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APPROXIMATE SOLUTION OF THE DIFFERENTIAL EQUATION FOR THE MIGRATION OF A REVERSIBLY REACTING SUBSTANCE

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A series solution is given for the differential equation describing the transport of a reversibly reacting substance in an infinite rectangular cell. The concentration dependence of the constituent transport coefficients has been approximated by polynomials. The solution converges for short time ($t < 1$ h). Several features of the leading and trailing boundary of monomer–trimer and monomer–dimer–trimer systems are discussed.

1. Introduction

If a substance is subjected to sedimentation, electrophoresis or chromatography with frontal analysis, one usually observes a migrating Gaussian peak which in the ultracentrifuge is distorted due to boundary conditions and radial dilution. But if the substance undergoes a reversible monomer–polymer association the leading and trailing boundary in chromatography, the ascending and descending boundary in electrophoresis and the boundary in the ultracentrifuge deviate strongly from Gaussian behaviour: one boundary is hypersharp whereas the other exhibits bimodality. This phenomenon has been clarified principally by Gilbert [1,2]. This author has solved the relevant differential equations, but because of the complexity of the equations he has neglected the diffusional spreading. The resulting boundary pattern holds for the asymptotic limit of infinite time because the migration and the diffusion proceed with time t and $\sqrt{t}$, respectively. The results of Gilbert have been verified and extended by Bethune and colleagues [3,4] with a countercurrent distribution analog which includes diffusion. Other aspects of the problem may be found in the literature [5–7].

In this paper we represent a solution which is valid for short times and for infinite rectangular cells. The advantages of this solution are that both leading and trailing boundaries can be calculated, that it can be constructed from tabulated functions and that any kind of deviation from ideal behaviour, i.e. frictional coupling between the species and non-ideal thermodynamic terms, can be included. Furthermore, other types of reversibly reacting systems, for example the transport of a component in a helix–coil equilibrium, may also be treated.

2. The differential equation and its solution

Tiselius [8] has introduced the concept of the constituent velocity in a reversibly reacting system. It is a weighted-average velocity, taken over all species $i = 1, 2, \ldots n$ participating in the reaction. With this concept the transport equations (in one direction x) for all species

$$J_i = -D_i \frac{\partial c_i}{\partial x} + v_i c_i, \qquad i = 1, 2, \ldots n, \tag{1}$$

are equivalent to one equation for the constituent [5–7]:

$$J = -D \frac{\partial c}{\partial x} + vc, \tag{2}$$

where

$$c = \sum_{i=1}^{n} c_i , \tag{3}$$

$$v = \left[\sum c_i v_i\right]/c, \tag{4}$$

$$D = \left[\sum D_i \partial c_i/\partial x\right]/(\partial c/\partial x) . \tag{5}$$

Here we have used the notation J_i = diffusion current density of species i, D_i = diffusion coefficient of species i, v_i = migration velocity of species i, c_i = concentration (density) of species i, in mass/volume; and likewise the symbols without subscript for the constituent.

Inasmuch as the concentrations of the species are given by a mass-action law $c_i = c_i(K_i, c)$, the transport coefficients $D(c)$ and $v(c)$ of the constituent are functions of the constituent concentration c. These functions can be calculated if the equilibrium constants K_i and the species coefficients D_i and v_i are given.

It is shown in the appendix that for a reversibly polymerising system D can be simplified to

$$D = \sum i D_i c_i / \sum i c_i , \tag{6}$$

which is a limiting form of a more complex expression derivable from the theory of irreversible thermodynamics [9].

Combining eq. (2) with the continuity equation we obtain

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left\{D(c)\frac{\partial c}{\partial x} - v(c)c\right\}. \tag{7}$$

This is the starting equation for our solution. It is quite general and is applicable in a rectangular cell to many kinds of transport measurements, for example sedimentation, electrophoresis and chromatography, by giving $v(c)$ its appropriate meaning.

The solution is sought for an infinite cell. This avoids more complicated boundary conditions. The initial boundary condition states that at zero time two solutions with different concentrations are separated by a sharp boundary:

$$\begin{array}{ll} c = c_A, & -\infty < x < 0 \\ c = c_B, & 0 < x < +\infty \end{array} , \quad t = 0. \tag{8}$$

The concentration jump is

$$\Delta c = c_B - c_B, \tag{9}$$

and the average concentration is

$$\bar{c} = \tfrac{1}{2}(c_A + c_B). \tag{10}$$

By giving c_A and c_B special values this includes leading and trailing boundaries in the usual sense as well as differential boundaries.

