Spherical particles obtained by dispersion polymerization: model calculations

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A model of particles formed in dispersion polymerization is suggested and the Gibbs energy of a single particle at infinite dilution is calculated. By minimizing the energy at fixed particle mass and composition, the particle dimensions are calculated and the degree of swelling of the particles is predicted. The estimated geometric radii are somewhat smaller than the experimental values of the hydrodynamic radii.

(Keywords: dispersion polymerization; modelling; spherical polymer particles)

INTRODUCTION

In dispersion polymerization the monomer (M) is completely miscible with the solvent (S), but the forming polymer (P) is insoluble. The polymer is protected from macroscopic precipitation by a steric stabilizer[1–3] (an appropriate block or graft copolymer, C), which distinguishes dispersion polymerization from precipitation polymerization. In some cases, the steric stabilizer is added to the reaction system in advance[4], while in others it is formed during the polymerization by grafting to a polymer present in the system[5,6]. To work satisfactorily, the steric stabilizer must consist of parts that have different affinities to the solvent.

Dispersion polymerization produces particles that have a comparatively compact body consisting of the polymer and an insoluble block of the steric stabilizer (both swollen by a certain amount of solvent), and a shell composed of soluble blocks strongly swollen by the solvent. Consider a polymer particle stabilized in solution by molecules of the diblock copolymer A–B located on the particle surface. The insoluble anchor blocks A are assumed to be uniformly spread over the whole surface of the particle, and the shell of the soluble chains B ensures the steric stability of the particle (*Figure 1*). Blocks A on the surface of the core of the dispersion particle are either partly entangled with chains P in the core, or adsorption of the chains A on the surface of the core is very strong due to the effort to replace the thermodynamically unfavourable contacts A–S and P–S by less disadvantageous contacts A–P. The stability of a system of dispersion particles is not perturbed even when these particles are transferred into a solvent that is good for both stabilizer blocks, A and B, and a precipitant for the polymer[7,8]. Consequently, the transfer of mass between the individual particles can be, at least in the cases quoted, neglected.

Using results of a fluorescence study, which revealed very fast diffusion of small molecules between the core of the dispersion particle and the surrounding solvent, Pekcan *et al.*[9] suggested a non-homogeneous, 'porous' structure of the core. A more recent study showed, however, that this phenomenon can be explained by the existence of a thick diffusion interlayer between the core of the dispersion particle and its shell, which contains both polymer chains and soluble blocks of the steric stabilizer[10]. Higgins *et al.*[11] interpreted their results of neutron scattering as the occurrence of clusters of stabilizer chains on the surface of the core of the dispersion particle. To include these observations into the model would be quite complicated.

In our previous theoretical studies, we investigated a model of block copolymer micelles in a selective solvent[12]. Certainly, there will be a close relation between the state of solution before polymerization (e.g. whether or not the stabilizer forms micelles) and the mechanism of formation of dispersion particles, which determines their final structure. The objective of this study is to extend our recent approach[12] for the description of the swelling behaviour of dispersion particles at fixed particle mass and composition. The results of the model calculations will be compared with experimental results obtained for poly(methyl methacrylate) dispersion particles stabilized by a polystyrene-*block*-poly(ethylene-*co*-propylene) diblock copolymer in decane[1,13].

THEORETICAL

Assume that the dispersion particles are monodisperse (which in real cases need not quite be true[1]) and that each of them contains n_C chains of the steric stabilizer (diblock copolymer) and n_P chains of polymer P (*Figure 1*). The core of the particle consists only of polymer P and has radius R^C. The core is surrounded by a spherical interlayer having thickness D^I, composed of insoluble chains A of the block copolymer, which are chemically different from the polymer. The core and the interlayer form the body of the particle, the radius of which is $R = R^C + D^I$. Both the core and the interlayer are swollen

