Short Communications

On the Peak Broadening in Chromatography

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In a recent article by Sørensen [1] on the mechanisms behind peak broadening in gel chromatography, some earlier work in the field was critically reviewed. In this connection a comment concerning the present author's work was somewhat misleading, which occasions the following clarifying remarks.

According to the author's theory peak broadening is expressed in terms of the variance $\mu_2(t)$ for the concentration profile in the mobile phase within the column. The expression was derived in Ref. 2 and was developed further in Refs. 3, 4. It may be written as follows:

$$\mu_2(t) = \mu_2(0) + 2Dt \qquad (1)$$

where t is the time (with an arbitrary zero point), and D is the generalized diffusion coefficient:*

$$D = D_1'w_1 + D_2 w_2 + \frac{v^2 V_2^2 w_1^2 (1-w_1)}{2D_2} \qquad (2)$$

Here w_1 and w_2 are the amounts of solute in the mobile and stationary phases, respectively, expressed as fractions of the total amount of solute in the column. In Sørensen's terminology

$$w_1 = \frac{1}{1+K} \qquad (3)$$

In eqn. (2) D_1' is a composite diffusion coefficient characterizing axial diffusion in the mobile phase. It represents two different effects, the Brownian diffusion and eddy diffusion. If the effects are separated we may write for moderate flow rates [4]

$$D_1' = D_1 + kv \qquad (4)$$

where D_1 is the ordinary diffusion coefficient, k the eddy diffusion coefficient and v the translational velocity of the mobile phase.

Although most investigators seem to favor this (linear) form of velocity dependence of the eddy diffusion effect, its validity may be questioned. Eqn. (4) is obviously not invariant with respect to flow reversal (as it should be if the conditions in the column are identical in both flow directions, and eqn. (1) is valid). A quadratic dependence of eddy diffusion on velocity may therefore be more appropriate. It is also possible that in a rigorous treatment of eddy diffusion the simple form of eqn. (1) cannot be retained. In any case, eqn. (4) should be considered as an approximation.

The second term in eqn. (2) represents axial Brownian diffusion in the stationary phase. In most columns this term should be omitted (as explicitly stated in Ref. 4). However, it has to be retained if the stationary phase has large unbroken dimensions in the axial direction of the column. As examples we may consider a column filled with threadlike gel particles, ordered coaxially in the column, or a column having the form of a capillary tubing, with its walls coated with absorbing material.

Finally, the third term in eqn. (2) represents the "chromatographic dispersion", which is due to non-equilibrium in the process of mass transfer between the mobile and stationary phases. This term is essentially identical to the corresponding term in Sørensen's equation.

With eqns. (2) and (3) in mind we may thus conclude that the results obtained by Sørensen and the author are substantially in agreement. It should be noted that results very similar to those discussed here have also been obtained by Giddings and Mallik.[5]

1. Sørensen, T. S. Acta Chem. Scand. A 28 (1974) 753.
2. Vink, H. J. Chromatogr. 20 (1965) 305.
3. Vink, H. J. Chromatogr. 25 (1966) 71.
4. Vink, H. J. Chromatogr. 52 (1970) 205.
5. Giddings, J. C. and Mallik, K. L. Anal. Chem. 38 (1966) 997.
6. Vink, H. Makromol. Chem. 116 (1968) 241.

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* Unfortunately, eqn. (2) was incorrectly reproduced in Ref. 6.