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Self-Consistent Field Theory of Micelle Formation by Block Copolymers

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ABSTRACT: A self-consistent field theory was developed to account for the micellization of block copolymers in selective solvents. The mean-field expression used successfully by Edwards in treating the polymer excluded-volume problem was modified to enable it to be applied to chains in bad solvents without the generation of unrealistically high segment densities. Full consideration was given to the issue of standard states so that a meaningful comparison could be made between theoretical and experimental results. The theory was able to account in a consistent and satisfactory manner for the thermodynamics of micellization of two polystyrene-*block*-polyisoprene copolymers in *n*-hexadecane which is a selectively bad solvent for polystyrene.

1. Introduction

When a block copolymer is dissolved in an organic liquid that is a bad solvent for one of the polymer components but a relatively good solvent for the other, the copolymer chains associate reversibly to form micelles.[1–6] For such systems it has been shown experimentally that it is a large negative enthalpy change on association which gives micelle stability.[7] This thermodynamic behavior is in strong contrast to the association of amphiphilic block copolymers and other synthetic surfactants in aqueous media for which a favorable entropy change arising from the hydrophobic effect is normally responsible for micelle formation occurring.[8]

From the studies carried out to-date it appears that block copolymers tend to form spherical micelles in dilute solution, although metastable wormlike micelles have been observed under certain conditions.[9] By ultracentrifugation,[10] gel permeation chromatography,[11] and transmission electron microscopy,[6,11] it has been shown that block copolymers which are fairly uniform in mass and composition form micelles with very narrow molar mass distributions; the molar mass distribution of the micelles is generally significantly narrower than that of the unassociated block copolymer. The presence of solvent in the core regions of block copolymer micelles in organic solvents has been studied by small-angle scattering[5] and ^{1}H and ^{13}C NMR methods.[12]

A number of theoretical treatments of micelle formation by block copolymers have led to predictions of scaling laws for micellar properties. To obtain mathematically tractable expressions, rather severe approximations had to be made about the segment density distributions and the nature of the interface.[13–21] Whilst the scaling predictions might be expected to be valid under special circumstances, in order to obtain a reasonably quantitative account of micellar behavior under more general conditions one must relax the highly simplified assumptions and develop a more comprehensive theory. As the theory must deal with the behavior of a polymer chain both in good and bad solvents, a self-consistent field approach would seem to be the theory of choice. Although such theories do not for example predict the exact exponents characterizing the behavior of an isolated homopolymer chain in a good solvent, the values obtained are good approximations in three dimensions,[22–24] and recent studies have shown that with an appropriate choice for the mean-field potential, quite good agreement can be achieved between theory and simulation over a range of solvent conditions.[25] A theory of this type has been used to study end-adsorbed polymer brushes in polymeric matrices,[26] and a lattice version of a mean-field theory has been applied to copolymeric micelles.[27]

In this paper we present a continuous space self-consistent theory for micelles. Unlike much past work, we treat the micelle and the isolated chain in a unified manner. As micellar properties depend critically upon the difference between the standard Gibbs energies of a micelle and that of the isolated chains, we believe it is important to treat the isolated chain at the same theoretical level as the micelle.[18] In common with all self-consistent theories, however, no assumptions need to be made about the micellar structure–density profiles since these can be predicted. In this paper, we compare our theoretical predictions with experimental results[18,28] for solutions of two polystyrene-*block*-polyisoprene copolymers in *n*-hexadecane (which is a selectively bad solvent for polystyrene), full attention being given to the issue of standard states. In later publications, we hope to present further comparisons with experimental results and also to investigate numerically whether the theory predicts any scaling laws.

2. Chemical Potential of Unassociated Chains

The chemical potential of an unassociated block copolymer chain in solution at the infinitely dilute solution limit can be written as

$$\mu_1 = -kT \ln z_{\rm p} - kT \ln z_{1{\rm c}} - kT \ln [\lambda_1^{-3} \rho_1^{-1}] \qquad (1)$$

where $z_{\rm p}$ is the internal partition function of the chain made up of rotational, vibrational, and electronic contributions and short-range intramolecular interactions. $z_{1{\rm c}}$ is the configurational partition function of a chain with fixed center of mass; it is termed for reference the coupling partition function since it accounts for long-range intramolecular interactions of the unassociated copolymer chain and for the intermolecular interactions of the copolymer chain with the solvent.

The last term on the right-hand side of eq 1 accounts for the translational motion of the chain within the volume, V, of the system. The de Broglie wavelength λ_1 for classical fluids depends only on the mass of the chains and the temperature; $\lambda_1 = h/(2\pi M L^{-1} kT)^{1/2}$, where M is the molar mass of the chains, h is the Planck constant, and L the Avogadro number. ρ_1 $(=N_{\rm f}/V)$ is the number density of the unassociated chains.

Expressed per mole of chains and in terms of a molar density, $\tilde{\rho}_1$ $(=N_{\rm f}/LV)$, eq (1) becomes

$$\tilde{\mu}_1 = -RT \ln z_{\rm p} - RT \ln z_{1{\rm c}} - RT \ln [\lambda_1^{-3} \tilde{\rho}_1^{-1} L^{-1}] \qquad (2)$$

If we choose an ideally dilute standard state of unit molar concentration, the standard chemical potential (expressed per mole) of the unassociated chains, $\tilde{\mu}_1{}^{\circ\rho}$, is given by

$$\tilde{\mu}_1{}^{\circ\rho} = -RT \ln z_{\mathrm{p}} - RT \ln z_{1\mathrm{c}} - RT \ln [\lambda_1{}^{-3}L^{-1}] \quad (3)$$

Alternatively, eq 2 can be written in terms of the mole fraction of unassociated chains, x_1, in which case

$$\tilde{\mu}_1 = -RT \ln z_{\mathrm{p}} - RT \ln z_{1\mathrm{c}} - RT \ln [\lambda_1{}^{-3}x_1{}^{-1}\tilde{V}_{\mathrm{s}}L^{-1}] \quad (4)$$

where $\tilde{V}_{\mathrm{s}}$ is the molar volume of the solvent.

If we choose an ideally dilute standard state of unit mole fraction, the standard chemical potential (expressed per mole) of the unassociated chains, $\tilde{\mu}_1{}^{\circ x}$, is given by

$$\tilde{\mu}_1{}^{\circ x} = -RT \ln z_{\mathrm{p}} - RT \ln z_{1\mathrm{c}} - RT \ln [\lambda_1{}^{-3}\tilde{V}_{\mathrm{s}}L^{-1}] \quad (5)$$

3. Chemical Potential of Chains in the Micellar State

The chemical potential of a block copolymer chain within a micelle, assuming intermicellar interactions can be neglected, can be written

$$\mu_m = -kT \ln z_{\mathrm{p}} - kT \ln z_{mc} - kT \ln \left[\lambda_1{}^{-3}\rho_m{}^{-1/m}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (6)$$

where z_{p} and λ_1 remain the same as for the unassociated chain on micellization (in contrast to chemical association); z_{mc} is the coupling partition function for a single chain within a micelle and accounts for long-range intramolecular interactions and for intermolecular interactions between a chain and solvent in a micelle as well as between the chain and other polymer chains in the same micelle.

