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Behavior of Micellar Solutions in Gel Permeation Chromatography. A Theory Based on a Simple Model*

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Summary

Gel permeation chromatograms are interpreted in terms of V, the peak elution volume, which is characteristic for the size of the solute species. If solute association takes place, V may become extensively concentration dependent. To further the understanding of this effect a simple theory, which ignores axial diffusion, has been developed, the model for molecular association being a micellar surfactant in equilibrium with its monomer.

INTRODUCTION

Gel permeation chromatography (GPC) separates molecules according to size. The method has therefore found wide application in the study of molecular weight distribution of polymers and oligomers. A special situation arises if two or more species, being in a dynamic equilibrium with each other, enter into the GPC process. An example with certain unique properties is micellar surfactant (A_n) in equilibrium with its monomer (A), $nA \rightleftharpoons A_n$. Micelles, being larger than the monomer, tend to move faster down the GPC column than the monomer, but in this event they dissociate to regenerate the equilibrium concentration of monomer. As a result, the surfactant front will emerge from the column at times which should be distinctly dependent on the concentration of the sample that had

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been injected into the column. In the following an attempt will be made to give a quantitative description of the process, based on a very simple model. This model ignores band spreading, a simplification that appears justified if a very broad band of solute is introduced in the column. This has been the experimental approach of Tokiwa et al. (*1*) The complications arising from band spreading will be discussed although rigorous treatment cannot be given at the present time.

THEORY

It is usually assumed that the association of surfactant molecules is approximately governed by the law of mass action,

$$K \simeq c_2/c_1^n \tag{1}$$

where K is an equilibrium constant and c_2 and c_1 are the mass concentrations of the micelles and monomer molecules, respectively. The association number, n, is usually larger than 10. It then follows from Eq. (1) that up to the so-called critical micelle concentration (cmc) the surfactant is almost exclusively present as the monomer, while at a total concentration larger than the cmc the monomer concentration remains essentially constant ($c_1 \simeq$ cmc).

We shall assume the micelles to be monodisperse, and further, that equilibration between micelles and monomer is virtually instantaneous. On the other hand, we tentatively assume that longitudinal diffusion in the column which gives rise to the familiar broadening of peaks to be insignificant. Thus, a solution introduced into the column as a band of discrete width is assumed to give rise to a square-wave signal in the detector monitoring the column effluent. The width of the signal is to be the same as that of the sample band (expressed as cubic centimeters of effluent). Although this assumption appears to be rather unrealistic, we believe that some of the essential features of the GPC process are still represented despite this simplification.

Figure 1A represents the concentration profile of a sample band just introduced in the column. As this band moves along, three velocities can be distinguished: the monomer velocity, u_1; the velocity of the undissociated micelle, u_2; and a velocity, u_2^*, of the dissociating micelles. Generally, $u_1 < u_2^* < u_2$. The velocities are expressed as centimeters per second. They can be immediately converted into

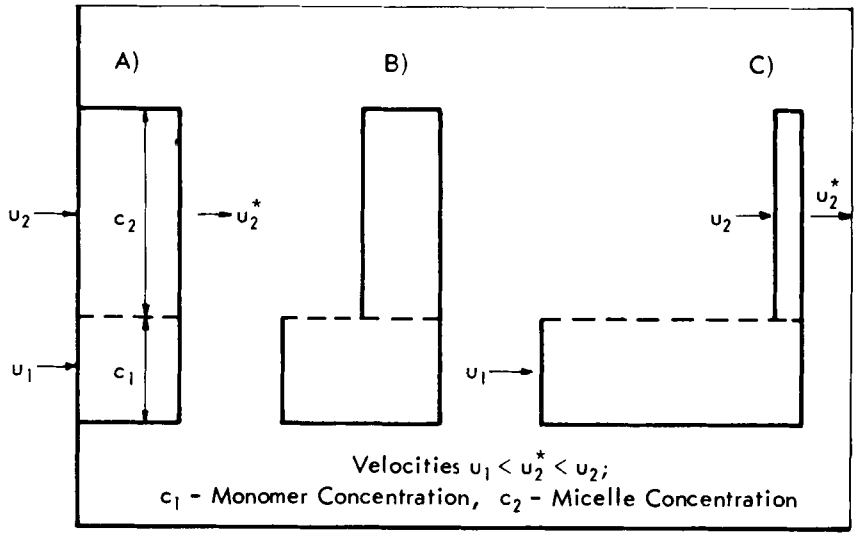

FIG. 1. Concentration profile of micellar solute in the GPC column.

flow rates (cubic centimeters per second) by multiplying with the (constant) cross sectional area, A, of the mobile phase in the column.