At the infinite ends of the cell the following boundary conditions prevail:

$$\begin{array}{ll} c = c_A, & x \longrightarrow -\infty \\ c = c_B, & x \longrightarrow +\infty \end{array} , \quad t > 0. \tag{11}$$

Following a procedure which has been used by Gosting and Fujita [10] in solving Ficks law for concentration-dependent diffusion, the two transport coefficients $D(c)$ and $v(c)$ are developed into a truncated Taylor series:

$$D(c) = \bar{D}\{1 + k_1(c-\bar{c}) + k_2(c-\bar{c})^2 + k_3(c-\bar{c})^3 + k_4(c-\bar{c})^4\}, \tag{12}$$

$$cv(c) = \bar{v}\,\{1 + h_1(c-\bar{c}) + \ldots + h_5(c-\bar{c})^5\}. \tag{13}$$

Likewise, the solution $c(x, t)$ is approximated by a Taylor series:

$$c(x, t) = \bar{c} + \tfrac{1}{2}\Delta c f_0(x, t) + (\tfrac{1}{2}\Delta c)^2 f_1(x, t) + \cdots . \tag{14}$$

With the help of eqs. (12), (13) and (14), the differential equation (7) splits up into a series of differential equations which can be solved successively. The result is [11]:

$$\frac{\partial c(z, t)}{\partial x} = \tfrac{1}{2}\Delta c \frac{1}{2\sqrt{\bar{D}t}} \times \sum_{i=0}^{4} (\tfrac{1}{2}\Delta c)^i \varphi_i(z)\psi_i(\delta)\alpha_i(k_j, h_j). \tag{15}$$

The functions $\varphi_i(z)$ are tabulated [11]; they depend only on a reduced variable z,

$$z = (x - \bar{v}h_1 t)/2\sqrt{\bar{D}t} , \tag{16}$$

which is the Boltzmann variable $x/2\sqrt{\bar{D}t}$ for diffusion in a coordinate system moving with constant velocity $\bar{v}h_1$ along the x-axis. The first term $\varphi_0(z)\alpha_0\psi_0$ in eq. (15) is the well-known error-function expression

$$\frac{\partial c}{\partial x} = \tfrac{1}{2}\Delta c \frac{1}{2\sqrt{\bar{D}t}}\, \varphi_0(z) + \cdots, \qquad (\psi_0 = 1, \alpha_0 = 1)$$

$$= \tfrac{1}{2}\Delta c \frac{1}{2\sqrt{\bar{D}t}} \frac{2}{\sqrt{\pi}}\, e^{-z^2} + \cdots \tag{17}$$

showing that in a transport experiment with sufficiently small Δc one observes Gaussian behaviour.

The functions $\psi_i(\delta)$ with $\delta = \frac{1}{2}\bar{v}\sqrt{t/\bar{D}}$ are growing with time. They are responsible for the fact that for $t \to \infty$ the solution (15) becomes meaningless. The coefficients α_i are known for given Taylor series coefficients k_j and h_j. Additional details along with tables for the φ_i, ψ_i and α_i are published elsewhere [11].

If the migration $\bar{v}$ is zero, eq. (15) reduces to

$$\frac{\partial c(z,t)}{\partial x} = \tfrac{1}{2}\Delta c \frac{1}{2\sqrt{\bar{D}t}} \sum_{i=0}^{4} (\tfrac{1}{2}\Delta c)^i \varphi_i(z) \alpha_i(0, h_i),$$

$$z = x/2\sqrt{\bar{D}t}$$

which is an extended form of the Gosting–Fujita [10] solution for concentration-dependent diffusion.

To calculate $\partial c/\partial x$ for a given time as a function of x one proceeds as follows: from a model for the reaction to be studied and the model properties of the species – i.e., with K_i, D_i, v_i – one determines the coefficients $k_j, h_j, \bar{D}, \bar{v}$ of eqs. (12) and (13), using eqs. (3), (4) and (5). From this and the tabulated functions a gradient $\partial c(z, t)/\partial x$ can be calculated and transformed into $\partial c(x, t)/\partial x$ with the help of eq. (16).

