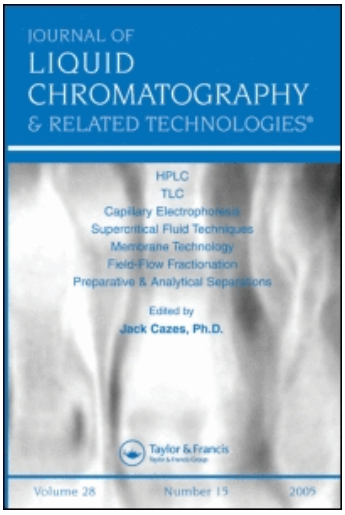

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SIZE EXCLUSION CHROMATOGRAPHY OF ASSOCIATING SYSTEMS. I. THE THEORETICAL MODEL

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ABSTRACT

Block copolymers in dilute solutions in selective solvents form micelles via closed association which is characterized by equilibrium between unimer and n-mer. A simple theoretical model has been proposed describing the behavior of such a system in the size exclusion chromatography (SEC). Chromatograms have been calculated varying association number and relative rates of association and dissociation. The results are compared with those of Coll´s theory for SEC of surfactants and Gilbert´s theory of associating systems.

INTRODUCTION

Block copolymers in dilute solutions in selective solvents (i.e., good solvents for one block, which are poor solvents for the other block) associate reversibly to form micelles, resembling thus the behavior of soaps and surfactants (1,2). It has been recognized (3) that the block copolymer micellization obeys the model of closed association, characterized by an equilibrium between unimer (molecularly dissolved copolymer) and spherical micelles (having a core from insoluble blocks and a shell from solvated blocks with a narrow molar mass and size distribution). Two- or three-block copolymers of AB or ABA types consist of several tens of molecules, while the association number of micelles from multiblock (e.g., star-shape) copolymers (4) may be lower.

Although the detailed information about size, mass and internal structure of block copolymer micelles has been reviewed in literature (1,2), only scarce and rather confused data on the kinetics of block copolymer micellization have been reported so far. While the rate of micellization of soaps and detergents has been found fast (2) (on the time scale always below one second), the results of the rate of block copolymer micellization, based on sedimentation velocity (3,4) and size exclusion chromatography (4-8), are puzzling. Some authors (4,8) have found the micelle formation or decomposition to be fast processes as compared with the time of experiment (in paper (8) even a rate in ms has been specified), others (5,6) have found the processes to be extremely slow, on the time scale of minutes. The mechanism of micelle formation or decomposition is probably more complex in case of block copolymers as compared with soaps and surfactants, due to inevitable entanglements of polymer chains in micellar cores. Besides, the rate of micellization of block copolymers may be influenced by various factors, e.g., by block incompatibility, block length, and selectivity of solvent system.

The sedimentation or chromatographic diagrams reflect the constantly disturbed and re-established unimer/micelle equilibrium

during transport. Theories trying to describe this very complex phenomenom are based on simplified models. A theory of the separation of unimer and micelles during a sedimentation velocity experiment assuming a slow transport and an instantaneous establishment of the unimer/micelles equilibrium has been developed by Gilbert (9,10). Ackers and Thompson's extention of Gilbert's theory to a SEC method (11) assumed a relatively large zone of the solution under study. Expressions of the leading and trailing edges have been derived for a rapidly associating system. Coll's theory (12) applies to surfactant transport in SEC experiment. Instead of mass action law, Coll postulates that below c.m.c. only unimer is present in solution, and above c.m.c., the unimer concentration is constant (and equal to c.m.c). Results of Coll's theory (in the form of rectangular zones) qualitatively agree with those of Ackers and Thompson's theory (smooth curves). The theories mentioned above (9,11,12) are based on the assumption of a very fast establishment of the unimer/micelle equilibrium, without specifying the lower speed limit of the "fast" process, from where the theories should be applicable.