If V_0 is the interstitial (void) volume of the column packing, V_1 the emergence volume of the monomer, V_2 the emergence volume of the undissociating micelles, and u_0 the velocity of the solvent in the interstices, then $u_1 = u_0V_0/V_1$ and $u_2 = u_0V_0/V_2$. Furthermore, it is easy to show that the surfactant front moves with a velocity

$$u_2^* = u_1 + (u_2 - u_1)c_2/(c_1 + c_2) \tag{2}$$

The factor $c_2/(c_1 + c_2)$ accounts for the slowing down of the micellar front as a result of dissociation. The concentrations, c_1 and c_2, of monomer and micelles are related to the total surfactant concentration, c_0, in the sampling loop by

$$c_0V_0 = c_1V_1 + c_2V_2 \tag{3}$$

Equation (3) accounts for the dilution effect once the surfactant enters the column and disperses into the accessible pores in the gel: $c_1 \simeq$ cmc is a constant for a given system.

As the surfactant band travels down the column, the micellar "hump" in Figs. 1B and 1C becomes increasingly narrower. We define a time t^* when the back of the "hump" has caught up with the front,

and micelles disappear altogether from the system. At times greater than t^* only monomer at concentration c_1 is present in the column. Micelles cannot reform since no concentrating process occurs in the column. If τ_0 is the time interval during which sample is injected into the column, we can equate distances of travel

$$u_2^* t^* = u_2(t^* - \tau_0) \tag{4}$$

Substitution for u_2 and u_2^* yields

$$t^* = \tau_0 a(k - a + b)/b(a - b) \tag{5}$$

introducing the dimensionless parameters $a = V_1/V_0$, $b = V_2/V_0$, and $k = c_0/c_1$.

Next we must compare t^* with the emergence time of the micellar front from the column, $t_e = V_0/u_2^* A$. Writing $t_0 = V_0/Au_0$ for the time required by the solvent to traverse the column, we obtain again by substitution

$$t_e = t_0 ab(k + b - a)/(ak + b^2 - a^2) \tag{6}$$

We may then discern three cases with respect to the emergence of the solute front in the column effluent:

(a) Monomer and micelles elute from the column. The condition is $t_e < t^*$. The relative elution volume (= elution volume divided by V_0), v_I, can be calculated from

$$v_I = u_0 A t_e/V_0 = ab(k + b - a)/(ak + b^2 - a^2) \tag{7}$$

(b) Although micelles were originally present in the column, only monomer emerges. The condition for this is $t_e \geq t^*$. The relative elution volume for this case, v_{II}, can be found from the following consideration: up to time t^* the solute front travels at a velocity u_2^*, thereafter, for a period t_1, until leaving the column, the velocity is that of the monomer, u_1. Hence,

$$v_{II} = u_0 A(t^* + t_1)/V_0 \tag{8}$$

t_1 can be expressed by means of the relationship $u_1 t_1 + u_2^* t_2^* = u_0 t_0$, and t^* by means of Eq. (5). One obtains

$$v_{II} = a - (ak - a^2)w/b^2 \tag{9}$$

where $w = \tau_0 u_0 A/V_0$, the volume of solution injected divided by the void volume of the column.

(c) The original sample concentration was $c_0 \leq a \times$ cmc, in which case monomer only is transported in the column. Therefore,

$$v_{III} = a \tag{10}$$

These equations show that, depending on the case, the emergence volume of the sample front may not only be a function of the emergence volumes of the particle species (a, b), but also of the total sample concentration relative to the cmc (k), and of the sample volume relative to the void volume of the column (w).

It follows from Eq. (7) that in the case of the cmc being very small compared to the concentration of the sample ($k >> 1$),

$$v_I \simeq b$$

since a, b are of the order of unity. The parameter b, by definition, is the relative elution volume of undissociating micelles, and in this case the surfactant should behave like an ordinary polymer. This situation may, for instance, be expected in the case of ethylene oxide alcohols which were found to be very stable by measurements of osmotic pressure (*2*).