The third term on the right-hand side of eq 6 is the contribution from the translational motion of the chains, account being taken of the restrictions imposed by micellar association. ρ_m ($=N_m/V$) is the number density of micelles, m is the number of chains in a micelle (i.e. the association number), and v_m is the volume of a micelle through which the center of mass of a chain is effectively free to move. (The derivation of eq 6 is described in the Appendix.) Expressed per mole of micelles and in terms of the molar density of micelles, $\tilde{\rho}_m$ ($=N_m/LV$), eq 6 becomes

$$\tilde{\mu}_m = -RT \ln z_{\mathrm{p}} - RT \ln z_{mc} - RT \ln \left[\lambda_1{}^{-3}\tilde{\rho}_m{}^{-1/m}L^{-1/m}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (7)$$

If we choose an ideally dilute standard state for the micelles with a number density of 1 mol of micelles per unit volume, the standard chemical potential of the micelles expressed per mole of copolymer chains is given by

$$\tilde{\mu}_m{}^{\circ\rho} = -RT \ln z_{\mathrm{p}} - RT \ln z_{mc} - RT \ln \left[\lambda_1{}^{-3}L^{-1/m}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (8)$$

Expressing eq 7 in terms of the mole fraction of micelles, x_m, gives

$$\tilde{\mu}_m = -RT \ln z_{\mathrm{p}} - RT \ln z_{mc} - RT \ln \left[\lambda_1{}^{-3}x_m{}^{-1/m}\tilde{V}_{\mathrm{s}}{}^{1/m}L^{-1/m}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (9)$$

If we choose an ideally dilute standard state of unit mole fraction of micelles, the standard chemical potential (expressed per mole) of the micelles, $\tilde{\mu}_1{}^{\circ x}$, is given by

$$\tilde{\mu}_m{}^{\circ x} = -RT \ln z_{\mathrm{p}} - RT \ln z_{mc} - RT \ln \left[\lambda_1{}^{-3}\tilde{V}_{\mathrm{s}}{}^{1/m}L^{-1/m}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (10)$$

4. Thermodynamics of Micellization

At thermodynamic equilibrium

$$\tilde{\mu}_1 = \tilde{\mu}_m \quad (11)$$

for all values of m. Hence from eqs 2, 3, 7, and 8

$$-RT \ln [\tilde{\rho}_m{}^{1/m}/\tilde{\rho}_1] = \tilde{\mu}_m{}^{\circ\rho} - \tilde{\mu}_1{}^{\circ\rho} \quad (12)$$

$$= -RT \ln [z_{mc}/z_{1\mathrm{c}}] - RT \ln \left[L^{1-(1/m)}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (13)$$

where $\tilde{\mu}_m{}^{\circ\rho} - \tilde{\mu}_1{}^{\circ\rho}$ is the standard Gibbs energy, $\Delta G_m{}^{\circ\rho}$ (and Helmholz energy, $\Delta A_m{}^{\circ\rho}$ since the volume is assumed to be constant) of micellization per mole of copolymer defined with reference to ideally dilute standard states of the micelles and unassociated chains of unit molarity.

Alternatively, from eqs 4, 5, 9, and 10

$$-RT \ln [x_m{}^{1/m}/x_1] = \tilde{\mu}_m{}^{\circ x} - \tilde{\mu}_1{}^{\circ x} \quad (14)$$

$$= -RT \ln [z_{mc}/z_{1\mathrm{c}}] - RT \ln \left[\tilde{V}_{\mathrm{s}}{}^{(1/m)-1}L^{1-(1/m)}\left(\frac{v_m}{m-1}\right)^{1-(1/m)} e^{1-(1/m)}\right] \quad (15)$$

where $\tilde{\mu}_m{}^{\circ x} - \tilde{\mu}_1{}^{\circ x}$ is the standard Gibbs energy of micellization per mole of copolymer with reference to ideally dilute standard states of the micelles and unassociated chains of unit mole fraction. The choice of standard states is a matter of convenience, and results can readily be interconverted as seen by comparison of eqs 13 and 15. In the present work we express results in terms of ideally dilute standard states of unit molarity.

The SCF theory described below was used to determine $\Delta G_m{}^{\circ\rho}$ and its enthalpy component, $\Delta H_m{}^{\circ}$, for the two polystyrene-*block*-polyisoprene copolymers in hexadecane over a range of m. (Note: the standard enthalpy of micellization, $\Delta H_m{}^{\circ}$, is not affected by the choice of ideally dilute standard state, hence the label ρ is omitted.) The $\Delta G_m{}^{\circ\rho}$ values were used to obtain association number distributions for different overall solution concentrations. Plots of the reciprocal weight-average association number, $\bar{m}_{\mathrm{w}}{}^{-1}$, versus solution concentration were constructed from the SCF results and used to determine the standard Gibbs energies of micellization by the critical micelle concentration method.[18,28]

5. SCF Theory

5.1. Homopolymer Chain with One End Fixed. Let us first consider the calculation of the coupling partition function $\Omega_{1\mathrm{c}}$ for a homopolymer chain with one end fixed at the origin. Short-range effects between neighboring chemical units in the chain (such as bond lengths and angles and potential barriers to internal rotation) can be accounted for by coarse graining through use of an equivalent freely-hinged chain consisting of N segments each of length b. To determine N and b, it is assumed in the usual way that the root-mean-square end-to-end distances of the real and freely-hinged chains are the same and also the two chains have the same fully extended length. From which

$$b = \langle R_e^2 \rangle_0 / D_e \tag{16}$$

$$N = D_e^2 / \langle R_e^2 \rangle_0 \tag{17}$$

where $\langle R_e^2 \rangle_0$ is the unperturbed mean-square end-to-end distance and D_e is the fully extended length of the real chain, respectively.

The statistical properties of the equivalent chain are described using the diffusion equation in the form used by Edwards:[22,23]

$$\left[\frac{\partial}{\partial n} - \frac{b^2}{6}\nabla_{\mathbf{R}}^2 + \beta\omega(\mathbf{R})\right] G(\mathbf{R},0;\, n,0) = \delta(\mathbf{R})\delta(n) \qquad 0 < n \leq N \tag{18}$$

where $\omega(\mathbf{R})$ is the mean field which accounts for the excluded-volume interactions, $\beta = (kT)^{-1}$, b is the Kuhn statistical length, $G(\mathbf{R},0;n,0)$ is the unnormalized probability that a chain with the initial segment at the origin has its nth segment at position vector $\mathbf{R}$ in space. Fixing one end of the chain at the origin leads to a polymer segment distribution which is spherically symmetric about the origin, and the mean field has the same symmetry.

The mean-field expression used by Edwards has the following form:

$$\omega(\mathbf{R}) = \beta^{-1} A_2 \rho_L(\mathbf{R}) \tag{19}$$

where

$$A_2 = \nu(1 - 2\chi) \tag{20}$$

A_2 is the second virial coefficient, χ is the thermodynamic interaction parameter,[29,30] $\rho_L(\mathbf{R})$ is the number density of segments, and ν is the volume of a segment. In poor solvents, A_2 is negative and use of this mean field gives rise to unrealistically high densities. This can be avoided if we take[25]

$$\omega(\mathbf{R}) = -\beta^{-1}\{\ln\,[1 - \nu\rho_L(\mathbf{R})] + 2\chi\nu\rho_L(\mathbf{R})\} \tag{21a}$$

This potential enforces the condition that $\rho_L(\mathbf{R}) < \nu^{-1}$.

Expanding the logarithmic term in eq 21a gives

$$\omega(\mathbf{R}) = \beta^{-1}\left\{(1 - 2\chi)\nu\rho_L(\mathbf{R}) + \frac{1}{2}\nu^2\rho_L^{\,2}(\mathbf{R}) + \frac{1}{3}\nu^3\rho_L^{\,3}(\mathbf{R}) + \ldots\right\} \tag{21b}$$

$$= \beta^{-1}\{A_2\rho_L(\mathbf{R}) + A'_3\rho_L^{\,2}(\mathbf{R}) + A'_4\rho_L^{\,3}(\mathbf{R}) + \ldots\} \tag{21c}$$

where A_2 is the second virial coefficient and A'_3, A'_4, etc. are approximations to the higher virial coefficients. If $\nu\rho_L(\mathbf{R}) \ll 1$, the effect of the higher terms is negligible and eq 21c reduces to eq 19.