Equations resulting form Ackers and Thompson's modification of Gilbert's theory can be solved analytically either for an infinitely mobile equilibrium unimer $\rightleftharpoons$ micelles, or for association number n=1 (isomerization), regardless of the rate of isomerization. For higher association numbers and finite rates of micelle formation or decomposition, an analytical solution is impossible and the numerical solutions published so far (Bethune and Kegeles) (13) concern only the comparision of the fast closed trimerization unimer $\rightleftharpoons$ trimer, with the progressive trimerization unimer $\rightleftharpoons$ dimer $\rightleftharpoons$ trimer.

The aim of this work was: a) to develop a theoretical model of the transport of a micellizing system in a SEC experiment, covering also the various rates of micelle formation and decomposition and b) to find limits of applicability of the existing theories.

THEORETICAL PART

A set of equations describing mathematically the chromatographicprocess of a reversibly associating system may be derived on the basis of the mass balance in the cross-sectional layer or thickness dx.

In the present model, the following assumptions have been made:

a) The mobile phase of a constant density moves along the axis of the bed (coordinate x) at a constant velocity v.

b) A semifinite bed of uniform spherical gel particles of radius R is characterized by a fractional volume of a mobile phase α and by a fractional void volume β of gel particles.

c) Reversible micellization of block copolymers can be described by a closed association

$$n\ U \underset{k_d}{\overset{k_{as}}{\rightleftharpoons}} M, \qquad (1)$$

where U and M represent unimer and micelles, respectively, n is the association number, and k_{as} and k_d are the rate constants of micelle formation or dissociation, respectively.

d) Micelles are supposed to be monodisperse in molar mass and size.

e) Micellization equilibrium takes place in the mobile phase only.

f) Unimer may penetrate freely (by diffusion) into pores of gel particles, but no micelle may enter the gel phase (due to sterical reasons).

g) All pores are accessible for unimer (with an equal probability), and the size exclusion principle is the only mechanism of the separation process.

Having taken into account all concentration changes in a fiven cross-sectional column layer, it is possible to formulate the following differential equations:

$$(\partial c_U^{(m)}/\partial t)+v(\partial c_M^{(m)}/\partial x)-D_U^{(m)}(\partial^2 c_U^{(m)}/\partial x^2)=(Q_U)_R+Q_d \ , \qquad (2)$$

$$(\partial c_M^{(m)}/\partial t)+v(\partial c_M^{(m)}/\partial x)-D_M^{(m)}(\partial^2 c_M^{(m)}/\partial x^2)=Q_{as} \ , \qquad (3)$$

and

$$(\partial c_U^{(s)}/\partial t) = D_U^{(s)}\left[(2/r)(\partial c_U^{(s)}/\partial r)+(\partial^2 c_U^{(s)}/\partial r^2)\right], \qquad (4)$$

where $c_U^{(m)}$, $c_M^{(m)}$ and $c_U^{(s)}$ represent the concentrations of unimers (U) and micelles (M) in mobile (m) and stationary (s) phases, respectively, expressed in terms of polymer masses per unit volume, t is the time, x represents the position in a column in the flow direction, and r is the distance from the center of a gel particle. Symbols $D_U^{(m)}$ and $D_U^{(s)}$ stand for diffusion coefficients of the species in the respective phases, and v is the constant velocity of mobile phase.

In accordance with the above reaction scheme (eq. (1)), the rate of micelle formation, Q_{as}, or dissociation, Q_d, is given by eq.(5)

$$Q_{as}= -Q_d = -k_D c_M^{(m)} + k_{as}(c_U^{(m)})^n \ . \qquad (5)$$

For unimer, no resistance to fluid mass transfer between mobile and stationary phases is assumed. Thus it holds at the fluid - -particle interface that

$$K_s c_U^{(m)} = c_U^{(s)} \quad \Big| r = R \ , \qquad (6)$$

where K_s is the distribution factor for the interface, and R is the radius of a gel particle.

The source term , $(Q_U)_R$, due to sorption of polymer in gel particles can be expressed as

$$(Q_U)_R = -(3\gamma/R)D_U^{(s)}(\partial c_U^{(s)}/\partial r) \quad \Big| r = R \ , \qquad (7)$$

where $\gamma = \beta(1-\alpha)/\alpha$.