The peak width can readily be calculated (disregarding diffusional peak spreading, as stipulated earlier). In Case I the relative width of the micellar "hump," h_I, as it emerges from the column is given by

$$h_I = w - b^2(a - b)/(ak - a^2 + b^2) \tag{11}$$

the total width by

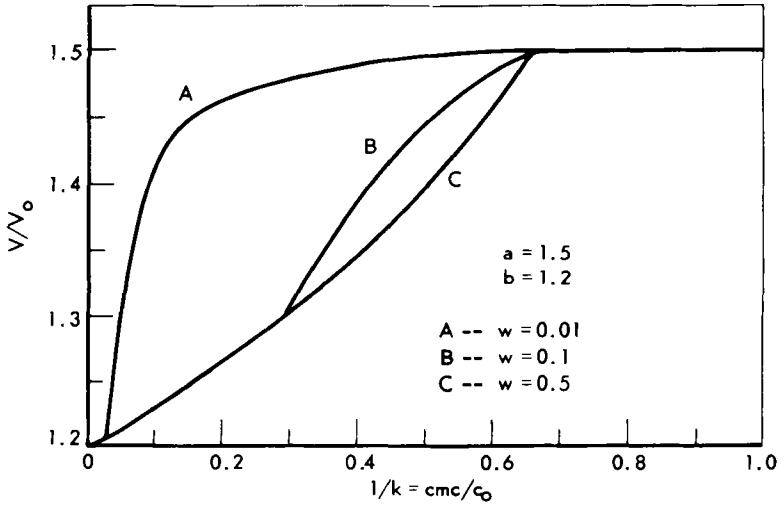

FIG. 2. Plot of relative elution volume against reciprocal reduced concentration.

$$H_{\mathrm{I}} = w + a(a - b)(k - a)/(ak - a^2 + b^2) \tag{12}$$

The total width in Case II is

$$H_{\mathrm{II}} = w + (ak - a^2)w/b^2 \tag{13}$$

In Case III the width is simply equal to w.

Figure 2 shows a plot of the reduced emergence volume of the surfactant front, calculated by means of Eq. (8) and (9). Curves A and B exhibit three segments, corresponding to the three cases discussed above. In Curve C, where $w = 0.5$, only two segments are apparent.

SPREADING OF SOLUTION BANDS

Considerable complications arise if band spreading (axial dispersion) has to be taken into account. Since chromatographic elution curves of monodisperse solutes are usually Gaussian, it appears justified to treat broadening as a diffusion problem. If the reduced width of the solution band (width divided by length of column) is denoted as $2\bar{h}$, one may consider as a starting point for a discussion the equation (*3*).

$$2c(\bar{x},t) = c(0)\{\mathrm{erf}\,[(\bar{h} - \bar{x})/2(\bar{D}t)^{\frac{1}{2}}] + \mathrm{erf}\,[(\bar{h} + \bar{x})/2(\bar{D}t)^{\frac{1}{2}}]\} \tag{14}$$

$c(0)$ is the initial concentration at $t = 0$, $\bar{x}$ and $\bar{D}$ (sec^{-1}) are the reduced space coordinate and the reduced diffusion coefficient, respectively. The latter may be obtained from calibration with some reference solute if one assumes that $\bar{D}$ is the same for all solutes in a given column system. Equation (14) expresses lowering of concentration as a consequence of diffusion, an effect particularly pronounced if the solution band is very narrow (Fig. 3). In this case micelles in the column will evidently disappear sooner than follows from Eq. (5). The frontal velocity of the surfactant, u_2^*, will not only be affected by the lowering of concentration but also by the concentration profile of the band, which is no longer square. A complete treatment of the combined processes of diffusion and chromatographic transport seems to be out of question. The most important effect of axial dispersion of a narrow band appears to be the lowering of the micelle concentration, and an approximation by numerical calculation may be feasible.

An experimental alternative suggests itself if one introduces a very broad band into the column. As shown in Fig. 3, the peak concentration shows only relatively little lowering in this case. However, if the micellar "hump" considerably narrows during its passage down the column, diffusion effects should again become significant.