The density distribution of the segments may be calculated from the relationship

$$\rho_L(\mathbf{R}) = \frac{\int_0^N \mathrm{d}n\, G(\mathbf{R},0;\, n,0) \int \mathrm{d}\mathbf{R}'\, G(\mathbf{R}',\mathbf{R};\, N,n)}{\int \mathrm{d}\mathbf{R}'\, G(\mathbf{R}',0;\, N,0)} \tag{22}$$

Equations 18, 21a, and 22 form a closed set, and the self-consistent solution can be readily obtained by numerical methods.[25] The partition function is given by

$$\Omega_{1c} = \int \mathrm{d}\mathbf{R}'\, G(\mathbf{R}',0;\, N,0) \tag{23}$$

5.2. Block-Copolymer Chain with One End Fixed. The equations considered above for the homopolymer case can be extended to account for block-copolymer chains. Let us consider a diblock copolymer formed by connecting a block A comprising N_A statistical segments to a block B with N_B segments. The short-range interactions between segments of the diblock copolymer are coarse grained into the statistical Kuhn lengths, b_A and b_B. The additional difficulty in calculating the properties of a copolymer as opposed to a homopolymer arises from the presence of three interaction parameters, χ_{SA}, χ_{SB}, and χ_{AB}.

Consider first a single diblock copolymer (in the unassociated state) with the unattached end of the A block fixed at the origin, the other end of the A block (the joint with the B block) at space point $\mathbf{R}_J$ and the unattached end of the B block at $\mathbf{R}_B$. The coupling partition function for all possible conformations of the copolymer chain containing $N = N_A + N_B$ segments is given within the SCF approximation by

$$\Omega_{1c}(N_A,N_B) = \int \mathrm{d}\mathbf{R}_B \mathrm{d}\mathbf{R}_J\, G_C(\mathbf{R}_B,\mathbf{R}_J,0;\, N_B,N_A,0) \tag{24a}$$

$$= \int \mathrm{d}\mathbf{R}_B \mathrm{d}\mathbf{R}_J\, G_A(\mathbf{R}_J,0;\, N_A,0)\, G_B(\mathbf{R}_B,\mathbf{R}_J;\, N_B,N_A) \tag{24b}$$

where the Greens functions G_A and G_B satisfy the following SCF equations:

$$\left[\frac{\partial}{\partial n_A} - \frac{b_A^2}{6}\nabla_{\mathbf{R}}^2 + \beta\omega_A(\mathbf{R})\right] G_A(\mathbf{R},0;\, N_A,0) = \delta(\mathbf{R})\delta(n_A) \qquad 0 < n_A \leq N_A \tag{25a}$$

$$\left[\frac{\partial}{\partial n_B} - \frac{b_B^2}{6}\nabla_{\mathbf{R}}^2 + \beta\omega_B(\mathbf{R})\right] G_B(\mathbf{R},\mathbf{R}_J;\, n_B,N_A) = G_A(\mathbf{R}_J,0;\, N_A,0)\delta(\mathbf{R} - \mathbf{R}_J)\delta(n_B) \qquad 0 < n_B \leq N_B \tag{25b}$$

For the A block the mean-field potential in eq 25a is given by

$$\omega_A(\mathbf{R}) = -\beta^{-1}(\nu_A/\nu_S)\{\ln\,[1 - \nu_A\rho_A(\mathbf{R}) - \nu_B\rho_B(\mathbf{R})] + 2\chi_{SA}\nu_A\rho_A(\mathbf{R}) + (\chi_{SA} + \chi_{SB})\nu_B\rho_B(\mathbf{R}) - \chi_{AB}(\nu_S/\nu_A)\nu_B\rho_B(\mathbf{R})\} \tag{26a}$$

where ν_A and ν_B are the volumes of statistical segments A and B and $\rho_{1A}(\mathbf{R})$ and $\rho_{1B}(\mathbf{R})$ are the number density distribution functions of the statistical segments. $\omega_A(\mathbf{R})$ is the energy change which would occur if an A-statistical segment was transferred from limiting dilute solution conditions to a location at which the volume fraction of A-statistical segments was $\nu_A\rho_A(\mathbf{R})$ and the volume fraction of B-statistical segments was $\nu_B\rho_B(\mathbf{R})$.

In eq 26a, χ_{SA} and χ_{SB} are interaction parameters (dimensionless) defined per solvent molecule, whilst χ_{AB} is defined per A-statistical segment. Written in terms of interaction parameters expressed per unit volume (which is preferred in this study) eq 26a becomes

$$\omega_A(\mathbf{R}) = -\beta^{-1}\{(\nu_A/\nu_S)\ln\,[1 - \nu_A\rho_A(\mathbf{R}) - \nu_B\rho_B(\mathbf{R})] + 2\alpha_{SA}\nu_A^{\,2}\rho_A(\mathbf{R}) + (\alpha_{SA} + \alpha_{SB} - \alpha_{AB})\nu_A\nu_B\rho_B(\mathbf{R})\} \tag{26b}$$

where $\alpha_{AB} = \chi_{AB}/\nu_A$, $\alpha_{SA} = \chi_{SA}/\nu_S$, and $\alpha_{SB} = \chi_{SB}/\nu_S$; ν_S is the volume of a solvent molecule.

Similarly, for the mean-field potential of B segments we have

$$\omega_B(\mathbf{R}) = -\beta^{-1}(\nu_B/\nu_S)\{\ln\,[1 - \nu_A\rho_A(\mathbf{R}) - \nu_B\rho_B(\mathbf{R})] + 2\chi_{SB}\nu_B\rho_B(\mathbf{R}) + (\chi_{SA} + \chi_{SB})\nu_A\rho_A(\mathbf{R}) - \chi_{AB}(\nu_S/\nu_B)\nu_A\rho_A(\mathbf{R})\} \tag{27a}$$

or, equivalently

$$\omega_B(\mathbf{R}) = -\beta^{-1}\{(\nu_B/\nu_S)\ln[1-\nu_A\rho_A(\mathbf{R})-\nu_B\rho_B(\mathbf{R})] + 2\alpha_{SB}\nu_B{}^2\rho_B(\mathbf{R}) + (\alpha_{SA}+\alpha_{SB}-\alpha_{AB})\nu_A\nu_B\rho_A(\mathbf{R})\} \quad (27b)$$

The number densities of the A and B segments within the volume occupied by a chain can be calculated from

$$\rho_{1A}(\mathbf{R}) = \frac{\int_0^{N_A} dn_A G_A(\mathbf{R},0;n_A,0)\int d\mathbf{R}_J d\mathbf{R}_B G_A(\mathbf{R}_J,\mathbf{R};N_A,n_A)G_B(\mathbf{R}_B,\mathbf{R}_J;N_B,N_A)}{\Omega_{1c}(N_A,N_B)} \quad (28)$$

$$\rho_{1B}(\mathbf{R}) = \frac{\int_0^{N_B} dn_B \int d\mathbf{R}_J d\mathbf{R}_B G_A(\mathbf{R}_J,0;N_A,0)G_B(\mathbf{R},\mathbf{R}_J;n_B,N_A)G_B(\mathbf{R}_B,\mathbf{R};N_B,n_B)}{\Omega_{1c}(N_A,N_B)} \quad (29)$$

Equations 24a–29 constitute a closed set which can readily be solved by standard numerical methods to predict the statistical properties of the single diblock copolymer chain having one end fixed.