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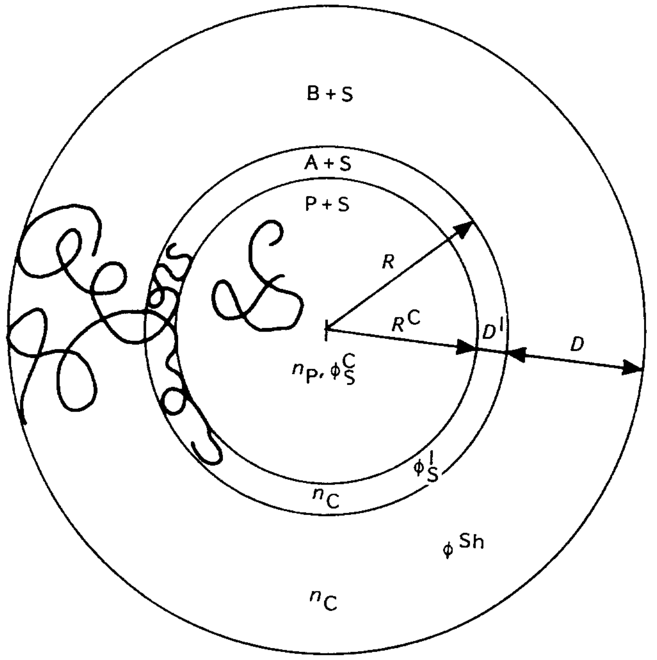

Figure 1 Model of a dispersion polymer particle formed by n_P and n_C chains of polymer P and diblock copolymer C, respectively. The core of the dispersion particle has the radius R^C and consists of polymer P. The insoluble blocks A of the A–B two-block copolymer act as an anchor and form an interlayer of thickness D^I. The soluble blocks B create the shell of thickness D. All parts are swollen by solvent S: its volume fractions are ϕ_S^C, ϕ_S^I and ϕ_S^{Sh}, respectively

with solvent S (volume fractions of the solvent ϕ_S^C and ϕ_S^I, respectively). The body of the dispersion particle is surrounded by a shell of chains B having geometric thickness D and strongly swollen by the solvent (volume fraction of the solvent ϕ_S^{Sh}).

Both in the interlayer and in the shell, the chains A and B are in a deformed state. The average end-to-end distances of the deformed chains projected in the radial direction are defined as D^I and D, respectively[14].

Dilution of the dispersion from the preparation conditions to the conditions of characterization is accompanied neither by a desorption of the steric stabilizer nor by a redistribution of the polymer[7,8], i.e. the mass of particles does not change. A frozen equilibrium is obviously operative in this case. Once formed, the particle mass can be regarded as constant and experimental values can be used for n_C and n_P. With respect to parameters characterizing the dimensions, such as R^C, D^I and D, the dispersion particle is regarded as being in thermodynamic equilibrium, i.e. the particle can change its degree of swelling, and its size is determined by the minimal standard Gibbs energy of the dispersion particle[14]

$$F_d^\circ(R^C, D^I, D) = \min. \qquad (1)$$

The Gibbs energy of a dispersion particle

The diblock copolymer A–B consists of blocks having molecular volumes v_A, v_B, and the molecular volume of the polymer chain is v_P. All chains are assumed to be sufficiently long and flexible. The molecular volume of the solvent is v_S. The numbers of segments in the polymer chain P and in blocks A and B are defined, respectively, as $m_P = v_P/v_S$, $m_A = v_A/v_S$ and $m_B = v_B/v_S$. For the volume of the core of a dispersion particle composed of n_P molecules of the polymer P:

$$V^C = \frac{4}{3}\pi(R^C)^3 = n_P v_P/(1-\phi_S^C) \qquad (2)$$

where

$$n_P = n_C(c_P/c_C)(M_{n,A} + M_{n,B})/M_{n,P} \qquad (3)$$

c_P, c_C are the mass concentrations of the polymer and block copolymer in the system, respectively, and $M_{n,A}$, $M_{n,B}$, $M_{n,P}$ are the corresponding number-average molar mass of blocks A, B and of polymer P. The volume of an interlayer consisting of n_C chains of block A is defined by

