

Investigation of Flow Injection Analysis in Terms of Segment Flow, Double Peaks and Friction

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Abstract

A theoretical description of flow injection analysis (FIA) has been developed and it was tested experimentally on the on-line reaction between chromate and 1,5-diphenylcarbazide (DPC). The flow is of segment type and the injected sample expands exponentially with time and it expands both in upstream and in the downstream direction. The symmetry of the expansion is destroyed only by transfer of solute molecules from the front to the rear of the segment, as caused by friction. It was found that the FIA peak, fundamentally, consists of two individual peaks that develop upon sample injection as a result of sample molecules mixing with the carrier, predominantly at the front of the segment and at the rear of the segment. Useful equations kinetics were obtained for a detailed description of the FIA trace and for providing characteristic time parameters of the system, by approximating the segment with a rectangular shape and convoluting with the expansion. It is shown that the shape of the FIA peak depends on the physical dimensions of the manifold and on a single parameter of friction, as given by (α_D) . The ability of the model to provide information about chemical kinetics is discussed.

Keywords Flow injection analysis, theory, spectrophotometry, segment flow, friction

1. Introduction

In the classical work of Taylor [1-2], the flow of fluid and the dispersion of molecules in tubes of small bores was described in terms of convection and diffusion. In that model, convection is responsible for the shape of the injected sample plug, and it exhibits a parabolic-velocity profile according to the vast majority of investigations [1-9]. The assumption of a parabolic-velocity profile of the fluid at steady flow is imposed by the Poiseuille model [10], which, in addition, predicts a FIA signal [7] with a tail of infinite length [3, 10]. By contrast in FIA, no tails are observed and adjustments to the simple Poiseuille model is required, as to model experiments [8-9]. By including the diffusion term in the equations of motion, the shape of the FIA peak may be described by a Gaussian function [1-2, 7, 10-11], which also allows modelling of FIA peaks with a double-peaked structure [11].

Recently, a description was introduced, which does not specifically assume convection as the primary source of shaping the FIA peak but friction, diffusion and the response of the detector

were found to be of equal importance [12-13]. The theory thus developed, was applied to non-reacting species and the main deviation between theory and experimental data of FIA was found along the rear section of the peak [12]. The theory of the present work is an improvement of the previous model and it applies to dispersion traces as well as to FIA traces of chemical reactions with a double-peak structure. In this manner, an excellent correspondence between theory and experiments was found.

2. Experimental

The measurements were performed by a single-line FIA manifold where the samples of chromate species were injected into a carrier of DPC reagent at room temperature [12-14]. A single-line manifold with straight tubes (Microline™, 0.5 mm diameter) was used in order to investigate laminar flow and diffusion without obstructions, i.e., without indentations or protrusion in the tubular system. Reynolds numbers below 200 define laminar conditions of the system [7]. Two series of experiments were applied, as to test the

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theory. In the first series the dispersion of chromate molecules was investigated without DPC in the reagent, that is, the chromate samples (3 mg/L or 50 mg/L) were injected into the carrier and the measured signal represented the actual dispersion of sample molecules in the absence of chemical reaction. In these experiments, the samples were monitored at 350 nm by a UV-VIS spectrophotometer with diode array detection in a quartz-detection cell of 1 cm width. In the second series of experiments DPC was present in the carrier, which initiated the chromate-DPC reaction. The chromate-DPC chelate, thus formed, was monitored at 548 nm. The carrier was prepared by dissolving 0.25 g of 1,5-diphenylcarbazide (Merck 98% purity) in 50 ml acetone (Merck, p.a.) followed by dilution with sulphuric acid to 500 ml at a concentration of 0.036M. The samples were prepared by dissolution of potassiumchromate (The British Drug Houses, p.a.) in sulphuric acid (0.036M) and acetone.