If we set $\nu_A = \nu_B = \nu$ and $\alpha_{SA} = \alpha_{SB} = \alpha_{AB} = \alpha$ (or $\chi_{SA} = \chi_{SB} = \chi_{AB} = \chi$), the SCF equations given above reduce to the case of the homopolymer chain.

However, fixing the first segment of the chain at the origin is not a good assumption to make when the coupling partition functions of relevance in the present study are estimated since it leads to an unrelistic buildup of segment density around the fixed segment. Therefore, when we treat the coupling partition function for AB block copolymers in both associated and unassociated states, some degree of freedom for the end segment is introduced as described below, but the center of gravity of the unassociated chain, or the center of gravity of the whole micelle in the case of associated chains, is effectively fixed.

5.3. Block-Copolymer Micelles. The problem to be considered before the SCF theory can be used to treat micelles is that of the distribution of the ends of the A block within the micellar core (assuming the solvent is selectively poor for the A blocks and good for the B blocks). This initial condition is needed for a fully defined set of equations. A methodology might be to assume the form of the distribution (say for example a Gaussian or a uniform distribution with a sphere of a given radius) and then to find the values of the parameters characterizing the distribution (the width of the Gaussian or the radius of the sphere taking the previous examples) that minimized the Gibbs energy. This is an approach that we hope to explore further in the future, but here we use a different ansatz.

We assume that the distribution of the A-block ends has the same form as that of the A-block segments as a whole, so that it is determined as part of the self-consistent treatment; i.e. the probability of the end segment of the A block of each chain occurring at a radius $\mathbf{R}_0$ from the center of mass of the micelle depends only on the overall density distribution of the A segments:

$$G_A(\mathbf{R}_0;0,0) = \rho_{mA}(\mathbf{R}_0)/\int \rho_{mA}(\mathbf{R}_0)\, d\mathbf{R}_0 \quad (30)$$

The distribution of the ends of the B blocks is not subject to any such input and is determined uniquely. (It may be noted that an SCF calculation yielding the distribution of the ends of grafted polymer brushes has been reported by Milner et al.[31]). A second assumption made in the present treatment is that the behavior and the environment of every copolymer chain in a micelle are identical.

The partition function of a chain within the confines of the micelle volume is given by

$$z_{mc} = \int d\mathbf{R}_J \int d\mathbf{R}_B G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)G_B(\mathbf{R}_B,\mathbf{R}_J;N_B,N_A) \quad (31)$$

$$= \int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)q_B(\mathbf{R}_J;N_B,N_A) \quad (32)$$

where

$$q_B(\mathbf{R};N_B-n_B,n_B) = \int d\mathbf{R}' G_B(\mathbf{R}',\mathbf{R};N_B-n_B,n_B) \quad (33)$$

and if $n_B = 0$, $q_B(\mathbf{R};N_B,0) = q_B(\mathbf{R};N_B,N_A)$. Green's functions $G_A(\mathbf{R},\mathbf{R}_0;n_A,0)$ and $q_B(\mathbf{R};n_B,N_A)$ satisfy the following equations:

$$\left[\frac{\partial}{\partial n_A} - \frac{b^2{}_A}{6}\nabla_R{}^2 + \beta\omega_A(\mathbf{R})\right]G_B(\mathbf{R},\mathbf{R}_0;n_A,0) = \delta(n_A)\delta(\mathbf{R}-\mathbf{R}_0) \qquad 0 < n_A \le N_A \quad (34)$$

$$\left[\frac{\partial}{\partial n_B} - \frac{b^2{}_B}{6}\nabla_R{}^2 + \beta\omega_B(\mathbf{R})\right]q_B(\mathbf{R};N_B-n_B,n_B) = \delta(n_B) \qquad 0 < n_B \le N_B \quad (35)$$

In the above equations, the potentials of mean force are given by eqs 26 and 27 whilst the segment density distributions are given by

$$\rho_{mA}(\mathbf{R}) = \frac{m\int_0^{N_A} dn_A G_A(\mathbf{R},\mathbf{R}_0;n_A,0)\int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R};N_A,n_A)q_B(\mathbf{R}_J;N_B,N_A)}{\int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)q_B(\mathbf{R}_J;N_B,N_A)} \quad (36)$$

$$\rho_{mB}(\mathbf{R}) = \frac{m\int_0^{N_B} dn_B \int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)G_B(\mathbf{R},\mathbf{R}_J;n_B,N_A)q_B(\mathbf{R};N_B-n_B,n_B)}{\int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)q_B(\mathbf{R}_J;N_B,N_A)} \quad (37)$$

If we define the additional Green's functions

$$H_A(\mathbf{R};N_B,n_A) = \int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R};N_A,n_A)q_B(\mathbf{R}_J;N_B,N_A) \quad (38)$$

$$H_B(\mathbf{R};n_B,N_A) = \int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)G_B(\mathbf{R},\mathbf{R}_J;n_B,N_A) \quad (39)$$

then, eqs 36 and 37 can be rewritten as

$$\rho_{mA}(\mathbf{R}) = \frac{m\int_0^{N_A} dn_A G_A(\mathbf{R},\mathbf{R}_0;n_A,0)H_A(\mathbf{R};N_B,n_A)}{\int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)q_B(\mathbf{R}_J;N_B,N_A)} \quad (40)$$

$$\rho_{mB}(\mathbf{R}) = \frac{m\int_0^{N_B} dn_B H_B(\mathbf{R};n_B,N_A)q_B(\mathbf{R};N_B-n_B,n_B)}{\int d\mathbf{R}_J G_A(\mathbf{R}_J,\mathbf{R}_0;N_A,0)q_B(\mathbf{R}_J;N_B,N_A)} \quad (41)$$

Green's functions $H_A(\mathbf{R};N_B,n_A)$ and $H_B(\mathbf{R};n_B,N_A)$ can be obtained from the following equations:

$$\left[\frac{\partial}{\partial n_{\mathrm{A}}}-\frac{b^{2}{}_{\mathrm{A}}}{6}\nabla_{\mathbf{R}}{}^{2}+\beta\omega_{\mathrm{A}}(\mathbf{R})\right]H_{\mathrm{A}}(\mathbf{R};N_{\mathrm{B}},n_{\mathrm{A}})= q_{\mathrm{B}}(\mathbf{R};N_{\mathrm{B}},N_{\mathrm{A}})\delta(n_{\mathrm{A}}) \qquad 0<n_{\mathrm{A}}\leq N_{\mathrm{A}} \tag{42}$$

$$\left[\frac{\partial}{\partial n_{\mathrm{B}}}-\frac{b^{2}{}_{\mathrm{B}}}{6}\nabla_{\mathbf{R}}{}^{2}+\beta\omega_{\mathrm{B}}(\mathbf{R})\right]H_{\mathrm{B}}(\mathbf{R};n_{\mathrm{B}},N_{\mathrm{A}})= G_{\mathrm{A}}(\mathbf{R},\mathbf{R}_0;N_{\mathrm{A}},0)\delta(n_{\mathrm{B}}) \qquad 0<n_{\mathrm{B}}\leq N_{\mathrm{B}} \tag{43}$$

Equations 26, 27, 30, 32, 34, 35, and 40–43 form a closed set. Discrete versions of the equations were obtained using the Crank–Nicholson scheme.[15,25] In the SCF calculations the initial trial functions used for the density distributions of the A and B blocks were Gaussian. In the first instance segment density distributions were determined self-consistently for the case in which the A blocks had their unattached end segments fixed at the origin rather than as described by eq 30, i.e. $G_{\mathrm{B}}(\mathbf{R};0,0)=1$ for $\mathbf{R}=0$ and $G_{\mathrm{B}}(\mathbf{R};0,0)=0$ for $\mathbf{R}>0$. The fixed-end condition was then relaxed by introducing eq 30 into the SCF scheme. Calculations were carried out for a range of m; the case when $m = 1$ was taken to describe unassociated chain behavior.

