. The contribution $(\Delta\mu_g^0)_{A,dil}$ can be written as the difference between the Gibbs energy of mixing of the block A in a micellar core and in a unimolecular globule:

$$\frac{(\Delta\mu_g^0)_{A,dil}}{kT}=\frac{V^C-gv_A}{gv_A}\ln\varphi_S^C+\chi_{AS}m_A\varphi_S^C-\frac{V_A^u-v_A}{v_S}\ln\varphi_S^u-\chi_{AS}m_A\varphi_S^u-\frac{\sigma_{AS}}{kT}4\pi(R_A^u)^2(1-\varphi_S^u) \tag{14}$$

The last term in equation (14), depicting the interfacial energy of the unimolecular globule, is expressed as the product of the globule surface and the effective surface tension, $\sigma_{AS}(1-\varphi_S^u)$; σ_{AS} is the interfacial tension between pure component A and solvent, which Helfand and Tagami[5] estimated from χ_{AS}:

$$\sigma_{AS}=\frac{kT}{l^2}\left(\frac{\chi_{AS}}{6}\right)^{1/2} \tag{15}$$

where $l=v_S^{1/3}$ is the characteristic segment length. The decrease in the interfacial energy caused by the presence of solvent inside the globule is taken into account by the factor $(1-\varphi_S^u)$.

Change in deformation of block A. The deformation of block A in the unimer state is characterized by the ratio of diameter of the globule, $2R_A^u$, to its unperturbed dimensions. In the micellar state we suppose that both block A/block B joints are located in the core/shell interface and that blocks A are distributed uniformly in the core volume. To satisfy this demand, we use an approximation employed by ten Brinke and Hadziioannou[6]: we represent (for this purpose only) the middle block by two separate linear chains, each half the length of the original one, their root mean square end-to-end distance being equal to the core radius. The reduction in entropy (per chain) due to loop formation of the middle block is:

$$\frac{(\Delta\mu_g^0)_{loop}}{kT}=\tfrac{3}{2}\beta\ln m_A$$

where β is unity as long as the excluded volume effects can be neglected, and $\beta > 1$ when excluded volume effects become important[6]. As this term does not depend on g, R and D, we do not include it in our calculations.

The following relation for the deformation energy has been derived under two assumptions: the chains in a micellar core are subject to one-directional deformation; and in the unimer state, the chain forming a globule is bulk compressed:

$$\frac{(\Delta\mu_g^0)_{A,\mathrm{def}}}{kT}=\left[\frac{2R^2}{m_A l^2}+\frac{(m_A/2)^{1/2}l}{R}-3\right]-\left[\frac{3}{2}\left(\frac{4R_A^{u^2}}{m_A l^2}-1\right)-3\ln\left(\frac{2R_A^u}{m_A^{1/2}l}\right)\right] \qquad (16)$$

Change in dilution of blocks B. This contribution to the Gibbs energy of micellization can be estimated in the same way as in the case of block A, only it should be kept in mind that there are two blocks B in one copolymer molecule. In the unimer state, each block B is supposed to form a coil of volume V_B^u $(=(4/3)\pi(R_B^u)^3)$, where $2R_B^u$ equals the root mean square end-to-end distance. The degree of swelling of block B in the good solvent, expressed by the expansion coefficient α_B $(=2R_B^u/m^{1/2}l)$, can be evaluated from the Flory equation modified by Stockmayer[7]:

$$\alpha_B^5-\alpha_B^3=0.88(0.5-\chi_{BS})m_B^{1/2} \qquad (17)$$

The contribution from both blocks to the Gibbs energy reads:

$$\frac{(\Delta\mu_g^0)_{B,\mathrm{dil}}}{kT}=\varphi_S^{Sh}\frac{V^{Sh}}{v_S}\ln\varphi_S^{Sh}+\chi_{BS}2m_B\varphi_S^{Sh}-2\left[\frac{V_B^u-v_B}{v_S}\ln\frac{V_B^u-v_B}{V_B^u}+\chi_{BS}m_B\frac{V_B^u-v_B}{V_B^u}\right] \qquad (18)$$

Change in deformation of blocks B. The micellar shell thickness, D, is defined as the root mean square end-to-end distance of block B. The deformation energy of block B is then a function of $D/m_B^{1/2}l$.