The boundary and initial conditions characterizing the SEC process outlined above are:

$$c_U^{(m)}(x,t) = c_M^{(m)}(x,t) = 0, \quad \text{for } x=0,\ t \geq 0, \tag{8}$$

$$c_U^{(m)}(x,t) = c_M^{(m)}(x,t) = 0, \quad \text{for } x \to \infty,\ t \geq 0 \tag{9}$$

$$c_U^{(m)}(x,t) = c_{oU}^{(m)}\, f(x), \quad \text{for } x \geq 0,\ t=0, \tag{10}$$

$$c_U^{(m)}(x,t) = (k_{as}/k_d)(c_{oU})^n f(x)^n, \quad \text{for } x>0,\ t=0, \tag{11}$$

In eqs. (10) and (11), $c_{oU}^{(m)}$ represents the maximum value of $c_U^{(m)}$ and function $f(x)$ describes the normalized initial concentration profile in a mobile phase.

Equilibrium Chromatography of a Reversibly Associating System

In the present paper, we will treat the simplified model of SEC of a micellar system. We assume that:

a) Axial dispersion is neglected since it has only a minor effect on the shape of the concentration profiles in a mobile phase, as compared with other factors (such as micellization in combination with the sieve filtration mechanism).

b) The solute equilibration between the mobile and stationary phases can be regarded as an instantaneous process, at least in comparison with the time of SEC experiment. This assumption simplifies considerably the mathematical solution of the equations. The concentration of unimer in a stationary phase $c_U^{(s)}$, is then proportional to $c_U^{(m)}$, $c_U^{(s)} = K\, c_U^{(m)}$, and equation (4) need not be solved.

For better manipulation of mathematical equations (see Appendix) the reduced dimensionless variables are introduced

$$\tau = tv/L, \quad X = x/L, \tag{12}$$

$$S=c_U^{(m)}/c_{oU} \quad , \quad F=(k_d/k_{as})c_M^{(m)}/(c_{oU})^n \quad , \qquad (13)$$

$$K=\gamma K_s \quad , \quad w_{as}=(k_{as}\, c_{oU}^{n-1}\, L)/v \quad , \quad w_d = (k_D L)/v \quad , \qquad (14)$$

where L is the length of a column. The simplified equations may then be written

$$(1+K)(\partial S/\partial \tau)+(\partial S/\partial X) = w_{as}(F-S^n) \quad , \qquad (15)$$

$$(\partial F/\partial \tau)+(\partial F/\partial X) = w_d(S^n-F) \quad . \qquad (16)$$

Parameters w_{as} and w_d represent the relative rates of association and dissociation with respect to flow velocity. The shape of function f(X) used in equations (10) and (11) is shown in Fig.1a (for details see Appendix).

RESULTS AND DISCUSSION

The numerical solution of equatioes (15) and (16), discussed in this section, were carried out varying the following *parameters:*

a) association number n:

n=1, (isomerization - although not important for SEC of micellar systems, theoretically interesting case),

n=2, (dimerization),

n=4, 8, 16 (micellization - formation of relatively small micelles)

b) relative rates of micelle formation or dissociation w_{as} and w_d, respectively:

$w_{as}= w_d= 1$ (slow reactions with respect to the flow rate);

$w_{as}= w_d= 10, 40$ (moderately fast reactions);

$w_{as}= w_d= 400$ (fast reactions).

Results presented in the following figures cover only $w_{as}/w_d=1$ (the calculations for other values of the ratio do not