$$V^I = \frac{4}{3}\pi[R^3 - (R^C)^3] = n_C v_A/(1-\phi_S^I) \qquad (4)$$

Similarly, for the shell volume:

$$V^{Sh} = \frac{4}{3}\pi[(R+D)^3 - R^3] = n_C v_B/(1-\phi_S^{Sh}) \qquad (5)$$

The Gibbs energy of a dispersion particle can be divided into a number of contributions[14]:

$$F_d^\circ = (F_d^\circ)^C_{mix} + (F_d^\circ)^I_{mix} + (F_d^\circ)^{Sh}_{mix} + (F_d^\circ)^I_{def} + (F_d^\circ)^{Sh}_{def} + (F_d^\circ)^C_{int} + (F_d^\circ)^I_{int} \qquad (6)$$

where $(F_d^\circ)^C_{mix}$, $(F_d^\circ)^I_{mix}$ and $(F_d^\circ)^{Sh}_{mix}$ are the Gibbs energies of mixing of chains in the core, interlayer and shell of the dispersion particle, respectively. $(F_d^\circ)^I_{def}$ and $(F_d^\circ)^{Sh}_{def}$ are the respective elastic deformation energies of chains A and B in the dispersion particle; chains P are assumed to be undeformed. $(F_d^\circ)^C_{int}$ and $(F_d^\circ)^I_{int}$ are contributions that originate in the interfacial energies of the core–interlayer and interlayer–shell boundary.

The Gibbs energy of mixing of polymer P. In terms of the Flory–Huggins equation the contribution $(F_d^\circ)^C_{mix}$ has the form[15]

$$\frac{(F_d^\circ)^C_{mix}}{kT} = \frac{V^C - n_P v_P}{v_S}\ln\phi_S^C + n_P\ln(1-\phi_S^C) + \chi_{PS} n_P m_P \phi_S^C \qquad (7)$$

where χ_{PS} is the Flory–Huggins interaction parameter.

The interfacial energy of chains A of the core–interlayer interface. At the core–interlayer boundary the chains of polymer P are in contact with blocks A of the copolymer. The corresponding contribution to the Gibbs energy of a dispersion particle is proportional to the effective interfacial tension $\gamma_{PA}(1-\phi_S^C)(1-\phi_S^I)$ and to the interface area $4\pi(R^C)^2$

$$\frac{(F_d^\circ)^C_{int}}{kT} = 4\pi(R^C)^2\frac{\gamma_{PA}}{kT}(1-\phi_S^C)(1-\phi_S^I) \qquad (8)$$

For estimation of the interfacial tension γ_{PA}, it is possible with a good approximation to use the relation[16,17]:

$$\gamma_{PA} = \frac{kT}{l^2}\left[\frac{\chi_{PA}}{6}\right]^{1/2} \qquad (9)$$

where $l = (v_S)^{1/3}$ is the characteristic segment length. A decrease in the interfacial tension due to the presence of solvent in the core and interlayer is considered in the factor[18] $(1-\phi_S^C)(1-\phi_S^I)$.

The free energy of mixing of blocks A. The contribution $(F_d^\circ)^I_{mix}$ of blocks A to the free energy of a dispersion particle can be written as[15]

$$\frac{(F_d^\circ)^I_{mix}}{kT} = \frac{V^I - n_C v_A}{v_S} \ln \phi_S^I + \chi_{AS} n_C m_A \phi_S \qquad (10)$$

The deformation energy of blocks A. Assume that chains A are uniformly distributed throughout the whole volume of the interlayer and that they are subjected to deformation in the radial direction at constant coil volume[15]

$$\frac{(F_d^\circ)^I_{def}}{kT} = \frac{1}{2} n_C \left[\frac{(D^I)^2}{r_A^2} + 2\frac{r_A}{D^I} - 3 \right] \qquad (11)$$

where r_A is the mean end-to-end distance of chains A in the unperturbed state.