In the unimer state the blocks B are solvated by the thermodynamically good solvent and their conformation is characterized by the expansion coefficient α_B (cf. equation (19)). The difference between the energy of deformation of both blocks B in a micelle and in the unimer state is given by the relation[3]:

$$\frac{(\Delta\mu_g^0)_{B,\mathrm{def}}}{kT}=\left(\frac{D^2}{m_B l^2}+2\frac{m_B^{1/2}l}{D}-3\right)-[3(\alpha_B^2-1)-\ln\alpha_B^3] \qquad (19)$$

Localization of a copolymer molecule. In the process of micelle formation, the copolymer molecule is positioned in the micelle so that both block A/block B joints are anchored at the core/shell interface. The decrease in entropy connected with this localization can be estimated from the probability of finding both joints in the interface with the surface area $4\pi R^2$ and thickness l. The entropy decrease connected with the localization of one joint is given by the ratio of the interfacial volume to the volume of the whole micelle; that connected with the localization of the second joint is given by the probability of finding both ends of the block A in the same spherical concentric layer with diameter $2R$ and thickness l (see Appendix):

$$W(R)=\left(\frac{3}{2\pi m_A}\right)^{1/2}\left[1-\exp\left(-\frac{6R^2}{m_A l^2}\right)\right] \qquad (20)$$

The Gibbs energy contribution due to localization is given by:

$$\frac{(\Delta\mu_g^0)_{\mathrm{loc}}}{kT}=-\ln\left(\frac{3R^2l}{(R+D)^3}\right)-\ln\left\{\left(\frac{3}{2\pi m_A}\right)^{1/2}\left[1-\exp\left(-\frac{6R^2}{m_A l^2}\right)\right]\right\} \qquad (21)$$

Formation of the core/shell interface. Micellization is accompanied by the formation of an interface between the core containing blocks A and a small amount of solvent (segmental ratio φ_S^C), and the shell containing blocks B with a substantially higher amount of solvent. The corresponding contribution to the Gibbs energy can be expressed as the product of the interfacial area and the effective interfacial tension, $[\sigma_{AS}/(kT)](1-\varphi_S^C)$ (equation (15)):

$$\frac{(\Delta\mu_g^0)_{\mathrm{int}}}{kT}=\frac{\sigma_{AS}}{kT}\frac{4\pi R^2}{g}(1-\varphi_S^C) \qquad (22)$$

The last term in equation (14) should be logically included in equation (22); we are leaving it where it is for the sake of a clearer comparison with Nagarajan and Ganesh's study[1].

Comparison with experiment

We have chosen two micellizing B–A–B three-block copolymer/selective solvent systems, for which experimental data (weight-average molar mass, M_w, and mass fraction of component B, w_B) are known: (i) polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene ($M_w = 74\times10^3$ g mol^{-1}, $w_{PS}=0.72$) in 1,4-dioxane[8] (PS-PhB-PS/dioxane); and (ii) polystyrene-*block*-polybutadiene-*block*-polystyrene ($M_w=140\times10^3$ g mol^{-1}, $w_{PS}=0.49$) in methyl ethyl ketone[9] (PS-PB-PS/MEK). We have also evaluated a model system polybutadiene-*block*-polystyrene-*block*-polybutadiene ($M_w=64.7\times10^3$ g mol^{-1}, $w_{PS}=0.76$) in heptane (PB-PS-PB/heptane) for comparing the results with those of Nagarajan and Ganesh[1] for the system PB-PS/heptane (*Table 1*). Molecular volumes of the repeating units are: 108.5 Å^3 for hydrogenated butadiene[10], 161.2 Å^3 for styrene and 244.7 Å^3 for butadiene[1]. Molecular volumes v_S of solvents are given in *Table 1*. From those values v_A, v_B, m_A, and m_B for given molar masses, and l $(=v_S^{1/3})$, can be calculated.