The enthalpy change (=internal energy change) per chain on association of m chains to form a micelle is given by

$$\Delta H_m{}^{\circ}=m^{-1}(H_{m\mathrm{A}}+H_{m\mathrm{B}})-H_{1\mathrm{A}}-H_{1\mathrm{B}} \tag{44}$$

In eq 44

$$H_{m\mathrm{A}}=-\beta^{-1}\int\left[(\alpha_{\mathrm{SA}})_{\mathrm{h}}\nu_{\mathrm{A}}{}^{2}\rho_{\mathrm{A}}(\mathbf{R})+\frac{1}{2}\{(\alpha_{\mathrm{SA}})_{\mathrm{h}}+ (\alpha_{\mathrm{SB}})_{\mathrm{h}}-(\alpha_{\mathrm{AB}})_{\mathrm{h}}\}\nu_{\mathrm{A}}\nu_{\mathrm{B}}\rho_{\mathrm{B}}(\mathbf{R})\right]\rho_{\mathrm{A}}(\mathbf{R})\,\mathrm{d}\mathbf{R} \tag{45a}$$

$$H_{m\mathrm{B}}=-\beta^{-1}\int\left[(\alpha_{\mathrm{SB}})_{\mathrm{h}}\nu_{\mathrm{B}}{}^{2}\rho_{\mathrm{B}}(\mathbf{R})+\frac{1}{2}\{(\alpha_{\mathrm{SA}})_{\mathrm{h}}+ (\alpha_{\mathrm{SB}})_{\mathrm{h}}-(\alpha_{\mathrm{AB}})_{\mathrm{h}}\}\nu_{\mathrm{A}}\nu_{\mathrm{B}}\rho_{\mathrm{A}}(\mathbf{R})\right]\rho_{\mathrm{B}}(\mathbf{R})\,\mathrm{d}\mathbf{R} \tag{45b}$$

In writing eqs 45a and 45b in this form, it is recognized that interaction parameters determined experimentally can contain both enthalpic and entropic contributions, i.e.

$$\alpha_{\mathrm{SA}}=(\alpha_{\mathrm{SA}})_{\mathrm{h}}+(\alpha_{\mathrm{SA}})_{\mathrm{s}};\ \alpha_{\mathrm{SB}}=(\alpha_{\mathrm{SB}})_{\mathrm{h}}+(\alpha_{\mathrm{SB}})_{\mathrm{s}};\quad \alpha_{\mathrm{AB}}=(\alpha_{\mathrm{AB}})_{\mathrm{h}}+(\alpha_{\mathrm{AB}})_{\mathrm{s}}$$

When expressed in molar units the enthalpy changes calculated from combination of eqs 44, 44a, and 44b may be compared with the enthalpies of micellization reported from experimental studies.

The coupling free energy per chain of a micelle, A_{mc}, may be calculated from z_{mc} obtained via eqs 32 and 33 using

$$A_{mc}=-\beta^{-1}\ln z_{mc}-m^{-1}(E_{m\mathrm{A}}+E_{m\mathrm{B}}) \tag{46}$$

where

$$E_{m\mathrm{A}}=\frac{1}{2}\beta^{-1}\int\omega_{\mathrm{A}}(\mathbf{R})\rho_{\mathrm{A}}(\mathbf{R})\,\mathrm{d}\mathbf{R} \tag{47a}$$

$$E_{m\mathrm{B}}=\frac{1}{2}\beta^{-1}\int\omega_{\mathrm{B}}(\mathbf{R})\rho_{\mathrm{B}}(\mathbf{R})\,\mathrm{d}\mathbf{R} \tag{47b}$$

The second term on the right-hand side of eq 46 is to correct for overcounting that is known to be introduced by the type of SCF scheme used in this study.[24]

Table I
Predictions of SCF Theory Compared with Experimental Results for Polystyrene-*block*-polyisoprene Copolymers in Hexadecane at 40 °C

sample	SI(1)	SI(2)
$\bar{M}_{\mathrm{w}}$	24600	26800
$(\bar{M}_{\mathrm{w}})_{\mathrm{s}}$	7000	13600
$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$	1.08	1.10
$\Delta G_m{}^{\circ\rho}$(expt)/kJ mol^{-1}	−21.4 ± 0.5	−31.8 ± 0.5
$\Delta G_m{}^{\circ\rho}$(SCF)/kJ mol^{-1}	−24.2[a]	−46.8[b]
$\Delta G_m{}^{\circ\rho}$(SCF; cmc)/kJ mol^{-1}	−24	−46
$\Delta H_m{}^{\circ}$(expt)/kJ mol^{-1}	−40.7 ± 2.2	−86.4 ± 5.0
$\Delta H_m{}^{\circ}$(SCF)/kJ mol^{-1}	−47.3[a]	−76.6[b]

[a] Value for m = 41. [b] Value for m = 128.

The coupling free energy change per chain on association of m chains to form a micelle is given by

$$\Delta A_{mc}=-\beta^{-1}\ln(z_{mc}/z_{1\mathrm{c}})-m^{-1}(E_{m\mathrm{A}}+E_{m\mathrm{B}})+E_{1\mathrm{A}}+E_{1\mathrm{B}} \tag{48}$$

where $z_{1\mathrm{c}}$ is the coupling partition function of an unassociated chain (treated in the calculations as a unimolecular micelle).

The standard Gibbs energy of micellization per mole of chain is then given by

$$\tilde{\mu}_m{}^{\circ\rho}-\tilde{\mu}_1{}^{\circ\rho}=L\Delta A_{mc}- RT\ln\left[\tilde{V}_{\mathrm{s}}{}^{(1/m)-1}L^{1-(1/m)}\left(\frac{v_m}{m-1}\right)^{1-(1/m)}e^{1-(1/m)}\right] \tag{49}$$

The molar concentrations of unassociated copolymer chains and micelles with association number m in a solution with a total molar concentration of copolymer $\tilde{\rho}_{\mathrm{t}}$ can be determined from the calculated standard Gibbs energies using eqs 50 and 51. The molar concentration of copolymer chains to be found in the form of micelles with a given association number m is $\mathrm{m}\tilde{\rho}_{\mathrm{m}}$.

$$\tilde{\rho}_1=\tilde{\rho}_{\mathrm{t}}[1+m\sum_{m>1}\exp\{-m(\tilde{\mu}_m{}^{\circ\rho}-\tilde{\mu}_1{}^{\circ\rho})/RT\}]^{-1} \tag{50}$$

$$\tilde{\rho}_m=\tilde{\rho}_1\exp\{-m(\tilde{\mu}_m{}^{\circ\rho}-\tilde{\mu}_1{}^{\circ\rho})/RT\} \tag{51}$$

6. Comparison between Experiment and Theory

Calculations were carried out for two polystyrene-*block*-polyisoprene copolymers, designated SI(1) and SI(2). The weight-average and number-average molecular weights, $\bar{M}_{\mathrm{w}}$ and $\bar{M}_{\mathrm{n}}$, and the polydispersity ratio, $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$, for the copolymers in the unassociated state are give at the top of Table I. In the calculations the block copolymers were treated as monodisperse, the weight-average molecular weight values being used in the determination of the number of statistical segments per chain.