3. Results and discussion

In the following, the experiments where no chemical reactions were initiated, i.e. , the samples were injected into a carrier deprived from DPC, are denoted as dispersion experiments. In FIA experiments, DPC was a constituent of the carrier and, upon injection, a chemical reaction commenced. By assuming that the front of the injected segment reaches the detector at the time t_0 after injection and the rear of the segment leaves the detection cell at the time t_1 , it can be shown that the FIA trace follows the approximate relation [12]:

$$A(t) = \begin{cases} A(t_0 \leq t \leq t_1) = -A \cdot [\exp(D_x \cdot (t - t_0)) - 1]^2 \\ A(t \geq t_1) = A \cdot \exp(D_x \cdot t) \\ \bullet (\exp(-D_x \cdot t_0) - \exp(-D_x \cdot t_1)) \\ \bullet [2 - \exp(D_x \cdot t) \cdot (\exp(-D_x \cdot t_0) + \exp(-D_x \cdot t_1))] \end{cases} \quad (1)$$

where D_x is a constant that accounts for diffusion, for friction and includes the spatial resolution of the detector. The constant A is going to be investigated in further detail in the present work since it is supposed to contain information about

friction that might differ between FIA systems and dispersion systems [12, 14]. The time values , t_0 and t_1 (eq. 1), represent, together with the initial absorbance (A_0), the plug-like shape of the absorbance profile, as monitored by the narrow detection cell. In fact, eq. 1 was derived on the basis of a slow detector that registers a relatively fast moving rectangular-shaped-concentration profile, which was treated mathematically as a convolution [15] of the shape and dispersion/diffusion together with the spatial resolution of the instrument [12]. With implementation of these assumptions, experimental evidence has been given for the existence of a linear relationship between D_x and the linear flow rate, v_x [12-13], as given by:

$$D_x = \alpha_D \cdot v_x \quad \alpha_D < 0 \quad (2)$$

where α_D is a characteristic constant of the system, which is independent of distances and of flow rates.

If the kinetic-diffusion term were included, the time of onset may be approximated by [16]:

$$t_0 \cong \frac{2 \cdot x_0}{v_x \cdot (2 - \alpha_D \cdot L_0)} \quad (3)$$

where x_0 is the tube length from the point of injection to the point of detection and L_0 is the loop length. According to eqs. 1-3, the single parameter, apart from the physical dimensions of the system, that determines the trace of the FIA peak is given by α_D . In the dispersion experiments, it was found, by a fit of theory to experiments, that $\alpha_D = -2.6 \pm 0.2 \text{ m}^{-1}$ but in the FIA experiments two values of α_D were identified, which evidence that two different peaks were present; First peak $\alpha_{D1} = 1.5 \pm 0.1 \text{ m}^{-1}$ and second peak $\alpha_{D2} = 2.7 \pm 0.2 \text{ m}^{-1}$. The latter value do not differ from the value obtained in the dispersion experiments, which shows that a common peak exists, most likely originating from the content of unreacted chromate. Accordingly, the additional peak, i.e. the first peak, may be characterised by an α_D -value that is significantly different from that of the second peak and can thus be used as a parameter of discrimination. Despite the fact that the peaks are not completely separated, as measured experimentally, the discrimination is

greatly facilitated by extraction of α_D -values of the theory. The observation that, in many cases, the FIA trace consists of two peaks [4-5, 7, 10-11, 17], in the present work is promoted as being the prevailing structure of any FIA peak. In Fig. 1 is shown the dependence of the FIA peak on L_0 .

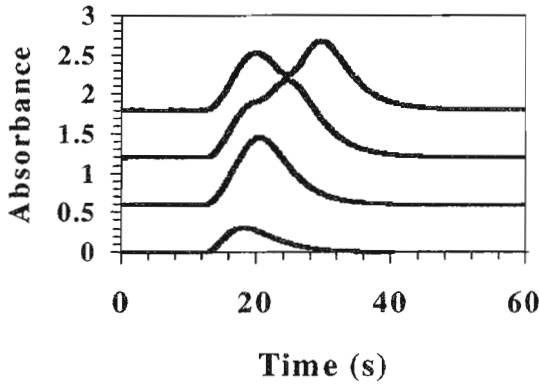


Fig. 1. Evolution of the second peak in FIA experiments as a function of L_0 . From bottom to top of figure: $L_0 = 0.1m, 0.5m, 1m$ and $1.5m$. For clarity, the traces were separated by 0.6 Abs. The small horizontal bars that represent the experiments are almost indistinguishable from the solid line of the theory ($x_0 = 2m, v_x = 0.19ms^{-1}$).