For the evaluation of $\Delta\mu_g^0$, numerical values of χ_{AS} and χ_{BS} must be known. Since they are not accessible from direct measurement, values based on the Hildebrant solubility parameters δ must be calculated[11]:

$$\chi_{IS}\cong0.35+\frac{V_S}{\mathcal{R}T}(\delta_I-\delta_S)^2 \qquad (23)$$

when estimated in this way, χ_{IS} cannot be taken as fully reliable, due to the limited applicability of δ parameters for systems with polar interactions, to a large scatter of their values for most polymers in the literature[10], and to the approximate character of the relation (23) (for example, $\chi_{PS\text{-heptane}}$ is 1.06 from the solubility parameters and 1.9, as quoted by Noolandi and Hong[12]). For this reason we have investigated and will demonstrate below the influence of χ_{IS} values on the micellar parameters.

Table 1 Input values for the evaluation of micellar parameters of copolymers B–A–B or B–A in a solvent. Extreme values of δ_i and χ_{iS} are in parentheses

	PS-PhB-PS/dioxane	PS-PB-PS/MEK	PB-PS/heptane
M (g mol^{-1})	74000	140000	64700
M_A (g mol^{-1})	53280	68600	15530
M_B (g mol^{-1})	10360	35700	49170
v_S (Å^3)	142.3 (ref. 10)	149.6 (ref. 10)	244.7 (ref. 1)
v_A (Å^3)	103040 (ref. 10)	119600 (ref. 1)	48100 (ref. 1)
v_B (Å^3)	16040 (ref. 1)	55280 (ref. 1)	85710 (ref. 1)
δ_S (cal$^{1/2}$ cm$^{-3/2}$)	10.0 (9.9) (ref. 10)	9.3 (ref. 10)	7.4 (ref. 10)
δ_A (cal$^{1/2}$ cm$^{-3/2}$)	8.1 (ref. 10)	8.1 (7.16) (ref. 10)	9.1 (ref. 10)
δ_B (cal$^{1/2}$ cm$^{-3/2}$)	9.1 (ref. 10)	9.1 (ref. 10)	8.1 (ref. 10)
χ_{AS}	0.87 (0.82)	0.57 (1.05)	1.06 (1.90) (ref. 12)
χ_{BS}	0.47 (0.44)	0.36	0.47 (0.50) (ref. 1)
g^{exp}	69 (ref. 8)	264 (ref. 9)	291[a]

[a] Calculated value from reference 1

Table 2 Calculated values of the micellar parameters. Values in parentheses correspond to the δ_i and χ_{iS} values in parentheses in *Table 1*

	PS-PhB-PS/dioxane	PS-PB-PS/MEK
g^{exp}	69	264
g^{calc}	415 (362)	42 (303)
R (Å)	259 (254)	262 (231)
(φ_S^C)	0.413 (0.459)	0.933 (0.297)
D (Å)	81 (83)	144 (273)
$\Delta\mu_g^0$ (kT)	−96.6 (−90.1)	−46.1 (−114.4)

Table 3 Calculated values of the micellar parameters of two model systems. Values in parentheses correspond to the δ_i and χ_{iS} values in parentheses in *Table 1*

	PB-PS-PB/heptane	
M (g mol^{-1})	64700	129400
M_A (g mol^{-1})	15530	31060
M_B (g mol^{-1})	24590	49170
g^{calc}	54 (93)	92 (165)
R (Å)	76 (84)	115 (127)
φ_S^C	0.308 (0.084)	0.300 (0.083)
D (Å)	137 (147)	231 (246)
$\Delta\mu_g^0$ (kT)	−19.4 (−34.0)	−36.0 (−60.3)

Table 4 Values of the micellar parameters calculated by means of equations (24) and (25) for $(\Delta\mu_g^0)_{A,def}$ and $(\Delta\mu_g^0)_{B,def}$. Values in parentheses correspond to the δ_i and χ_{iS} values in parentheses in *Table 1*

	PS-PhB-PS/dioxane	PS-PB-PS/MEK
g^{exp}	69	264
g^{calc}	157 (137)	20 (123)
R (Å)	187 (184)	188 (171)
φ_S^C	0.412 (0.458)	0.915 (0.299)
D (Å)	61 (63)	115 (181)
$\Delta\mu_g^0$ (kT)	−90.1 (−83.9)	−40.6 (−105.2)

RESULTS AND DISCUSSION

In our calculations, we have tried to find numerical values of the micellar parameters such that the conditions given by equations (9) and (10) are fulfilled, i.e. that the decrease in the standard Gibbs energy of micellization, $\Delta\mu_g^0$, is maximal.