It should be pointed out that D_i and v_i need not be constants. Thus, one may introduce a frictional coupling by either

$$v_i = v_i^0 \{1 - \textstyle\sum_i \mu_i c_i\},$$

$$\text{or} \quad v_i = v_i^0 \{1 - \mu c\}, \tag{18}$$

$$\text{and} \quad D_i = D_i^0 \{1 - \mu c\},$$

where μ is a constant. This changes only the values of $\bar{D}, \bar{v}, k_j, h_j$. It is obvious that other deviations may be taken into account, for example a thermodynamic factor as a driving force in diffusion or activity coefficients in the mass-action law.

3. Results and discussion

The foregoing treatment has been applied to the reversible polymerising systems monomer–trimer and monomer–dimer–trimer. The parameters K_i, D_i and v_i have been chosen according to data on α-chymotrypsin [12] in an ultracentrifugal field. The rectangular cell approximation of the Lamm equation is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial c}{\partial x} - s(\omega^2 \bar{x})\, c\right], \tag{19}$$

where s is the constituent sedimentation coefficient, ω the angular speed, x the distance from the rotor axis and $\bar{x}$ its average value. Comparison with eq. (7) yields

$$v(c) = s(c)\,(\omega^2 \bar{x}). \tag{20}$$

We have taken

$$\omega^2 \bar{x} = 2.5 \times 10^8\ \text{cm} \cdot \text{s}^{-2}.$$

The sedimentation coefficients s_i^0 and diffusion coefficients D_i^0 of the species (subscripts M, D, T for monomers, dimers, trimers) at infinite dilution were calculated according to the model of an equivalent sphere:

$$s_{\mathrm{M}}^0 / s_{\mathrm{D}}^0 = (\tfrac{1}{2})^{2/3}, \qquad (s_{\mathrm{M}}^0 / s_{\mathrm{T}}^0) = (\tfrac{1}{3})^{2/3},$$

$$D_i^0 / s_i^0 = RT/M_i(1 - \rho v),$$

$$\text{i.e.} \quad s_{\mathrm{M}}^0 = 2.4\ \text{S}, \qquad s_{\mathrm{D}}^0 = 3.81\ \text{S}, \qquad s_{\mathrm{T}}^0 = 5\ \text{S}, \tag{21}$$

$$D_{\mathrm{M}}^0 = 9.58 \times 10^{-7}, \quad D_{\mathrm{D}}^0 = 7.60 \times 10^{-4},$$

$$D_{\mathrm{T}}^0 = 6.64 \times 10^{-7}\ \text{cm}^2 \cdot \text{s}^{-1}.$$

This compares favourably with literature values [12–14].

In the monomer–trimer case the constituent transport coefficients are

$$s(c) = \frac{s_{\mathrm{M}}^0 c_{\mathrm{M}} + s_{\mathrm{T}}^0 c_{\mathrm{T}}}{c_{\mathrm{M}} + c_{\mathrm{T}}} (1 - \mu c), \tag{22}$$

$$D(c) = \frac{D_{\mathrm{M}}^0 c_{\mathrm{M}} + 3 D_{\mathrm{T}}^0 c_{\mathrm{T}}}{c_{\mathrm{M}} + 3 c_{\mathrm{T}}} (1 - \mu c). \tag{23}$$

Together with

$$K_3 = c_{\mathrm{M}}^3 / c_{\mathrm{T}} \tag{24}$$

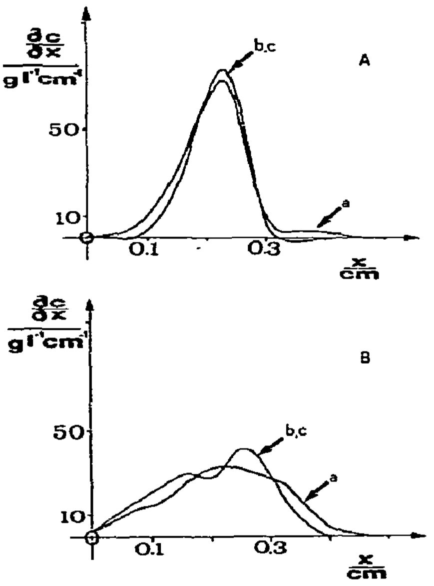

Fig. 1. Influence of a concentration dependence of the diffusion coefficient for a monomer–trimer reaction boundary: $K_3 = 50\ g^2 \cdot \ell^{-2}$, $\bar{c} = 4\ g \cdot \ell^{-1}$, $t = 2700$ s. (A) leading boundary, (B) trailing boundary. (a) D = const., (b) $D = \bar{D}\ \{1 + k_1(c-\bar{c})\}$, (c) $D = \bar{D}\{1 + k_1(c-\bar{c}) + k_2(c-\bar{c})^2\}$.