The interfacial energy of the particle body–shell interface. At the interface interlayer–shell, the chains of blocks A are in contact with the solvent. The respective contribution to the Gibbs energy of a dispersion particle is proportional to the effective interfacial tension $\gamma_{AS}(1 - \phi_S^I)$ and to the interface area $4\pi R^2$:

$$\frac{(F_d^\circ)^I_{int}}{kT} = 4\pi R^2 \frac{\gamma_{AS}}{kT} (1 - \phi_S^I) \qquad (12)$$

Despite the fact that Helfand and Tagami[16] derived relation (9) for the interfacial tension in a symmetrical system of two polymers, many authors also use this relation for estimating the tension between a polymer and a solvent[19,20]. Munch and Gast[19] demonstrated that the error introduced by this assumption into the model calculation is small compared to the total Gibbs energy of the particle. Specifically, for the interface polystyrene–decane, the value of 4.5 mN m^{-1} is obtained for γ_{PA} according to equation (9). This value is comparable to those of the interfacial tension estimated for this pair by different procedures[17].

The free energy of mixing of blocks B. The mixing contribution of n_C blocks B to the total Gibbs energy is[15]:

$$\frac{(F_d^\circ)^{Sh}_{mix}}{kT} = \phi_S^{Sh} \frac{V^{Sh}}{v_S} \ln \phi_S^{Sh} + n_C m_B \chi_{BS} \phi_S^{Sh} \qquad (13)$$

The deformation energy of blocks B. The shell thickness of a dispersion particle D is defined[14] as the root-mean-square end-to-end distance of block B. The deformation energy is then a function of D/r_B, where r_B is the unperturbed mean end-to-end distance of chains B. The deformation energy n_C blocks B is then given by relation[15]:

$$\frac{(F_d^\circ)^{Sh}_{def}}{kT} = \frac{1}{2} n_C \left[\frac{D^2}{r_B^2} + 2\frac{r_B}{D} - 3 \right] \qquad (14)$$

RESULTS AND DISCUSSION

Comparison with experiment

The dispersion particles are regarded as fixed structures with respect to the number of chains of the block copolymer and polymer (once the particles are formed, no exchange of mass takes place), but as entities being in thermodynamic equilibrium with respect to their swelling and geometric dimensions. Characteristic dimensions of a dispersion particle R^C, D^I, D can be obtained by minimizing the standard Gibbs energy (equation (1)) at a fixed n_C and n_P. Dispersions of poly(methyl methacrylate) in decane with a polystyrene-*block*-poly(ethylene-*co*-propylene) as steric stabilizer[1,13] ($M_{n,A} = 42\,000$ g mol^{-1}, $M_{n,B} = 58\,000$ g mol^{-1}) will be discussed as an example. The molecular volumes of repeating constitutional units in the polymer and both copolymer blocks are 0.140 nm^3 for poly(methyl methacrylate), 0.166 nm^3 for polystyrene[21] and 0.124 nm^3 for the ethylene-*co*-propylene copolymer (hydrogenated polyisoprene)[22]. The characteristic ratios, $r/M^{1/2}$, are[21,23] 0.064 nm mol$^{1/2}$ g$^{-1/2}$, 0.067 nm mol$^{1/2}$ g$^{-1/2}$ and 0.096 nm mol$^{1/2}$ g$^{-1/2}$, respectively. The molecular volume of decane is $v_S = 0.323$ nm^3.