The results are shown in *Tables 2* to *4*. To demonstrate the influence of the χ parameters on the resulting micellar parameters, δ_i and χ_{iS} are introduced as the most frequent and, in parentheses, extreme values, both taken from the literature[10]. The resulting micellar parameters are shown accordingly.

When comparing the experimental values of the association number, g^{exp}, with those calculated, g^{calc}, it is obvious that in the system PS-PhB-PS/dioxane there is an apparent disagreement between g^{exp} and g^{calc}, while in the case of PS-PB-PS/MEK both values agree well, at least for $\chi_{AS} = 1.05$. The experimental data indicate that the association number for the three-block copolymer micelles (the type B–A–B/selective solvent for B) is higher than that for the diblock copolymer having a comparable molar mass and chemical composition[13]. A comparison of the model calculations by Nagarajan and Ganesh[1], for a diblock copolymer (*Table 1*), with our own results obtained for a three-block copolymer of the same molar mass or the same composition (*Table 3*) shows the same pattern, i.e. that the g calculated for the diblock copolymer is more than three to five times higher than the g^{calc} for three-block copolymer micelles. Similarly, if we consider a three-block copolymer molecule B–A–B to consist formally of two diblock copolymer molecules B–A, thus having the same chemical composition, but half the molar mass of the B–A–B copolymer, g_{BAB}^{calc} for the three-block copolymer micelles is half to one third of the corresponding value g_{BA}^{calc} for the diblock copolymer micelles. This result confirms the consistency of the two models.

To illustrate the influence of the individual contributions in equation (11) to the total Gibbs energy of micellization, $\Delta\mu_g^0$, we have expressed them as a function of the association number g (*Figures 2* and *3*). We have also sought such numerical values of the micellar dimensions R and D to get minimal values of $\Delta\mu_g^0$ for each g. As already discussed by Nagarajan and Ganesh[1], two types of contribution are necessary for the formation of micelles with a finite association number: (i) the contribution $(\Delta\mu_g^0)_{int}$, covering the interfacial energy of the core/shell interface for each copolymer chain, decreases with increasing g and thus leads to an increase in the micellar molar mass and size; (ii) the contributions pertaining to the deformation of copolymer blocks, $(\Delta\mu_g^0)_{A,def}$, and $(\Delta\mu_g^0)_{B,def}$, and to a lesser extent to the dilution of the block B, $(\Delta\mu_g^0)_{B,dil}$, increase with increasing