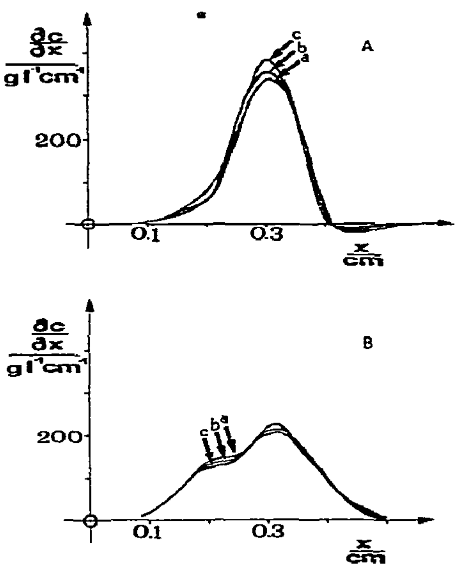

Fig. 2. Same as fig. 1, except $\bar{c} = 22\ g \cdot \ell^{-1}$.

they constitute the concentration dependence of the model.

First we have checked how well eq. (13) fits the function $s(c)$. Within the ranges

$$0 < c < 50\ g \cdot \ell^{-1},$$

$$1\ g^2 \cdot \ell^{-2} < K_3 < 100\ g^2 \cdot \ell^{-2},$$

$$0 < \mu < 0.008\ \ell \cdot g^{-1},$$

which correspond to solutions existing from 100% monomer up to about 10% monomer, the difference between the values of eqs. (22) and (13) is always less that 0.5% and in the average less than 0.1%. The same holds true for the monomer–dimer–trimer case. So it may be stated that the polynomial (13) has a sufficient number of terms to describe the constituent sedimentation coefficient.

A fourth-order polynomial (12) for $D(c)$ turned out to be more of a higher order than was necessary. The influence of a difference between a linear and parabolic approximation on the migrating patterns is nearly zero. This is illustrated in figs. 1 and 2 where we have plotted the leading and trailing boundary $\partial c/\partial x$ versus x with constant, linearly and parabolically varying D*. Fig. 1 refers to $\bar{c} = 4\ g \cdot \ell^{-1}$ and fig. 2 to $\bar{c} = 22\ g \cdot \ell^{-1}$, both with $K_3 = 50\ g^2 \cdot \ell^{-2}$ and for $t = 2700$ s. If the solution has about equal amounts of monomer and trimer in the plateau region, fig. 1, a constant D would give a completely wrong pattern. This is in accord with expectation because both monomer and trimer contribute to the diffusional spreading, but with different diffusion coefficients D_i^0. On the other hand, in the case of fig. 2 with only 20% monomers, the diffusion of the trimers dominates and so a constant D gives about the right answer. In general a parabolic $D(c)$ is sufficient to account for the main features.

After this discussion of the relevance of eqs. (12) and (13) we turn to the problem of the convergence of the series solution (15). It was already pointed out that because the functions $\psi_i(\delta)$ increase with time t, there is an upper limit t_v above which the series fails

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* In this and the following examples the boundary conditions are: $c_A = 0$, $\Delta c = c_B - c_A = c_B = 2\bar{c}$. With $\Delta c < 0$, this describes a leading boundary, where the substance migrates in the direction of zero concentration. With $\Delta c > 0$, on the contrary, a trailing boundary can be calculated, where the substance moves in the direction of the plateau concentration $2\bar{c}$.

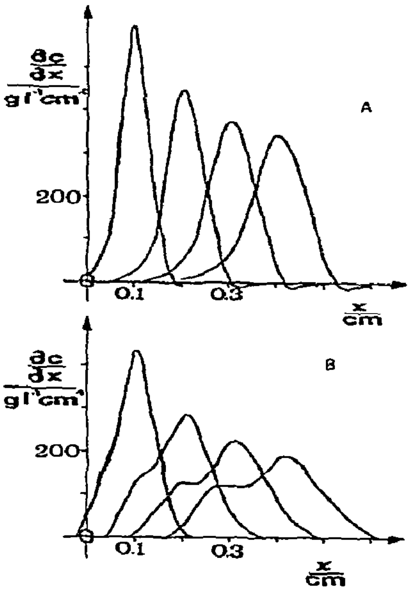

Fig. 3. Leading (A) and trailing (B) boundary for the monomer–trimer case, $K_3 = 50\ g^2 \cdot \ell^{-2}$, $\bar{c} = 22\ g \cdot \ell^{-1}$, $t = 900$, 1800, 2700, 3600 s.