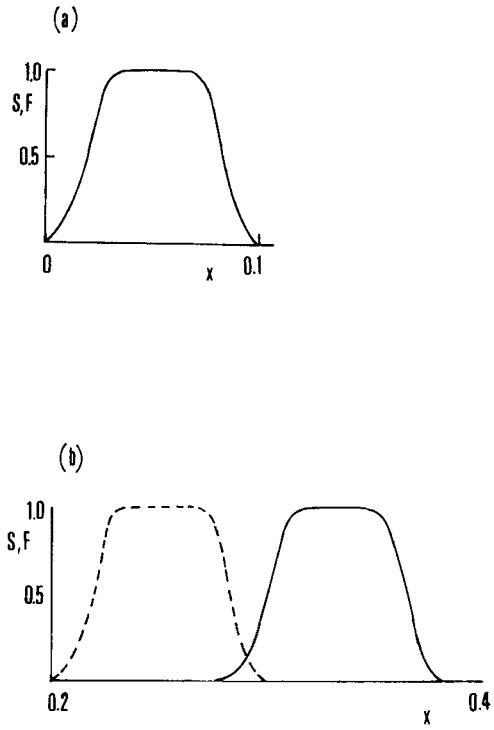

FIGURE 1. a) Original concentration profile (original peak) of the slow equilibrium component at the beginning of simulated SEC experiment.
S is the reduced concentration of the slow component (see eq. (13)); X is the reduced column length (see eq. (12)).
b) Calculated chromatogram of two independent components for $K_S=1$, $\gamma=0.5$.
Full line - fast component with the reduced concentration F; dashed line - slow component with the reduced concentration S.

exhibit qualitatively new features). In the subsequent discussion we will therefore use just one parameter $w=w_{as}=w_d$. In all cases, the value K=0.5 (which corresponds to $K_s=1$ and $\gamma=0.5$) (eq.(14)) was used. This value represents quite a high separation efficiency. In the present paper we assume the equal separation efficiency, regardless of the association number n, which simplifies considerably the comparison of theoretical chromatograms for different values of n. Unfortunately, this assumption cannot be realized in experimental SEC of micellar systems.

In the subsequent discussion, we use the following terminology:

a) a slow component - a component of a reversibly associating system which enters the gel pores (or more generally, which is slowed down by the interactions with a stationary phase);

b) a fast component - a component which neither enters the gel pores, nor interacts with a stationary phase (for $n>4$, it corresponds to small block copolymer micelles).

The terms slow independent component and fast independent component are reserved for species which may exist separately, i.e., they are not in mutual equilibrium ($w_{as}=w_d=0$).

The calculations for smaller n (n=1, 2, 4) are not important for SEC of micellar systems as the separation of the two equilibrium forms based on size-exclusion mechanism would be negligible for isomers or for associates scarcely bigger than unimers. Nevertheless, the results may find their application in other types of chromatography (gas or liquid chromatography of interacting systems). Furthermore, using the assumption of the separation efficiency independent of n, the results for small values of n may be compared readily with those for higher n and thus the influence of the association number on the chromatogram shape may be traced directly. The comparison of calculated chromatograms is carried out for the column section characterized by the reduced interval of the column length $X \in (0.2 - 0.4)$. In this column section the independent components are well separated (Fig.1b).

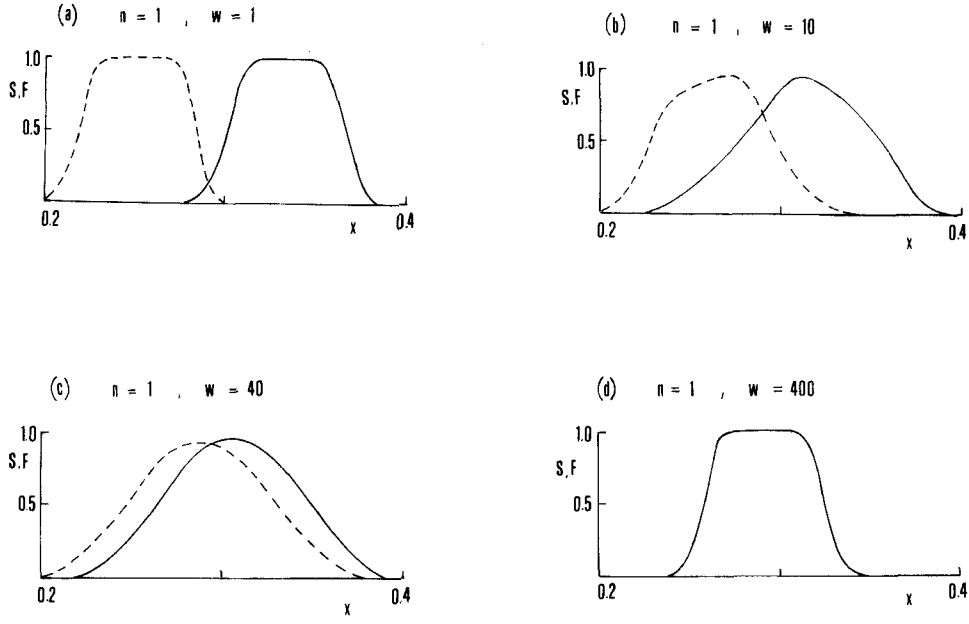

FIGURE 2. Calculated chromatograms for reversible isomerization. The meaning of symbols is the same as in Fig. 1.