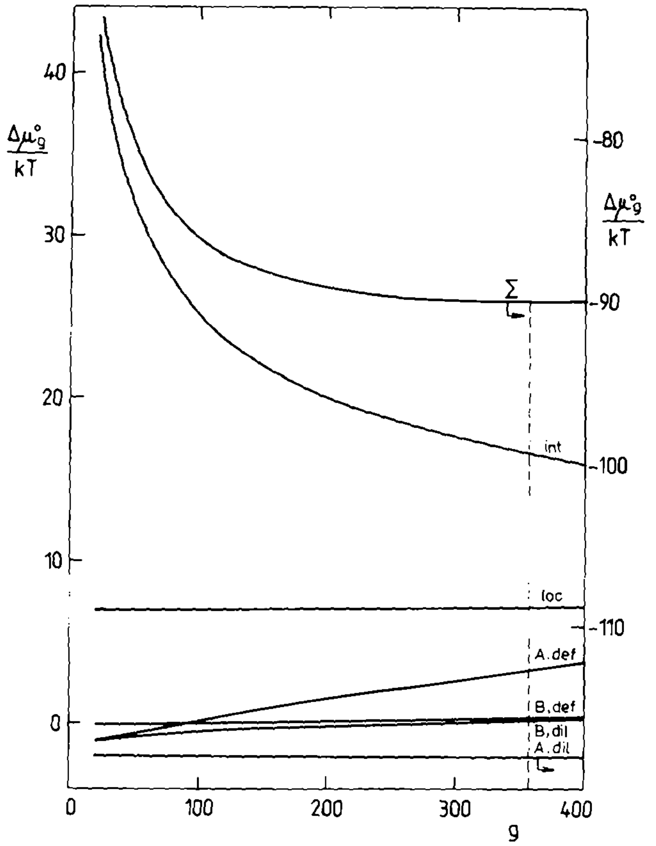

Figure 2 Contributions to the Gibbs free energy of micellization of a three-block copolymer PS-PhB-PS in 1,4-dioxane at 25°C. $\chi_{AS}=0.82$, $\chi_{BS}=0.44$. The individual contributions are described in the text. Curve Σ is the total $\Delta\mu_g^0/kT$ and the dashed line designates its minimum

g and thus constrain the micellar growth. At a certain g value, where the total $\Delta\mu_g^0$ assumes a minimum, the micellar growth is stopped and an equilibrium state is reached.

While the relations for the evaluation or estimation of the interfacial term, $(\Delta\mu_g^0)_{int}$, postulated by different authors are basically the same, the relations for the deformation energy differ from one paper to another. Some authors, for example, Leibler *et al.*[14] use the equations:

$$\frac{(\Delta\mu_g^0)_{A,def}}{kT}=3\left[\frac{2R^2}{m_A l^2}+\frac{m_A l^2}{2R^2}-2\right] -\left[\frac{3}{2}\left(\frac{4R_A^{u^2}}{m_A l^2}-1\right)-3\ln\left(\frac{2R_A^u}{m_A^{1/2}l}\right)\right] \tag{24}$$

$$\frac{(\Delta\mu_g^0)_{B,def}}{kT}=3\left[\frac{D^2}{m_B l^2}+\frac{m_B l^2}{D^2}-2\right] -\left[3(\alpha_B^2-1)-\ln\alpha_B^3\right] \tag{25}$$

which differ from (16) and (19), even though both are based on Flory's approach. The calculations using equations (24) and (25) on the one hand, and (16) and (19) on the other, lead to quite different results (*Table 4*, *Figure 4*): the contribution $(\Delta\mu_g^0)_{A,dil}$ increases with increasing g more steeply when using equations (24) and (25) than when using equations (16) and (19) (*Figure 2*). As a consequence, the minimum of the total Gibbs energy

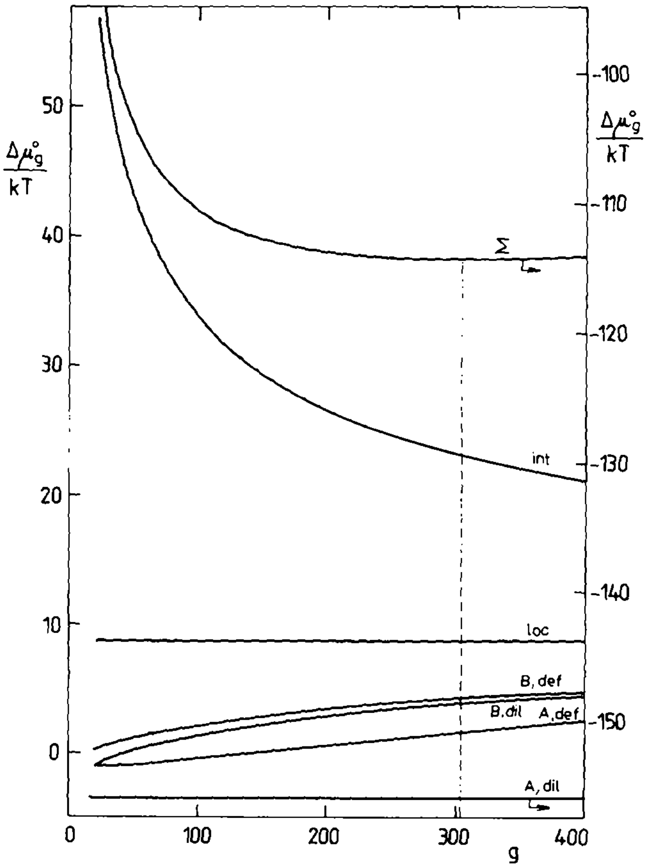

Figure 3 Contributions to the Gibbs free energy of micellization of a three-block copolymer PS-PB-PS in MEK at 25°C. $\chi_{AS}=1.05$, $\chi_{BS}=0.36$. The individual contributions are described in the text. Curve Σ is the total $\Delta\mu_g^0/kT$ and the dashed line designates its minimum