to converge. This limit cannot be calculated because of the complexity of the functions φ_i and ψ_i. But fortunately it can be estimated by plotting the boundaries for different times and having a look at the right end of the leading boundary, fig. 3. This has an overshoot with negative $\partial c/\partial x$ which is impossible in this model. So one would stop using this series if the overshoot becomes too great. It is more pronounced for higher values of n in $nA \rightleftarrows A_n$; it is less pronounced in those cases where intermediate polymerising steps are included. For times $t \gg t_v$ and/or $s_T^0 \gg s_M^0$ the trailing boundary also exhibits meaningless deviations.

Another criterion for convergence may be the numerical calculation of the two moments m_0 and m_1

$$m_0 = \int \frac{\partial c}{\partial x} dx, \qquad \frac{m_1}{m_0} = \frac{1}{m_0} \int x \frac{\partial c}{\partial x} dx$$

from the boundaries. For $t < t_v$ they deviate no more than $\frac{1}{2}$% from their theoretical values

$$m_0 = \Delta c \qquad m_1/m_0 = s(2\bar{c})(\omega^2 \bar{x}).$$

This is of course not a sufficient criterion for convergence but from this and the appearance of the overshoot we conclude that for $t < t_v \approx 2000$–4000 s, depending on the model parameters chosen, the overall accuracy is of the order of 1%.

In fig. 4 the two boundaries are depicted for various concentrations, keeping K_3 constant, at a fixed time $t = 2700$ s, the trailing boundary together with its aymptotic limit of the Gilbert theory [1,2]. The different concentrations cover a range of monomer fractions $\alpha_M = c_M/c$ from 81% to 26%. These patterns are principally in agreement with those of Bethune and colleagues [3,4] and the conclusions drawn from these authors need not be reconsidered here. It should only be remarked that for low plateau concentrations where the component is mainly in the form of monomers the boundary becomes Gaussian in shape and that the minimum is most clearly visible when monomers and trimers have about equal fractions. This becomes even clearer when looking at the gradients of the species $\partial c_M/\partial x$ and $\partial c_T/\partial x$, fig. 5. Therefore, in the following discussion of the influence of the model parameters with respect of the appearance of the minimum we in general choose $\bar{c} = 4\ g \cdot \ell^{-1}$ with $\alpha_M \approx 0.46$.

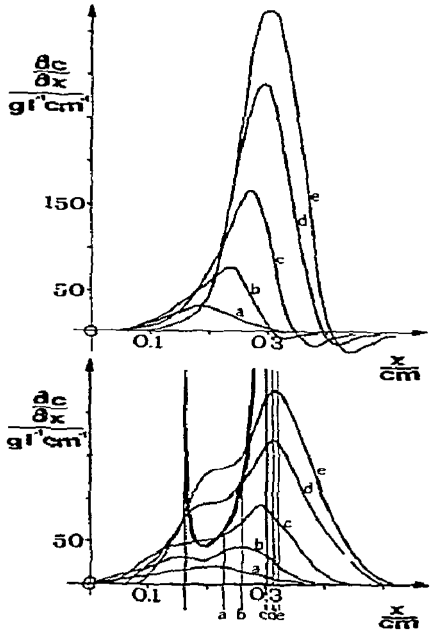

Fig. 4. Leading (A) and trailing (B) boundary for the monomer–trimer case, $K_3 = 50\ g^2 \cdot \ell^{-2}$, $t = 2700$ s. In (B) the Gilbert [1,2] sclution has been included. (a) $\bar{c} = 2\ g \cdot \ell^{-1}$, $\alpha_M = 0.81$, (b) $\bar{c} = 4\ g \cdot \ell^{-1}$, $\alpha_M = 0.65$, (c) $\bar{c} = 8\ g \cdot \ell^{-1}$, $\alpha_M = 0.46$, (d) $\bar{c} = 16\ g \cdot \ell^{-1}$, $\alpha_M = 0.31$, (e) $\bar{c} = 22\ g \cdot \ell^{-1}$, $\alpha_M = 0.26$.