Experimental values were used for all the thermodynamic interaction parameters required in the SCF calculations. Those for α_{SA} and $(\alpha_{\mathrm{SA}})_{\mathrm{h}}$ were obtained from swelling measurements made by us as a function of temperature in the range of interest on homopolystyrene samples in hexadecane and interpreted via the Flory–Huggins equation containing a Gibbs energy parameter: $\alpha_{\mathrm{SA}}=(\alpha_{\mathrm{SA}})_{\mathrm{h}}+(\alpha_{\mathrm{SA}})_{\mathrm{s}}=3.379T^{-1}-0.00\,390$ (in cm^{-3}), where T is temperature in degrees Kelvin.[32] This expression for α_{SA} is in fair accord with results established at higher temperatures by DiPaola-Baranyi et al.[33] using a gas chromatographic method. The information for the polyisoprene/hexadecane pair was obtained from polymer solution behavior and from microcalorimetrically determined heats of mixing of hexadecane and squalene:[32] within experimental error $\alpha_{\mathrm{SB}}=(\alpha_{\mathrm{SB}})_{\mathrm{h}}=0.45T^{-1}$. The

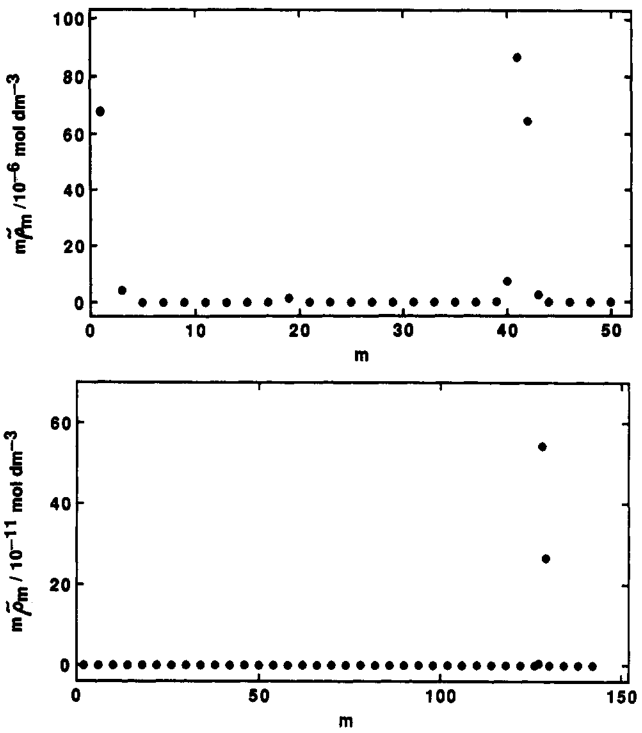

Figure 1. Molar concentration of block copolymer chains at different association numbers. (a, Top) solution of SI(1) with overall copolymer concentration, $\tilde{\rho}_t$ = 2.319 × 10^{-4} mol dm^{-3} and T = 40 °C. (b, Bottom) solution of SI(2) with $\tilde{\rho}_t$ = 1.345 × 10^{-8} mol dm^{-3} and T = 40 °C. The off-scale value for m = 1 is 1.260 × 10^{-8} mol dm^{-3}.

polyisoprene/polystyrene interaction parameter was obtained from phase behavior results and microcalorimetric studies carried out on oligomers:[32] $\alpha_{AB} = (\alpha_{AB})_h + (\alpha_{AB})_s = 0.658T^{-1} - 0.00107$ (in cm^{-3}). The expression is in good agreement with results determined by Mori et al. from an analysis of small-angle X-ray profiles determined for a polystyrene-*block*-polyisoprene copolymer in the disordered state.[34]

From average experimental values of polymer dimensions, the length of an equivalent polystyrene segment, b, and the number of monomer units per equivalent segment were calculated through eqs 16 and 17 to be 1.78 nm and 6.98, respectively, and those for polyisoprene 0.78 nm and 1.73. The molar volumes of polystyrene, polyisoprene, and hexadecane were $0.978M_A$ and $1.09M_B$ and 294.1 cm^3, respectively, where M_A is the molar mass of polystyrene and M_B the molar mass of polyisoprene.

The SCF procedure we have described was used to determine segment density distributions for micelles over a wide range of m (including the monomolecular micelle, m = 1) and values of ΔA_{mc} and $\Delta H_m{}^\circ$. Standard free energies of micellization, $\Delta G_m{}^{\circ p}$, were determined from the ΔA_{mc} values using eqs 48 and 49: the available micelle volume v_m was taken to be $(4/3)\pi(R_g)_{mA}{}^3$, where $(R_g)_{mA}$ is the radius of gyration (determined from the segment density distribution) of the polystyrene component of the micelle with association number m.

The molar concentrations of copolymer chains at different association numbers for a range of overall solution concentrations were calculated from the SCF results using eqs 50 and 51. Typical plots of $m\tilde{\rho}_m$ versus m for SI(1) (at $\tilde{\rho}_t$ = 2.319 × 10^{-4} mol dm^{-3}) and SI(2) (at $\tilde{\rho}_t$ = 1.345 × 10^{-8} mol dm^{-3}) in hexadecane at 40 °C are shown in Figure 1a,b. For each system there is seen to be a prominent micellar peak at high association number with a very narrow size distribution; the position of the prominent peak which is at m = 41 for SI(1) and m = 128 for SI(2) is independent of concentration. Significant concentrations of copolymer chains can also occur at m values immediately above m = 1 (see Figure 1a); the mole fractions of these lower species, as well as those of the large micelles, depend on the overall solution concentration.

The results in Figure 1a,b are in accord with experimental results which show that spherical block copolymer micelles with medium to high association number solvents can have narrow size distributions.[6,18,35] There are no accurate data with which to compare predicted distribution widths for the present system, but in any case such a comparison would not be straightforward since account would need to be taken of the finite size distribution of the block copolymer sample. An average association number has been determined experimentally for SI(1) in hexadecane by light scattering,[35] but not for SI(2). It was found that SI(1) had an average association number of 33. This experimental value was arrived at by fitting the light-scattering data in the region of the critical micelle concentration (cmc) to a model which assumed there were just two sizes of species present in solution, unassociated chains and micelles with a particular association number. When the SCF results are used to calculate the weight-average association number for all species in solution except m = 1 at the cmc, a value of m_w = 33.7 is obtained, which is close to the experimental value. Electron microscopy studies provide very approximate values for the association numbers of the prominent micellar species at high molar mass. Well-defined micellar particles having a narrow size distribution have been isolated[36] from solutions of both S(1) and S(2) in hexadecane and sized in the stained dry state (whilst mounted on carbon substrates) using transmission electron microscopy. From the results it was estimated that the association numbers of the S(1) and S(2) micelles were respectively 40 ± 15 and 138 ± 40; the values fall in the range predicted by theory, although clearly the results do not offer a stringent test because of the large uncertainty estimates attached to them.

As yet we have not used the SCF theory to investigate any scaling laws. However, for the SI/hexadecane system considered in this study, which is characterized by strongly segregated polystyrene blocks, the SCF calculations predict the association number of prominent micellar species is very dependent on the block length of the least soluble block. It is the difference in the molar masses of the polystyrene block lengths (7000:13 000) which is largely responsible for the large difference in the association numbers (41:128) of SI(1) and SI(2). It may be noted that for SI block copolymers in the microphase separated bulk state, there is an even stronger dependence of association number (in that case of the polystyrene blocks in spherical domains) on block length:[37,38] the domain radius $R_A \sim M_A{}^{2/3}$ and hence $m \sim M_A{}^2$.