To calculate F_d°, the values of the interaction parameters χ_{PS}, χ_{AS}, χ_{BS} and χ_{PA} are needed. Unfortunately, direct experimental values are not available and have to be estimated, e.g. by using the relation[24]:

$$\chi_{iS} \simeq 0.35 + \frac{V_S}{RT} (\delta_i - \delta_S)^2 \qquad (15)$$

in which δ_i (i = P, A, B) and δ_S are Hildebrant's solubility parameters of polymer components and solvent, and V_S is the molar volume of the solvent. The following values were chosen[21]: $\delta_S = 6.6$ cal$^{1/2}$ cm$^{-3/2}$ (= 13.5 J$^{1/2}$ cm$^{-3/2}$); $\delta_P = 9.08$ cal$^{1/2}$ cm$^{-3/2}$ (= 18.58 J$^{1/2}$ cm$^{-3/2}$) and $\delta_A = 8.56$ cal$^{1/2}$ cm$^{-3/2}$ (= 17.52 J$^{1/2}$ cm$^{-3/2}$). According to equation (15), the corresponding values are $\chi_{PS} = 2.4$ and $\chi_{AS} = 1.6$. The value for poly(ethylene-*co*-propylene) in heptane, $\chi_{BS} = 0.5$, reported by Nagarajan and Ganesh[20], has also been used for decane solutions because of the chemical similarity of both solvents. Otherwise, unrealistically high χ_{BS} values would ensue from the solubility parameters. The χ_{PA} value was calculated by using relation (15), with the difference that the empirical term 0.35 was absent for both polymeric components[24]: from values of δ_P and δ_A, it follows that $\chi_{PA} = 0.09$.

For each dispersion system[13], the dimensions of dispersion particles, R^C, D^I and D were calculated from the following data: concentration ratio of the polymer and block copolymer, c_P/c_C, number-average molar mass of poly(methyl methacrylate) in the core of the dispersion particle, $M_{n,P}$, and the average number of chains of the steric stabilizer per particle, n_C.

The calculated dimensions of the dispersion particles $(R + D)$ are approximately 20–25% smaller than the experimental hydrodynamic radii, R_h, obtained by quasielastic light scattering[13] (*Table 1*). This may be due to the fact that the dispersion particles are not completely uniform and the experimental values of the molar mass and size are mass averages or higher averages of these quantities. The calculated degrees of swelling of the particle core, expressed by the volume fraction of solvent, ϕ_S^C, are similar for all our systems and amount to about 0.05. These values are much smaller than those estimated by Stejskal *et al.*[1].

The calculated D^I values vary between 0.9 and 1.6 nm, and are thus small compared with the unperturbed end-to-end distance of the A blocks ($r_A = 14$ nm). The volume fraction of the solvent in the interlayer, ϕ_S^I, varies from 0.25 to 0.68 for the dispersions studied (extreme cases are shown in *Figure 2c*). The very small thickness