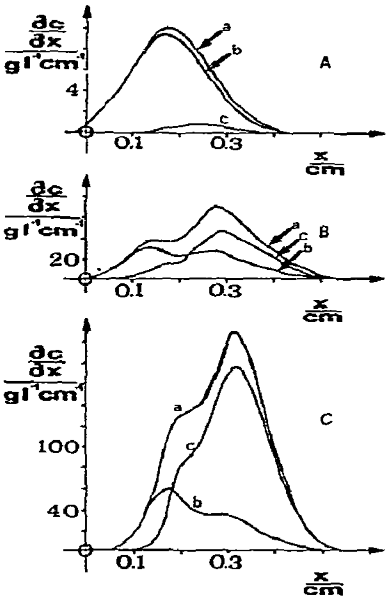

Fig. 5. The gradients of the total concentration (a), of the monomer (b) and trimer (c), in a trailing boundary, $K_3 = 50\ g^2 \cdot \ell^{-2}$, $t = 2700$ s, for different concentrations: (A) $\bar{c} = 1\ g \cdot \ell^{-1}$, (B) $\bar{c} = 8\ g \cdot \ell^{-1}$, (C) $\bar{c} = 22\ g \cdot \ell^{-1}$.

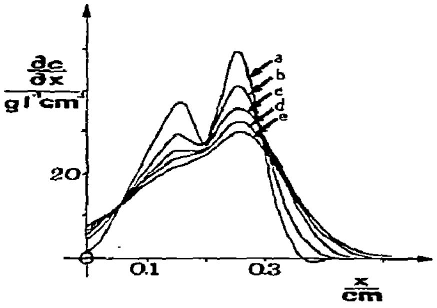

Fig. 6. Influence of the diffusion coefficient on a monomer–trimer trailing boundary; $K_3 = 50\ g^2 \cdot \ell^{-2}$, $t = 2700$ s, $\bar{c} = 4\ g \cdot \ell^{-1}$. (a) $\bar{D} = 7.5 \times 10^{-7}\ cm^2 \cdot s^{-1}$, (b) $\bar{D} = 9.58 \times 10^{-7}$ $10^{-7}\ cm^2 \cdot s^{-1}$, this is the appropriate value; (c) $\bar{D} = 12.5 \times 10^{-7}\ cm^2 \cdot s^{-1}$, (d) $\bar{D} = 15 \times 10^{-7}\ cm^2 \cdot s^{-1}$, (e) $\bar{D} = 17.5 \times 10^{-7}\ cm^2 \cdot s^{-1}$.

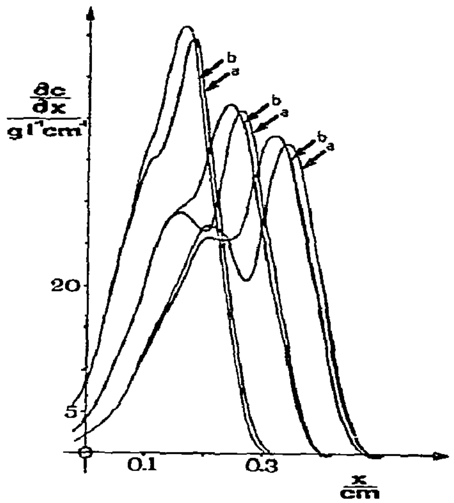

Fig. 7. Monomer–trimer trailing boundary at three times: $t = 1800$ s, 2700 s, 3600 s. Curves (a) hold for $\mu = 0$, no coupling; curves (b) describe a frictional coupling, $\mu = 0.008$ $\ell \cdot g^{-1}$, $K_3 = 50\ g^2 \cdot \ell^{-2}$, $\bar{c} = 4\ g \cdot \ell^{-1}$.

In fig. 6 the sedimentation coefficient, concentration and time are kept constant whereas the diffusion coefficient has been assigned varying values. This variation reflects changes of the molecular weight of the monomer, see eq. (21). It is obvious that with increasing diffusional spreading the minimum in $\partial c/\partial x$ disappears as one would expect it.

If the sedimentation and diffusion coefficients of the species decrease linearly with total concentration†, eqs. (22) and (23) with $\mu \neq 0$, this turns out to have a profound effect on the reaction boundary, fig. 7: the appearance of the minimum is delayed to longer times. The reason for this is that $s(c)$ with $\mu = 0$ increases faster with concentration than with $\mu > 0$.

Along the same line of reasoning one can show that a change of the ratio s_M^0/s_T^0 from its assumed value for equivalent spheres has a similar effect, fig. 8.

It is also possible to study the influence of an activity coefficient y_i in the mass-action law:

$$K_3 = (y_M c_M)^3 / y_T c_T .$$

This would change the concentration dependence of the constituent sedimentation and diffusion coefficient, but less pronounced than the introduction of the factor μ.