Segment density distributions expressed in terms of volume fractions of polymer segments are shown in Figures 2a–d for respectively SI(1), m = 41; SI(1), m = 1; SI(2), m = 128; SI(1), m = 1. The radii of gyration of these four species and the radii of gyration of their polystyrene and polyisoprene components are listed in Table II. As predicted in earlier theoretical studies,[15,27] there is seen to be a significant proportion of solvent present even at the centers of the micellar cores. The degree of solvent penetration, which has been studied experimentally for some systems,[5,12] has been noted as an important factor in enabling associating copolymer systems to attain equilibrium size distributions.[39]

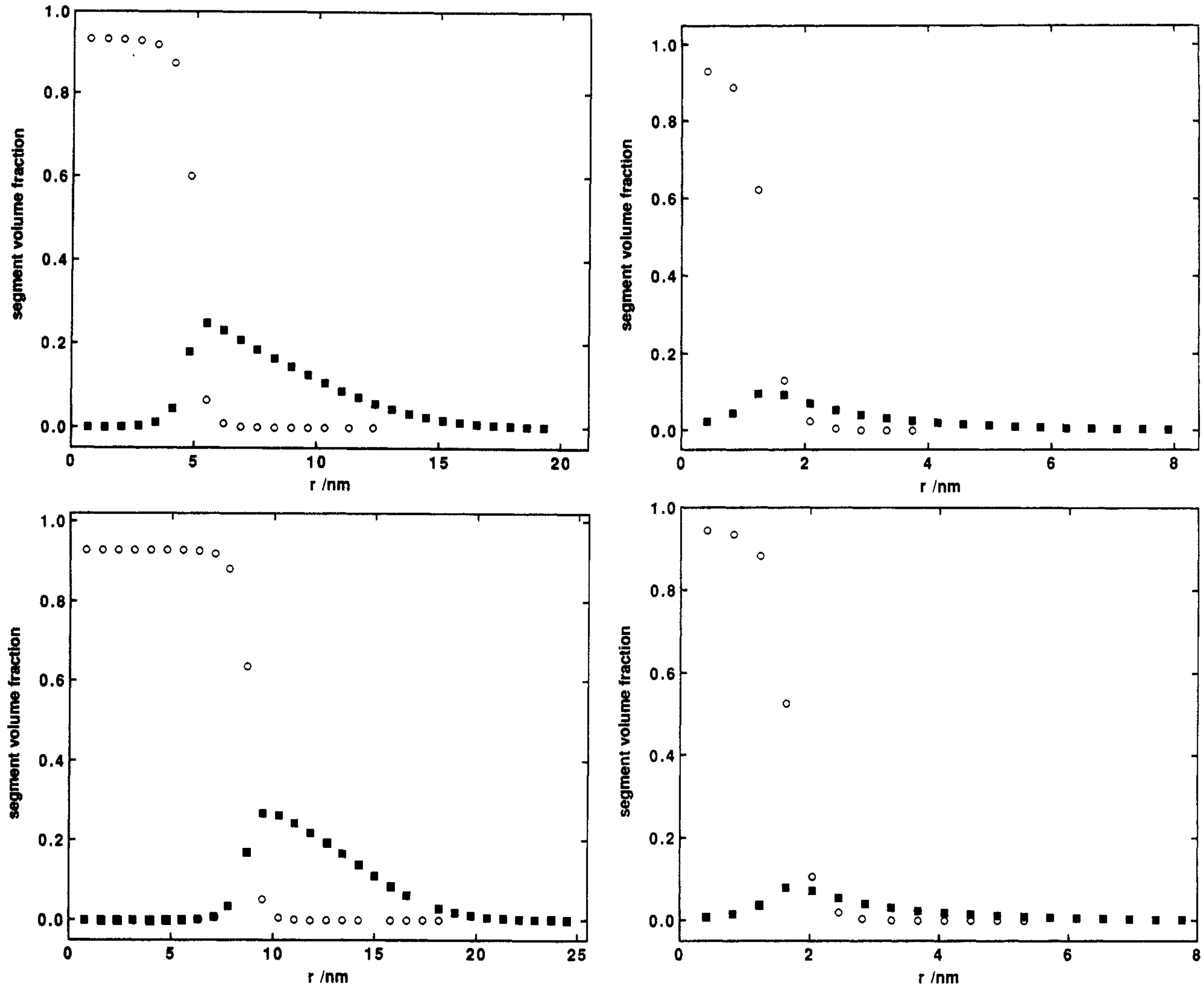

Figure 2. Volume fractions of polystyrene (○) and polyisoprene segments (■) versus the radial distance from the centers of micelles and monomolecular micelles for SI copolymers in hexadecane at 40 °C: (a, top left) SI(1), $m = 41$; (b, top right) SI(1), $m = 1$; (c, bottom left) SI(2), $m = 128$; (d, bottom right) SI(2), $m = 1$.

Table II
Radii of Gyration of Micelles and Monomolecular Micelles Predicted by SCF Theory for Polystyrene-*block*-polyisoprene Copolymers in Hexadecane at 40 °C, Together with the Predicted Radii of Gyration of the Polystyrene and Polyisoprene Components

		SI(1)	SI(2)
		$m = 41$	$m = 128$
micelle	$(R_g)_m$/nm	7.41	9.20
S component	$(R_g)_{mA}$/nm	2.73	4.85
I component	$(R_g)_{mB}$/nm	7.63	9.70
		$m = 1$	$m = 1$
monomolecular micelle	$(R_g)_1$/nm	4.34	3.76
S component	$(R_g)_{1A}$/nm	0.90	1.05
I component	$(R_g)_{1B}$/nm	4.49	4.03

Calculated values of $\Delta G_m{}^{\circ p}$ and $\Delta H_m{}^{\circ}$ determined via eqs 44, 45a, and 45b are given in Table I for SI(1) at $m = 41$ and SI(2) at $m = 128$; all the values are expressed per mole of chain, and for the standard Gibbs energies of micellization the ideally dilute standard states for unassociated chains and micelles are set respectively at concentrations of 1 mol (unassociated chains) dm^{-3} and 1 mol (micelles) dm^{-3}. Experimentally determined values[18,28] of the standard Gibbs energy and enthalpy of micellization, $\Delta G_m{}^{\circ p}$ and $\Delta H_m{}^{\circ}$, are also listed in Table I. Overall, the theoretical and experimental results are in satisfactory agreement, although the value predicted theoretically for the standard Gibbs energy of SI(2) is rather high. In consideration of the degree of agreement it should be noted that the values of $\Delta G_m{}^{\circ p}$ are particularly sensitive to the system interaction parameters used in the calculations and a better overall fit could undoubtedly be obtained by allowing some variation in these, rather than adopting the more satisfying but demanding procedure used here of taking only parameters determined from experimental studies of homopolymers/oligomers and their solutions. (It should also be noted that a 10% uncertainty must be attached to the block molar mass values reported in the experimental study.)