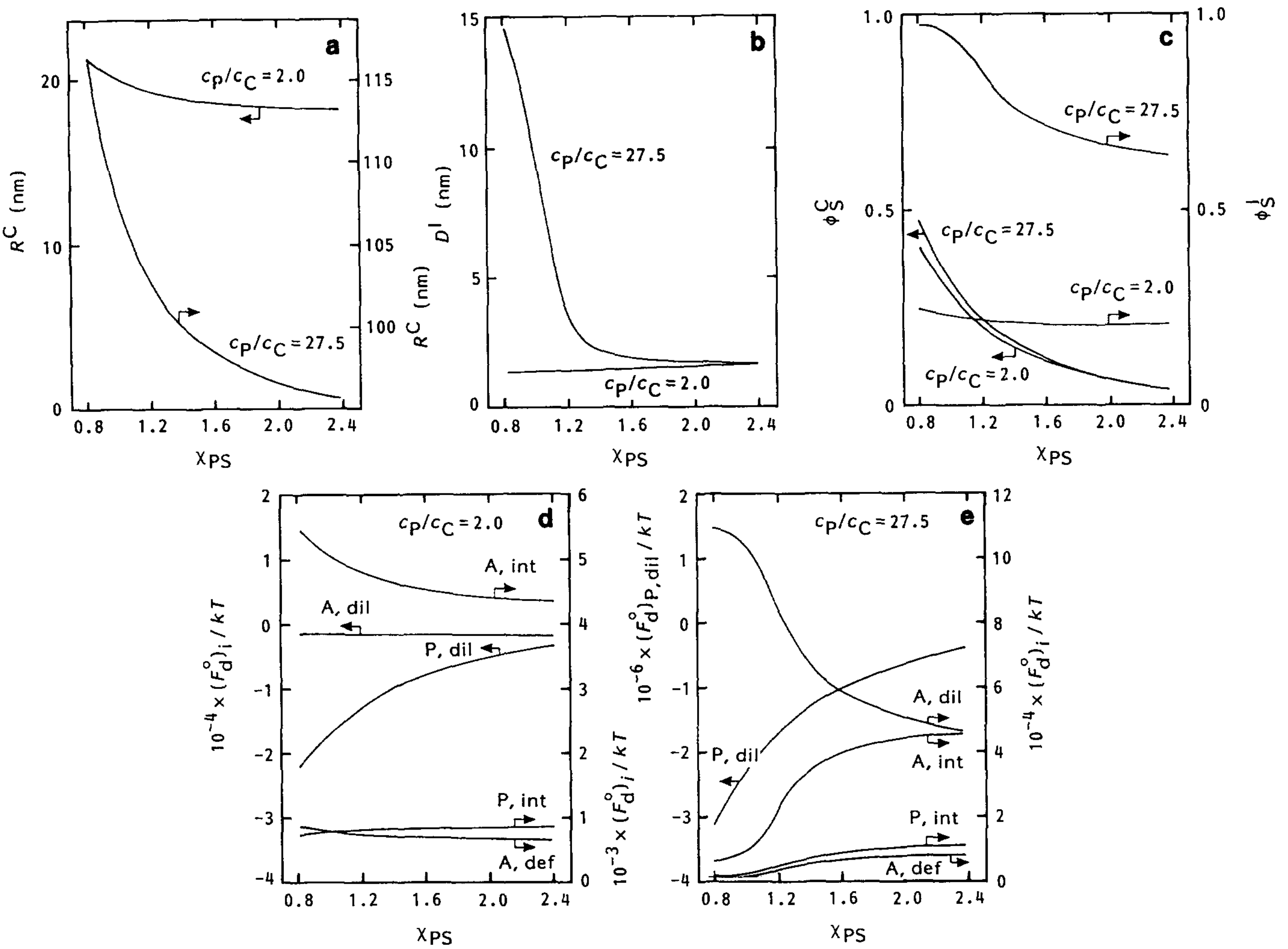

Figure 2 Dependence (a) of the radius of the core, R^C, (b) of the thickness of the interlayer, D^I, (c) of the volume fraction of solvent in the core and interlayer, ϕ_S^C and ϕ_S^I, respectively, and (d, e) of the individual contributions of the Gibbs energy $(F_d^o)_i$ (see text for meaning of i) on the interaction parameter χ_{PS} (c_P/c_C is the polymer–stabilizer mass ratio)

Table 1 Parameters of dispersion particles

	Experimental[13]				Calculated (*Figure 1*)			
Code	n_C	c_P/c_C	R_h (nm)	$10^{-3} \times M_{n,P}$ (g mol^{-1})	R^C (nm)	D^I (nm)	D (nm)	$R+D$ (nm)
DX1	150	8.06	72	47.2	35	1.1	22	57
DX2	115	4.03	61	56.9	25	1.3	22	49
DX3	103	2.69	59	69.4	21	1.5	22	45
DX4	89	2.02	50	68.0	18	1.6	22	42
D1	322	17.6	94	141.2	58	1.0	21	81
D2	132	8.80	73	116.2	34	0.9	21	56
D3	125	5.87	65	134.3	29	1.1	22	51
D4	131	4.40	65	161.4	27	1.3	22	50
D5	914	27.5	151	162.2	96	1.0	22	119
D6	735	13.8	121	212.5	71	1.2	22	94
D7	370	9.17	99	176.7	49	1.2	22	72
D8	284	6.88	92	230.0	41	1.2	22	64

of the interlayer D^I can be interpreted in terms of the 'pancake' model[25]. According to this model, the thickness of the layer formed by adsorbed insoluble chains may be of the order of magnitude of several segmental lengths, i.e. much smaller than the unperturbed chain dimensions. At the same time, the end-to-end distance in the direction parallel with the adsorption interface has the same order of magnitude as the unperturbed dimensions.