The results for isomerization are shown in Fig.2. They resemble those obtained previously by other authors (14,15). They are presented to demonstrate the mathematical correctness of the computation procedure used in the limiting case of n=1. For slow isomerization, w=1 (Fig.2a), the chromatogram coincides with that for the independent species (Fig.1b). For w=10 (Fig.2b), the changes in the shape of the peak become significant. Peaks are broader as compared with the initial one (Fig.1a). For w=40 the separation of the peaks, which are broad, smooth and symmetrical, is very poor (Fig.2c). In case of fast isomerization, w=400 (Fig.2d), both components move nonseparated through a column at a rate which is an average of the rates of independent components. The initial concentration profiles neither change nor separate during a simulated chromatographic experiment.

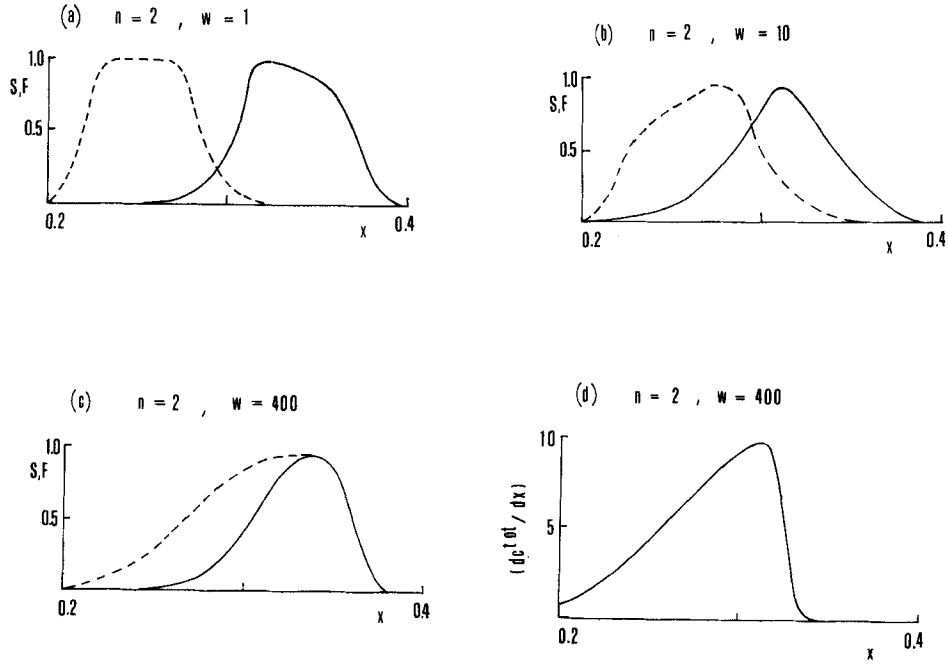

FIGURE 3. Calculated chromatogram for a reversible dimerization. a) slow dimerization, b) moderately fast dimerization, c) fast dimerization, d) the derivative of the total reduced concentration (c^{tot}=S+F) with respect to reduced column length X.

Fig.3 shows the chromatograms for the dimerization. The distortion of peaks is more pronounced than in case of isomerization. The faster peak is evidently distorted even for a slow reaction, e.g., w=1 (Fig.3a). For fast reactions, (e.g., w=400), the peaks differ in the leading edge and coincide in the trailing edge which is steeper than any of both leading edges. The first small rise of the concentration of the slow component corresponds, with respect to the position in the column, to that of the independent slow component. The derivate of the total concentration in the leading edge region is a smooth and monotonous curve which is in agreement with Gilbert´s theory for fast isomerization (9,10) (Fig.3d).