Because of the difficulty in measuring micelle and unassociated chain concentrations directly, standard Gibbs energies of micellization are normally obtained experimentally by determining the critical micelle concentration at a given temperature (or equivalently measuring the critical micelle temperature (cmt) at a given concentration) and using this result in combination with the approximate relationship

$$\Delta G_m{}^{\circ p} \approx RT \ln \text{cmc} \qquad (52)$$

which is based on the assumption that the molar concentration of micelles in the system can be neglected at the cmc and the molar concentration of unassociated chains can be set equal to the total molar concentration of block copolymer chains in the solution. It is of interest therefore to compare standard Gibbs energies of micellization determined from theoretical cmc plots with those deter-

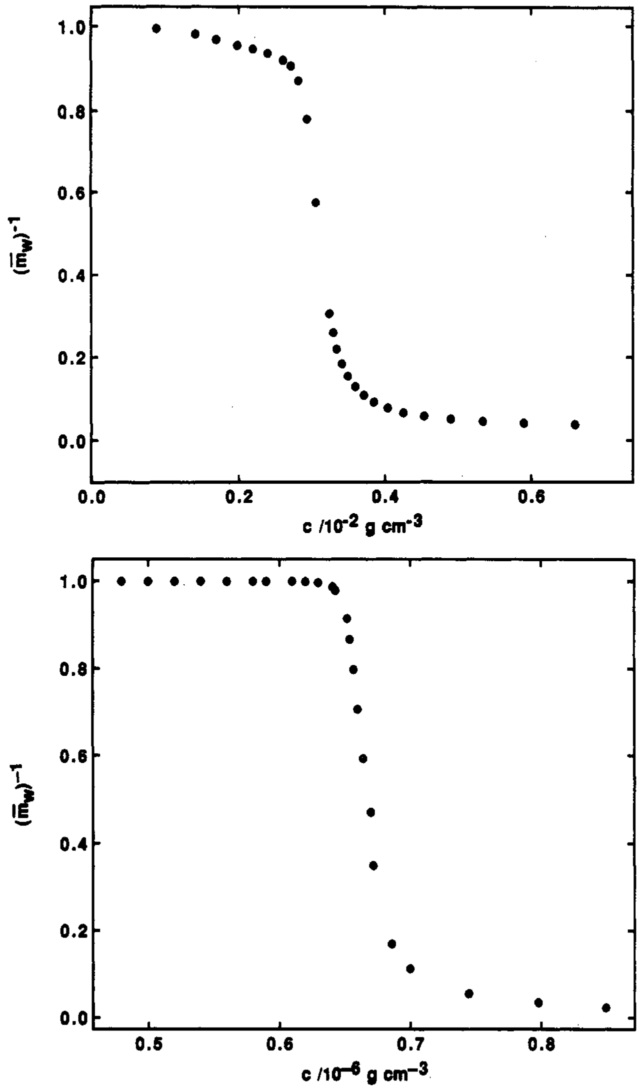

Figure 3. Variation of the reciprocal weight-average association number with total solution concentration for $T = 40$ °C: (a, top) SI(1) in hexadecane; (b, bottom) SI(2) in hexadecane. The cmc's for the SI(1) and SI(2) systems are respectively 2.66×10^{-3} and 6.32×10^{-7} g cm^{-3}.

mined theoretically for the prominent micellar species of high molar mass as described earlier.

The variation of $\bar{m}_w^{-1}$ (the average here being taken over all species, $m \geq 1$) with total solution concentration determined from SCF results is shown in Figure 3a,b for SI(1) and SI(2), respectively. The cmc's for the two systems can be identified with the concentrations at which $\bar{m}_w^{-1}$ begins to fall sharply on increasing the solution concentration and, combined with eq 52, give the $\Delta G^{\circ p}$ values listed in Table I. The values are in good agreement with the theoretical values determined by the direct approach, and lend support to the use of the cmc (or cmt) method for probing the thermodynamics of micellization of block copolymers.

From the comparison of experimental and theoretical results it is concluded that the SCF theory described here is able to account in a consistent and satisfactory manner for the main thermodynamic features of block-copolymer micellization in dilute solution, although there is now a need to compare the theory with more wide ranging experimental data and to investigate scaling behavior. These issues are currently being addressed by us and further work is underway to extend the theory to allow for different micellar shapes and the influence of intermicellar interactions.

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Appendix

The Helmholtz energy of N_f block copolymer chains in a solution of volume V is assumed to be the sum of internal and external contributions:

$$A = -kT \ln z_p^{N_f} - kT \ln Z_e \tag{1'}$$

where z_p is the internal molecular partition function of the chains and Z_e is a total partition function accounting for translational motion of the chains, intermolecular interactions, and long-range polymer intramolecular interactions.

$$Z_e = \frac{1}{\lambda_1^{3N_f} N_f!} \int \dots \int e^{-U/kT}\, \mathrm{d}\mathbf{R}_{1_{Ai}} \dots \mathrm{d}\mathbf{R}_{N_{Ai}} \mathbf{R}_{1_{Bi}} \dots \mathrm{d}\mathbf{R}_{N_{Bi}} \tag{2'}$$

where here $\mathbf{R}_{1_{Ai}}$ signifies the position vector of the first segment of the A block of the ith chain and the integration is taken over the positions of all segments of N_f chains, U is the potential energy of interaction due to N_f chains in a particular configuration, and the division by $N_f!$ allows formally for correct Boltzmann counting of states.

If the chains are unassociated and it is assumed that the molecular coupling partition function, z_{1c}, is independent of chain location and chain/chain intermolecular interactions are absent (i.e. at the infinite dilution limit), then eq 2′ reduces to

$$Z_e = z_{1c}^{N_f} \left\{ \frac{V^{N_f}}{\lambda_1^{3N_f} N_f!} \right\} \tag{3'}$$

where the term in braces accounts for the translational motion of the N_f chains within volume V.

The chemical potential of block copolymer chains in solution is given by

$$\mu_1 = (\partial A / \partial N_f)_{T,V} \tag{4'}$$

which combined with eqs 1′ and 3′ yields

$$\mu_1 = -kT \ln z_p - kT \ln z_{1c} - kT \ln \lambda_1^{-3} \rho_1^{-1} \tag{5'}$$

If the block copolymer chains associate into micelles, there is some restriction of translational motion. Only one chain in each of the N_m micelles can be treated as completely free. The remaining $N_f - N_m$ chains are restricted. The number of translational states for each restricted chain is reduced by a factor $N_m v_m / V$, where V is the total volume of the system and v_m is the volume per micelle within which a restricted chain is effectively free to move relative to that of the unrestricted chain. The total volume available to a restricted chain is $N_m v_m$ because the micelles are in dynamic equilibrium. Since the number of ways of dividing N_f chains into one group of N_m chains and a second group of $N_f - N_m$ chains is $N_f![N_m!(N_f - N_m)!]^{-1}$, it follows that the total translational reduction factor for a system of N_f chains is

$$\frac{N_f!}{N_m!(N_f - N_m)!} \left[\frac{N_m v_m}{V} \right]^{N_f - N_m}$$

If intermicellar interactions are absent and the coupling partition function, z_{mc}, for all micellar chains is the same at a given association number, m, then for N_f chains in the associated system the total partition function accounting for translational motion of chains and for chain/chain and chain/solvent interactions within the micelles is

$$Z_e = z_{mc}^{N_f}\left\{\frac{V^{N_f}}{\lambda_1^{3N_f}N_f!}\right\}\left[\frac{N_f!}{N_m!(N_f-N_m)!}\right]\left[\frac{N_m v_m}{V}\right]^{N_f-N_m} \quad (6')$$

where the $N_f!$ within the braces again allows for correct Boltzmann counting of states.

Combining eqs 1′, 4′, and 6′ gives the relationship for the chemical potential of block-copolymer chains within the micellar state:

$$\mu_m = -kT\ln z_p - kT\ln z_{mc} - kT\ln\left[\lambda_1^{-3}\rho_m^{-1/m}\left(\frac{v_m}{m-1}\right)^{1-(1/m)}e^{1-(1/m)}\right] \quad (7')$$

Setting $m = 1$ in eq 7′ recovers the chemical potential of block-copolymer chains in the unassociated state.

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