The calculated thickness of the particle shell (12–22 nm) is comparable with the unperturbed end-to-end distance for free chains of the same molar mass. The average volume fraction of solvent is $\phi_S^{Sh} = 0.96 - 0.98$.

Effect of the input parameters on the results of calculations

With respect to the equivocal character of choice of the values of the Flory–Huggins interaction parameters for the polymer and the two blocks in model calculations, their influence on the calculated dimensions of dispersion particles has to be assessed. Owing to the high values of the parameters χ_{PS} and χ_{AS}, the predominant role in the Gibbs energy of a dispersion particle is played by the very thermodynamically disadvantageous interactions of P and A chains with the solvent, balanced by the deformation energy of A chains and by minimization of the interfacial energy.

To demonstrate the effect of the interaction parameters χ_{PS} (*Figure 2*) and χ_{AS} (*Figure 3*), two systems[13] with the greatest difference in the polymer–stabilizer ratio, i.e. $c_P/c_C = 2.0$ and 27.5, were chosen. It can be seen in *Figures 2* and *3* that both systems basically differ not only in the size of the quantities represented there, but also in their dependences on Flory–Huggins interaction parameters. While for the system with $c_P/c_C = 27.5$, D^I

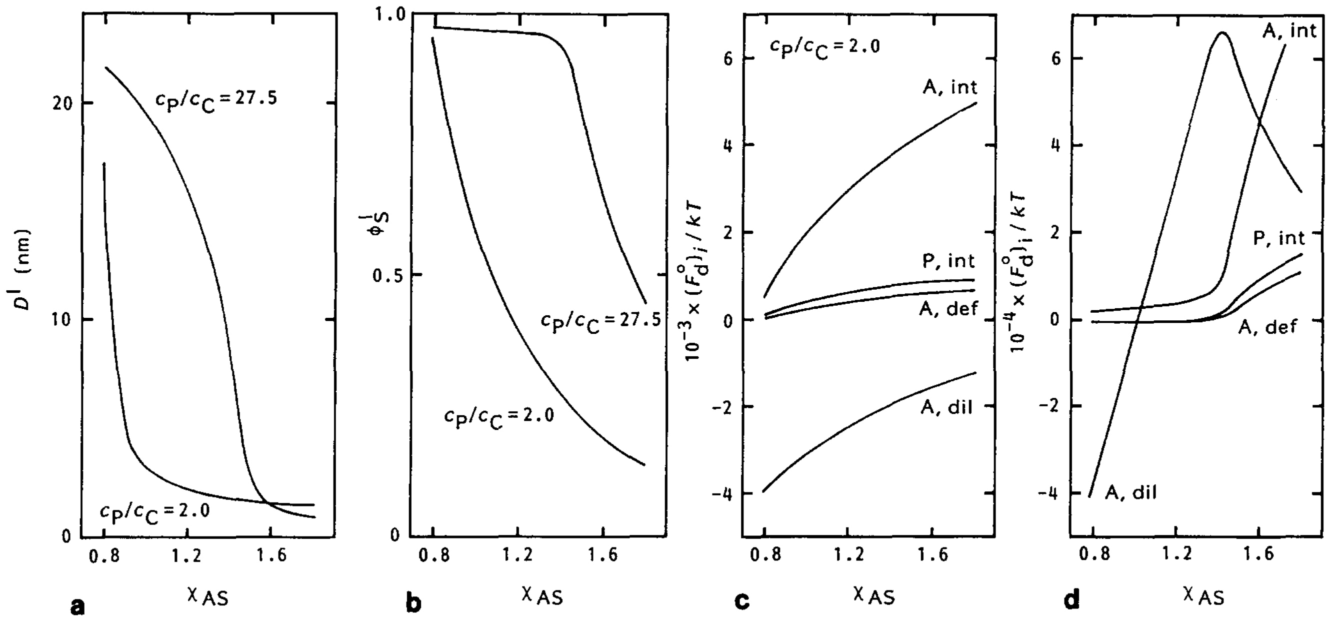

Figure 3 Dependence (a) of the thickness of the interlayer, $D^{\rm I}$, (b) of the volume fraction of solvent in the interlayer, ϕ_S^I, and (c, d) of the individual contributions of the Gibbs energy $(F_d^\circ)_i$ (see text for meaning of i) on the interaction parameter χ_{AS} (c_P/c_C is the polymer–stabilizer mass ratio)

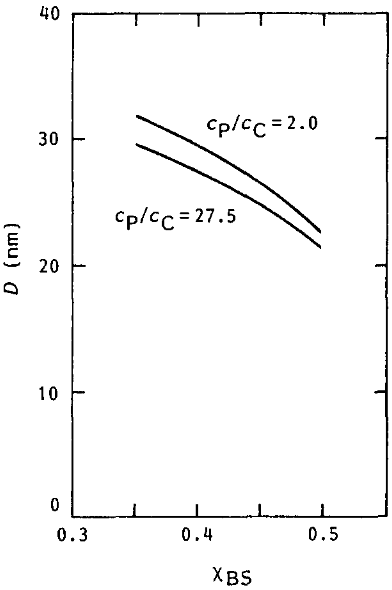

Figure 4 Dependence of the shell thickness D on the interaction parameter of the soluble block with the solvent, χ_{BS} (c_P/c_C is the polymer–stabilizer mass ratio)