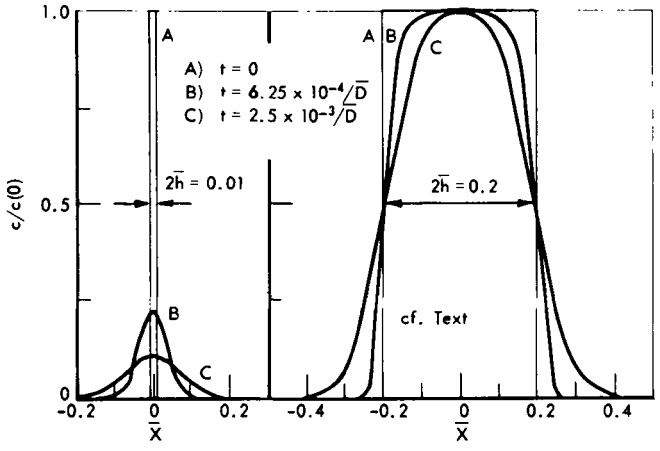

FIG. 3. Diffusive spreading of a narrow and a wide solution band.

Hence, Case II of the previous section will be most affected by band spreading. An evaluation of these effects must be left to experimental tests.

EXPERIMENTAL

A few preliminary experimental results obtained with narrow bands of sodium dodecyl sulfate (NaDDS) in aqueous sodium nitrate solution (0.03 *M*) are shown in Fig. 4.

These results were obtained with a column 120-cm long having an inside diameter of 0.33 cm. The column was packed with porous glass beads Corning CPG 10-240 (Water Associates, Framingham, Mass.), the particle size being 36–75 μ. The void volume, V_0, was calculated as 5.4 cc. The solvent flow rate was approximately 0.08 cc/min. A sensitive differential refractometer (*4*) served as the detector (temperature, 24°C).

In all cases the stock solution contained 5 g/liter of highly purified NaDDS (the critical micelle concentration is approximately 0.8 g/liter (*5*). The stock solution was charged for 10, 30, 60, and 120 sec, respectively, corresponding to relative band widths, w, of 0.0025, 0.0076, 0.0149, and 0.0304.

DISCUSSION

The curves in Fig. 4 have, at least qualitatively, the expected appearance. While in cases of A and B the concentration in the effluent

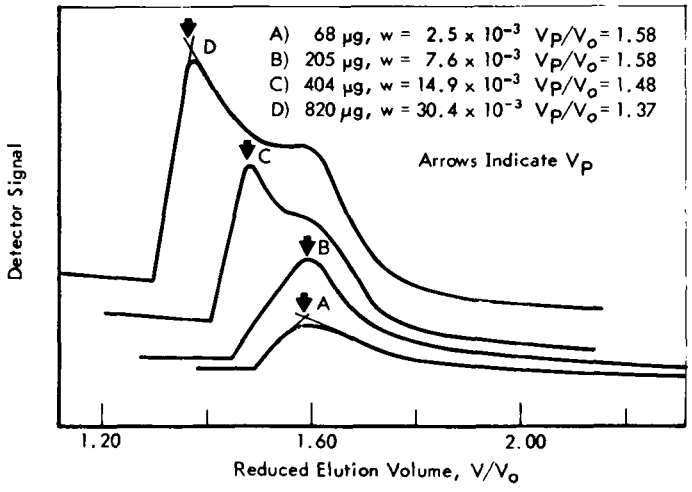

FIG. 4. Chromatographic peaks of NaDDS at different sample charges.

is below the cmc and the peak elution volumes are the same, micellar peaks are apparent in cases of C and D. Correspondingly, the peak elution volumes decrease with increasing concentration. The concentration differences are primarily brought about by band spreading, and a quantitative interpretation in terms of the present theory was not attempted. As mentioned before, the spreading effect can be minimized by injecting broad bands, for instance, with $w > 0.2$.

This latter approach was chosen by Tokiwa et al. (*1*), who studied the behavior of alkyl sulfates in aqueous solutions by means of Sephadex columns. The band width was larger than $w = 0.5$, and Case II, i.e., disappearance of micelles in the column, probably did not occur. The experimental results, expressed in terms of appearance volumes (V) of the surfactant front are, however, not in complete accord with the present theory: the ascending branch of the plot of V/V_0 versus reciprocal concentration was found to be linear, while the plot in Fig. 2 shows curvature. But more seriously, the break in the experimental curves of Tokiwa et al. occurred at the cmc, while according to our reasoning it should correspond to $a \times$ cmc.

CONCLUSION

The present treatment was restricted to the special case of an associating system where one could assume a constant equilibrium

concentration of monomer. An extension of the theory to include other types of association (e.g., dimer formation) would require a different mathematical approach.

Experimental data obtained under well-defined conditions are needed to verify the present theory and to assess the influence of band spreading on the peak elution volumes.

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