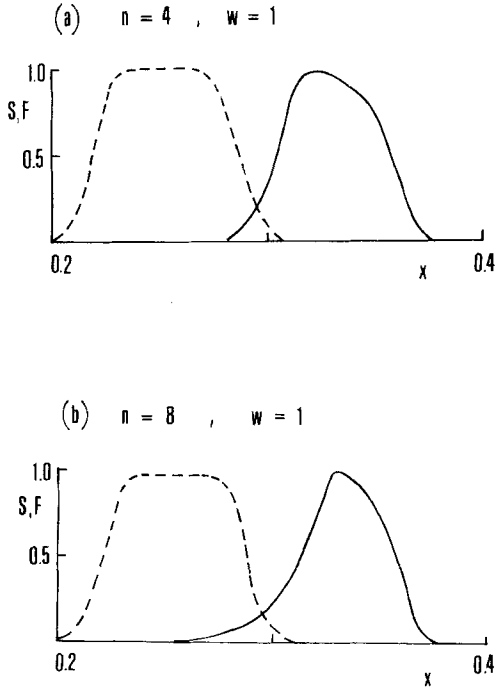

FIGURE 4. Calculated chromatograms for slow association equilibrium.
The meaning of the symbols is the same as in Fig.1.

Figs.4,5,6 and 7 show calculated chromatograms for higher association numbers (n=4, 8, 16). In case of slow reactions, w=1 (Fig.4), the simulated SEC experiments still lead to the separation of equilibrium components. The slower peak becomes broader and the faster peak sharper with the increasing value of n. For ten times faster association and dissociation rates, w=10 (Fig.5), the shapes of the peaks remain basically the same as in the previous case, nevertheless, the separation of the peaks is less pronounced.

For the fast reactions, w=400 (Fig.6), the curves have the typical shapes predicted by Gilbert´s theory for a fast association

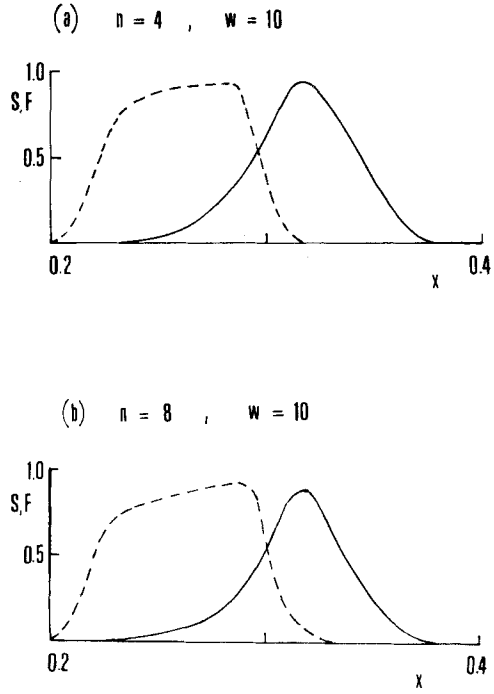

FIGURE 5. Calculated chromatograms for moderately fast association equilibrium.
The meaning of the symbols is the same as in Fig.1.

equilibrium. The resemblance of the concentration profiles calculated in our work and those predicted by the Gilbert´s theory is obvious especially for higher values of n (n=8, 16). The concentration of the slow component starts to grow up relatively quickly in the position corresponding to the position of the leading edge of the independent slow peak. Then, the rise slows down and a relatively broad region of very slowly growing concentration is reached. The final drop (trailing edge) is very steep and resembles a shockwave. The peak is broader than the original one. The fast peak, which is narrow and asymmetrical (leading edge is less steep than the trailing edge) grows up