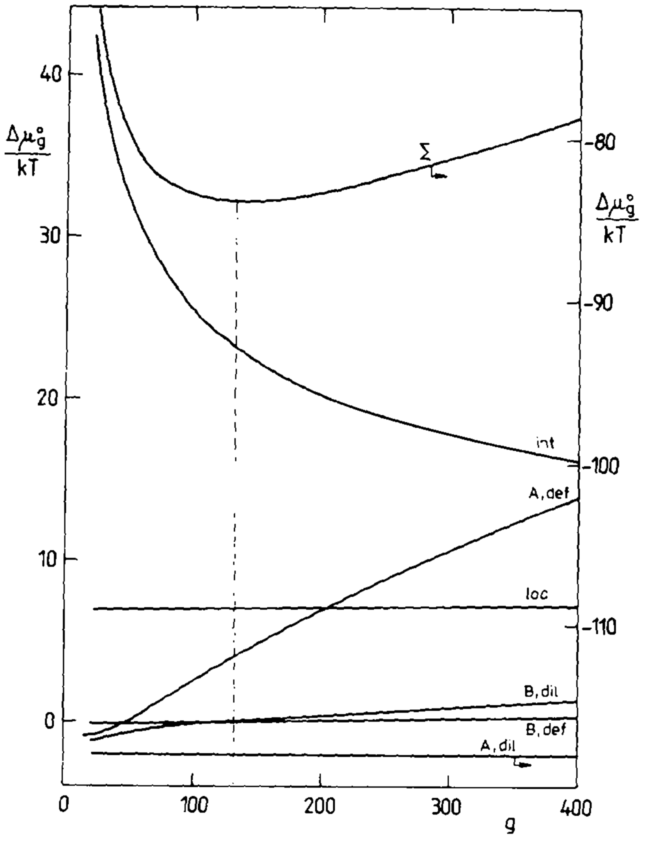

Figure 4 Contributions to the Gibbs energy of micellization of a three-block copolymer PS-PhB-PS in 1,4-dioxane at 25°C. $\chi_{AS}=0.82$, $\chi_{BS}=0.44$. The individual contributions are described in the text. Curve Σ is the total $\Delta\mu_g^0/kT$ and the dashed line designates its minimum. The contributions related to deformation energy are evaluated according to equations (24) and (25)

in the first case lies at lower g, and also the difference between g^{exp} and g^{calc} for the PS-PhB-PS/dioxane system is smaller. Nevertheless, it should be kept in mind that the block B in the system mentioned is too short ($M_B = 10360$ g mol^{-1}) to behave as a Gaussiain chain, which is the necessary condition for the validity of equations (19) and (25).

CONCLUSIONS

A theoretical model for micellization of a three-block copolymer B–A–B in a solvent selective for blocks B, based on the model for micellization of a diblock copolymer by Nagarajan and Ganesh[1], has been proposed. Results obtained with both models confirm the experimental findings (which are unfortunately scarce, but ref. 13 is an example) that the association number for micelles of a diblock copolymer is substantially higher than that for micelles of a three-block copolymer of a comparable molar mass and composition and in the same selective solvent.