In figs. 9 and 10 we show some results for the monomer–dimer–trimer case. The notation is

$$K_2' = c_M^2/c_D, \quad K_3' = c_M c_D/c_T, \quad K_2' K_3' = K_3 = \text{const.}$$

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† Other types of concentration dependence could be studied.

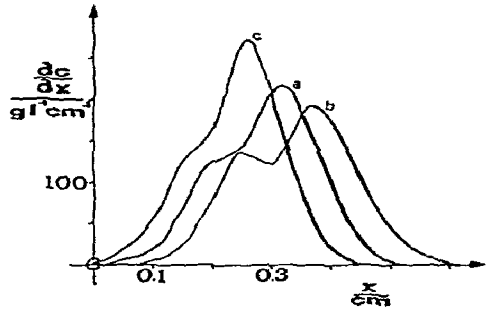

Fig. 8. Monomer–trimer trailing boundary, $K_3 = 50\ g^2 \cdot \ell^{-2}$, $t = 2700$ s, $\bar{c} = 22\ g \cdot \ell^{-1}$. (a) s_T^0/D_T^0 according to eq. (21), (b) s_T^0/D_T^0 increased by 20%, (c) s_T^0/D_T^0 decreased by 20%.

The weight fractions $\alpha_i = c_i/c$ of the different species in the plateau region are given in the legend.

The transport coefficients $s(c)$ and $D(c)$ are calculated with the numerical values given in eq. (21) and $\mu = 0$ and the eqs. (4), (6) and (20).

It is evident that with increasing fraction of dimer the minimum in the trailing boundary disappears, fig. 9, and the leading hypersharp boundary broadens. At high plateau concentrations with predominantly trimers the effect of the increasing dimer concentration in the shoulder is small, fig. 10. A stationary point, like the one in fig. 9B, has been found in other cases, but so far we are unable to state the conditions for the appearance of such a point.

4. Conclusions

The mathematical solution presented in this paper allows us to calculate the concentration gradient in a leading and trailing boundary of a reversibly reacting component. The appearance of a minimum of a reversibly polymerizing substance is strongly dependent on the parameters chosen, i.e. time, ratio of the frictional coefficients of the species, concentration dependence of the species mobility, activity coefficients.

Other types of boundaries for reversibly reacting systems could be calculated, for example for systems exhibiting infinite open association like glutamate dehydrogenase [15] or systems with concentration-dependent conformational transitions, where even diffusion without migration may lead to bimodal be-

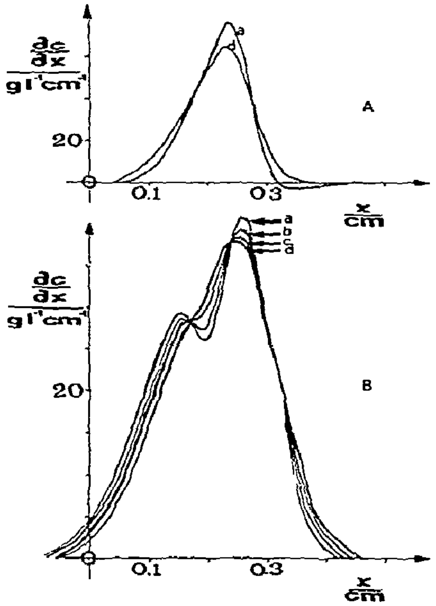

Fig. 9. Monomer–dimer–trimer, $t = 2700$ s, $\bar{c} = 4\ g \cdot \ell^{-1}$, $K_2'K_3' = 50\ g^2 \cdot \ell^{-2}$. Influence of increasing dimer fraction. (A) leading boundary, (B) trailing boundary.

	$K_2'(g \cdot \ell^{-1})$	$K_3'(g \cdot \ell^{-1})$	α_M	α_D	α_T
(a)	∞	0	0.64	0	0.36
(b)	50	1	0.66	0.06	0.32
(c)	20	2.5	0.59	0.14	0.27
(d)	10	5	0.55	0.24	0.21

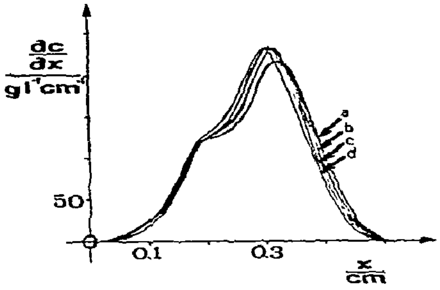

Fig. 10. Monomer–dimer–trimer, $t = 2700$ s, $\bar{c} = 22\ g \cdot \ell^{-1}$, $K_2'K_3' = 50\ g^2 \cdot \ell^{-2}$.