(*Figures 2b* and *3a*) begins to increase markedly at $\chi_{AS} < 1.5$ or $\chi_{PS} < 1.2$, in the system with $c_P/c_C = 2.0$ the increase sets in at only $\chi_{AS} < 1.0$. With increasing χ_{PS} there is even a slight decrease. The radius R^C (*Figure 2a*) increases with the χ_{PS} parameter more, when c_P/c_C is higher. The dependences of ϕ_S^C and ϕ_S^I (*Figures 2c* and *3b*) are also significant. The effect of the individual contributions to the total Gibbs energy of the dispersion system is illustrated by their dependence on the interaction parameters.

The interaction parameters χ_{PA} seems to exert a weak effect on the thickness of the interlayer, and this in a system with only a high c_P/c_C. $D^{\rm I}$ decreases from 1.5 nm at $\chi_{PA} = 0.09$ to 1.0 nm at $\chi_{PA} = 0$. As expected, the parameter χ_{BS} only affects the shell thickness, but the effect is quite considerable (*Figure 4*).

The similarity between the dependence of $D^{\rm I}$ on χ_{AS} (*Figure 3a*) and the dependence of the thickness of the adsorption layer on the effective chemical potential reported in a paper by Marques *et al.*[25] should be mentioned here (cf. Figure 3 in reference 23). Obviously, different approaches lead to similar results.

CONCLUSIONS

The model discussed describes the swelling of dispersion particles; the mass transport between particles is not considered. The calculated geometric dimensions of the dispersion particles are about 20–25% smaller than the experimental values of the hydrodynamic radii (*Table 1*). This difference can be attributed to the non-uniformity of the particles[1], which has been neglected in the calculations, and to the uncertainty in the values of the Flory–Huggins interaction parameters used in the computations. On the whole, the agreement between the experimental and predicted dimensions is acceptable. Model calculations of the present type are helpful in preparing required dispersion properties.

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