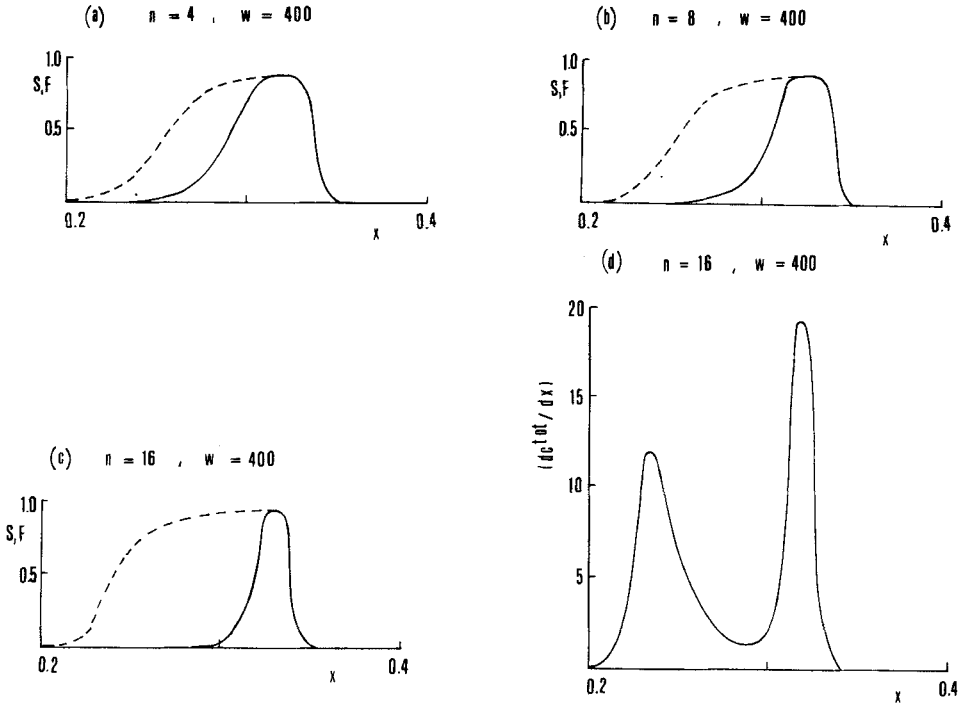

FIGURE 6. Calculated chromatograms for fast association equilibrium (a-c), d) the derivative of the total reduced concentration (c^{tot}=S+F) with respect to reduced column length X.
The meaning of the symbols is the same as in Fig.1.

quickly in the region of a constant concentration of the slow component. The trailing edge of the fast peak coincides with that of the slow peak in the position between the trailing edges of peaks belonging to the independent species. The derivative of the total concentration shows two maxima in the leading edge region (Fig.6d).

The peaks for the higher association number (e.g., n=8) and w=40 resemble in shape those of the fast reaction, only the trailing edge for the moderately fast reaction is less steep

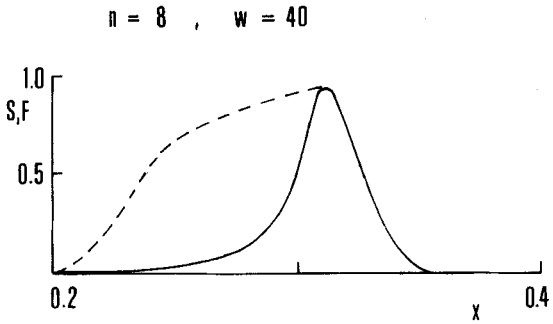

FIGURE 7. Calculated chromatogram for higher association number and moderately fast association.

and is shifted slightly to the higher values of X (Fig.7). This results is presented to demonstrate that the higher is the association number, the lower value of w would lead to the chromatogram resembling that of a fast association equilibrium.

The numerically simulated SEC experiments indicate further that the mass fraction of associates decreases as the solute passes through the column. This fact is evident mainly for the fast and moderately fast association equilibria. The slow peak becomes broader with increasing elution. The fast peak becomes narrower as the elution proceeds, nevertheless, the value of its maximum concentration does not decrease significantly. After a sufficiently long time (provided that the column secures an efficient separation), the associates (fast peak) may disappear from the system completely. This result is in agreement with Coll´s theory (12) of the chromatographic behavior of surfactants near the critical micelle concentration.