	$K_2'(g \cdot \ell^{-1})$	$K_3'(g \cdot \ell^{-1})$	α_M	α_D	α_T
(a)	∞	0	0.26	0	0.74
(b)	50	1	0.26	0.06	0.68
(c)	20	2.5	0.25	0.14	0.61
(d)	10	5	0.23	0.24	0.53

haviour [16]. These will be treated in another paper.

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Appendix A

For the ith polymerisation step we write

$$c_i = K_i c_M^i . \tag{A.1}$$

Therefore

$$\frac{\partial c_i}{\partial x} = K_i i c_M^{i-1} \frac{\partial c_M}{\partial x} = \frac{i c_i}{c_M} \frac{\partial c_M}{\partial x} . \tag{A.2}$$

The total concentration c is given by

$$c = \sum c_i$$

Hence

$$\frac{\partial c}{\partial x} = \sum \frac{\partial c_i}{\partial x} = \sum \frac{i c_i}{c_M} \frac{\partial c_M}{\partial x} = \frac{\partial c_M}{\partial x} \sum \frac{i c_i}{c_M} . \tag{A.3}$$

Solving for $\partial c_M / \partial x$ and substituting into (A.2) we obtain

$$\frac{\partial c_i}{\partial x} = \frac{i c_i}{\Sigma i c_i} \frac{\partial c}{\partial x} . \tag{A.4}$$

This converts eq. (5) into eq. (6).

Added note

One of the referees has drawn our attention to the work of Cox [17] who has devised a computer simulation method for solving this problem. He also uses the concept of constituent transport coefficients and except for the effect of radial dilution, incorporated by Cox, the starting equations are the same. A quantitative comparison of the results of the two different mathematical procedures is not possible, because of the radial dilution effect, but it is gratifying that the qualitative conclusions are the same. The following points especially should be mentioned: (i) details of the concentration dependence of the diffusion coefficient $D(c)$ do not show up in the gradient curves; instead it is sufficient to describe the overall decrease of $D(c)$ by a linear or some similar function. (ii) The minimum in a bimodal gradient curve predicted by Gilbert's asymptotic solution [1, 2] may disappear, if with decreasing monomer molecular weight the diffusion coefficient is increasing, if the concentration of intermediate species is increasing, and if the frictional coupling is increasing.

References

[1] G.A. Gilbert, Discuss. Faraday Soc. 20 (1955) 68.
[2] G.A. Gilbert, Proc. Roy. Soc. A250 (1959) 377.
[3] J.L. Bethune, J. Phys. Chem. 74 (1970) 3837.
[4] B.J. McNeil, L.W. Nichol and J.L. Bethune, J. Phys. Chem. 74 (1970) 3846.
[5] J.R. Cann, Interacting macromolecules (Academic Press, New York 1970).
[6] L.W. Nichol and D.J. Winzor, Migration of interacting systems (Clarendon Press, Oxford, 1972).
[7] H. Fujita, Mathematical theory of sedimentation analysis (Academic Press, New York 1962).
[8] A. Tiselius, Nova Acta R. Soc. Scient. Upsal. [4], 7 (1930) No. 4
[9] H. Schönert, Z. Naturfschg. 24b (1969) 1222.
[10] L.J. Gosting and H. Fujita, J. Amer. Chem. Soc. 79 (1957) 1359.
[11] H. Schönert, Forschungsber. d. Landes Nordrhein Westfalen, Nr. 2396 (Westdeutscher Verlag, Opladen, 1974).
[12] G. Kegeles and M.S.N. Rao, J. Amer. Chem. Soc. 80 (1958) 5724.
[13] G.W. Schwert and S. Kaufmann, J. Biol. Chem. 190 (1951) 807.
[14] G.W. Schwert, J. Biol. Chem. 179 (1949) 655.
[15] R. Josephs, H. Eisenberg and E. Reisler, in: Protein–protein interactions, ed. R. Jaenicke and E. Helmreich (Springer, Berlin, 1972) p. 57.
[16] H. Bittner, Diplomarbeit, Techn. Hochschule Aachen (1969).
[17] D.J. Cox, Arch. Biochem. Biophys. 119 (1967) 230; 129 (1969) 106; 142 (1971) 514; 146 (1971) 181.