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On the Fractionation of Polymers by Membrane-Diffusion

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In a recent article by Almin¹ the concentration change in a membrane-diffusion unit was considered and an exact solution for special boundary conditions was derived. In addition an approximate solution was presented and its use in connection with multi-stage fractionation was indicated. In the present note some complementary remarks on the subject are made. Especially, a comparison between Almin's formula and an earlier approximate for-

mula by the author² is made, and it is shown that for small values of the exponent $2bDl/v$ (i.e. for most cases of practical interest) the two formulae are nearly equal.

Using Almin's symbols and writing $2bDl/v = \alpha$ eqns. (14) and (15) in Ref.² give for small α

$$\frac{c(t)}{c(0)} = \exp\left(-\frac{1}{2}\alpha\gamma \frac{\alpha\gamma}{1+\gamma - (\alpha\gamma/4)}\right) \quad (1)$$

On the other hand, the variable r in Ref.¹ is defined by

$$\frac{1}{2}(1 + e^{-\alpha})\gamma e^{\gamma} = re^r \quad (2)$$

which gives for small α

$$r = \gamma - \frac{1}{2} \frac{\alpha\gamma}{1+\gamma} \quad (3)$$

With (3) eqn. (8) in Ref.¹ becomes

$$\frac{c(t)}{c_1(0)} = \frac{1}{1+\gamma - \frac{1}{2}[\alpha\gamma/(1+\gamma)]} \times \left(\exp - \frac{1}{2}\alpha\gamma \frac{\alpha\gamma}{1+\gamma}\right) \quad (4)$$

Comparing (1) with (4) we must keep in mind that in the two cases different boundary conditions are used. Eqn. (1) is a steady state solution with $c(0)$ being the steady state concentration at $t = 0$. In Almin's paper the exact formula (eqn. (7) in Ref.¹) refers to boundary conditions with solution of concentration $c_1(0)$ in the container A and pure solvent in the diffusion cell. The same boundary conditions are retained in the approximate formula (4), but the approximation requires that t is large, i.e. that steady state conditions are established. Thus, the initial (extrapolated) steady state concentration is according to (4)

$$c(0) = \frac{c_1(0)}{1+\gamma - \frac{1}{2}[\alpha\gamma/(1+\gamma)]} \quad (5)$$

With (5) in mind we see that for small α (1) and (4) are essentially the same. However, in multi-stage experiments (eqns. (16)–(23), Ref.²) the steady state concentration $c(0)$ has to be used in the interconnected fractionation units. Therefore, in this connection it is essential that a formula of the form of (1) is used.

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