The results of numerical calculations indicate that the rate limit, from which the association equilibrium may be considered as a fast process, is surprisingly low. For association numbers corresponding to small micelles of block copolymers (e.g., n=8, 16) the re lative rates such as, e.g., w=40 are sufficient to produce a chromatogram resembling that based

on Gilbert's theory. Systems with fast rates of association and dissociation, w=400, give chromatograms typical for a mobile association equilibrium.

From the experimental point of view it means that for common SEC experiments (when the total time of measurement is about 20-30 min.), the rates of micelle formation or dissociation (as a matter of fact it is the rate of the slower process which must be considered as a limiting factor) in the order of seconds are sufficient to produce the chromatogram typical for a fast association (micellization) equilibrium.

In the following paper we shall present a modified model covering also a hindered release of solute from the gel pores and some relevant experimental data.

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APPENDIX

Numerical Computations

Equations (15) and (16) are hyperbolic partial differential equations (PDEs) of the first order. For numerical calculations, they were replaced by finite-difference expressions (FDEs) and solved in the region of variables $X \in \langle 0,1 \rangle$ and $\tau \in \langle 0,1 \rangle$. To get a numerical solutions of FDEs, four points Wendroff scheme was used (16). A network of grid points (i,j) with the grid spacing, $\Delta X=(X_{i+1}- X_i)=10^{-3}$ and several different equidistant grid spacing in the time scale $\Delta\tau=(\tau_{j+1}- \tau_j)$, was defined. For all calculations, $\Delta\tau$ was always smaller than ΔX and $\alpha=(\Delta\tau/\Delta X) \in \langle 0.25\text{-}0.001 \rangle$. Diminution of α was used as a test of convergency of the calculations. From the theoretical point of view, the Wendroff formula is convergent for $\Delta X \to 0$ and $\Delta\tau \to 0$, regardless of the values of α, but for finite values of ΔX, the value of α as small as possible is favorable (it prevents numerical oscillations in case that the concentration profile is steep). The values of ΔX and α used in computer calculations were results of a compromise between sufficient precission (small discretization error) and a realistic time of numerical computations.

Using the Wendroff scheme, the values S_{i+1}^{j+1} and F_{i+1}^{j+1} (solutions of the equations (15) and (16) in the grid points (i+1, j+1)) are evaluated on the basis of the values in the grid points (i,j), (i+1,j) and (i,j+1) and the scheme gives the following finite-difference formulas

$$S_{i+1}^{j+1} = S_i^j + A_1(S_{i+1}^j - S_i^{j+1}) + B_1 Q \quad , \tag{A1}$$

$$F_{i+1}^{j+1} = F_i^j + A_2(S_{i+1}^j - F_i^{j+1}) + B_2 Q \quad , \tag{A2}$$

where constants A_1, A_2, B_1 and B_2 are given by

$$A_1 = [1-\alpha/(1+K)] \,/\, [1+\alpha/(1+K)] \quad , \tag{A3}$$

$$A_2 = (1-\alpha)/(1+\alpha) \quad , \tag{A4}$$

$$B_1 = [2\alpha X/(1+K)]\, w_{as}/[1+\alpha/(1+K)] \quad , \tag{A5}$$

$$B_2 = 2\alpha X\, w_d/(1+\alpha) \quad , \tag{A6}$$

and the nonlinear term Q

$$Q = F_{av} - S_{av}^n \quad , \tag{A7}$$

is evaluated using the average values F_{av}, S_{av} defined by the relations

$$S_{av} = 0.5(S_i^{j+1} + S_{i+1}^j) \quad , \tag{A8}$$

$$F_{av} = 0.5(F_i^{j+1} + F_{i+1}^j) \quad , \tag{A9}$$

The initial boundary conditions describing appropriately the SEC experiment should be given in form of shock-waves. To prevent numerical oscillations, which may arise in case that discontinuous initial and boundary conditions are applied

together with finite-difference formulas for hyperbolic PDEs, a slightly modified initial concentration peak is assumed (Fig.1a). This modification changes significantly neither the physical nature of the problem nor the mathematical solution of PDEs. From physical point of view, this initial concentration profile (defined by the function f(X)) may be regarded as an originally rectagular zone that was slightly affected by a free diffusion before entering the column.