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NOMENCLATURE

D	Thickness of the micellar shell (Å)
g	Association number of the micelle
G	Total Gibbs free energy (cal)
k	Boltzmann constant (cal K^{-1})
l	Effective length of the segment (Å)
m_A	Number of segments in block A of the copolymer
m_B	Number of segments in block B of the copolymer
M	Molar mass of the copolymer (g mol^{-1})
M_A	Molar mass of the A block of the copolymer (g mol^{-1})
M_B	Molar mass of the B block of the copolymer (g mol^{-1})
N_1	Number of singly dispersed copolymers (unimer molecules)
N_g	Number of micelles of the association number g
N_S	Number of solvent molecules
R	Core radius of the micelle (Å)
$\mathcal{R}$	Universal gas constant (cal mol^{-1} K^{-1})
R_A^u	Radius of the swollen block A in the unimer (Å)
R_B^u	Radius of the swollen block B in the unimer (Å)
T	Temperature of the system (K)
v_A	Molecular volume of the A block of the copolymer (Å^3)
v_B	Molecular volume of the B block of the copolymer (Å^3)
v_S	Molecular volume of the solvent (Å^3)
V^C	Volume of the micellar core region (Å^3)
V^{Sh}	Volume of the micellar shell region (Å^3)
V_A^u	Volume of the swollen A block in the unimer (Å^3)
V_B^u	Volume of the swollen B block in the unimer (Å^3)
V_S	Molar volume of the solvent (cm^3 mol^{-1})
w_A	Mass fraction of the A block in the copolymer
$W(R)$	Probability function
α_A	Chain expansion parameter for block A in unimer
α_B	Chain expansion parameter for block B in unimer
β	Correction factor for loop formation
δ_I	Hildebrant solubility parameter of a component I (cal$^{\frac{1}{2}}$ cm$^{-3/2}$)
μ_1, μ_g	Chemical potentials of the unimer and micelle (kT)
μ_1^0, μ_g^0	Standard chemical potentials of the unimer and micelle (standard state of pure components) (kT)
Π	Osmotic pressure (cal cm^{-3})
σ_{AS}	Interfacial tension between the micellar core block A and the solvent (cal cm^{-3})
ϕ	Total segmental fraction of the copolymer in the solution
ϕ_1, ϕ_g	Segmental fraction of the unimer molecules and micelles in the solution
$\varphi_S^C, \varphi_S^{Sh}$	Segmental fraction of the solvent in the micellar core and shell, respectively
φ_S^u	Segmental fraction of the solvent in the swollen block A in the unimer
χ_S	Average copolymer–solvent Huggins' interaction parameter
χ_{AS}	Flory–Huggins block A-solvent interaction parameter
χ_{BS}	Flory–Huggins block B-solvent interaction parameter

APPENDIX

Derivation of relation (21) for $(\Delta\mu_g^o)_{loc}$

The contribution $(\Delta\mu_g^o)_{loc}$ to the total Gibbs energy of the system is due to the decrease in entropy caused by the localization of the block A/block B joints in the core/shell interface. The probability p_1 of the occurrence of the first joint in a three-block copolymer molecule in the core/shell interface is given by the ratio of the volume of the interface to the total micellar volume:

$$p_1 = \frac{4\pi R^2 l}{\frac{4}{3}\pi(R+D)^3} \qquad \text{(A-1)}$$

The probability p_2 of the occurrence of the second joint in the interface can be estimated from the following reasoning: Assuming Gaussian distribution of chain segments, the probability of finding the second chain end in a volume element $\mathrm{d}V$ at a distance r is equal to:

$$w(r)\,\mathrm{d}V=\frac{b^2}{\pi^{3/2}}\exp(-b^2r^2)\,\mathrm{d}V \qquad \text{(A-2)}$$

where $b^2=3/(2m_\mathrm{A}l^2)$. The volume element can be derived as a function of r:

$$\mathrm{d}V=2\pi rl\,\mathrm{d}r \qquad \text{(A-3)}$$

By integrating equation (A-2) for r from zero to $2R$ we get:

$$p_2=\left(\frac{3}{2\pi m_\mathrm{A}}\right)^{1/2}\left[1-\exp\left(-\frac{6R^2}{m_\mathrm{A}l^2}\right)\right] \qquad \text{(A-4)}$$

p_2 is identical to $W(R)$ in equation (20).

Hence,

$$\frac{(\Delta\mu_\mathrm{g}^o)_\mathrm{loc}}{kT}=-\ln(p_1p_2)$$

$$=-\ln\left(\frac{3R^2l}{(R+D)^3}\right)-\tfrac{1}{2}\ln\left(\frac{3}{2\pi m_\mathrm{A}}\right)$$

$$-\ln\left[1-\exp\left(-\frac{6R^2}{m_\mathrm{A}l^2}\right)\right] \qquad (21)$$