The general structure of the FIA trace can be shown to be primarily dependent on L_0 , as evidenced by Fig. 1 where the evolution of the double peak is generated by increments in L_0 . This structure of the peak was found in dispersion experiments but it was also found in FIA experiments. The recognition of a general double-peaked structure of the FIA peak is interpreted as a confirmation of pure plug flow where mixing of solvent (or reagents of the carrier) proceeds at the front section and at the rear section of the segment in motion [12-13]. The mixing is assumed to proceed without formation of concentration gradient, which is an approximation, as compared to an earlier description including linear concentration gradients [13]. The notion of a double peak prompts an improvement description of the FIA trace given by eq. 1, which may be accomplished by applying two sets of equations that represent the mixing at the front and the mixing at the rear of the segment, respectively. Thus, the improved FIA-double peak may be described by adding two absorbances,

$A_1(t, t_{01}, t_{11})$ and $A_2(t, t_{02}, t_{12})$, as to obtain the sum of absorbances, $A(t)$:

$$A(t) = A_1(t, t_{01}, t_{11}, \alpha_{D1}) + A_2(t, t_{02}, t_{12}, \alpha_{D2}) \quad (4)$$

In eq. 4 the response is characterised by two values of α_D (eq. 2) and the time values associated with onset (t_{01} and t_{02}) and with the exit (t_{11} and t_{12}) may differ for the two peaks. By using eqs. 1 and 4, the correspondence between theory and experiment is excellent, as shown in Figs. 1 and 2 where the FIA peaks were investigated as a function of L_0 and of x_0 , respectively.

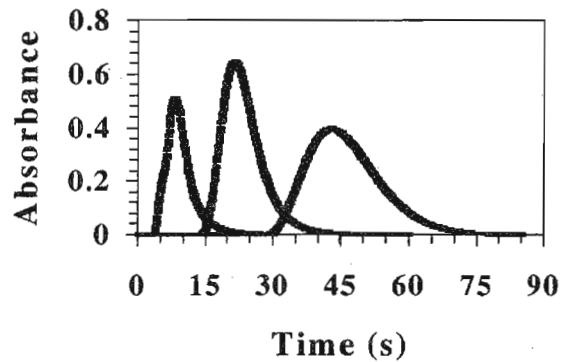


Fig. 2. The shape of the FIA peaks depicted as a function of x_0 . From left to right: $x_0 = 0.6m, 2.5m$ and $5m$. The horizontal bars are experimental values and the solid line are fitted values. ($L_0 = 0.5m, v_x = 0.19ms^{-1}$).

In both cases, the assumption of a double-peaked structure completely removes any discrepancy between theory and experiment, as compared to earlier results where single-peak structures were anticipated [12-13]. Although the results of Fig. 2 seem to exhibit single-peak structures, particularly at long distances x_0 , the double-peak is revealed for short distances and, thus, confirms the assumptions of eq. 4. From the fit of theory to experiment was extracted all the time values of eq. 4 and they are suitable for performing a comparison of the model of segment flow with the Poiseuille model. In Fig. 3 is shown that the time of onset (t_{01}) is very well predicted by eq. 3, that is close to the value given by x_0/v_x , which strongly indicates that the time of onset differs from the prediction of Poiseuille, i.e., differs from $x_0/2v_x$, as indicated in

the figure. The time of exit of the second peak (t_{12}) was also

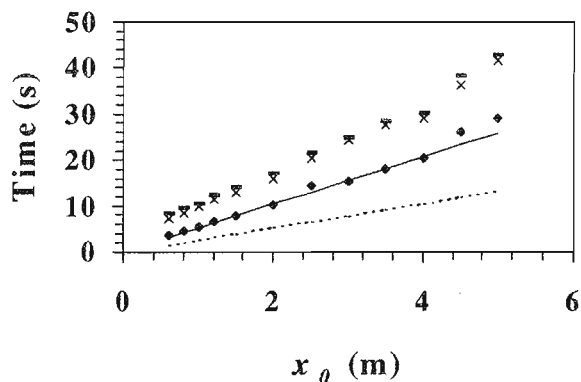


Fig. 3. Characteristic time values, as found by fitting the theory to FIA experiments obtained at various lengths of x_0 . (\blacklozenge) Experimental t_0 -values ($-$) Eq. 3 ($---$) Prediction of Poiseuille ($-$) t_{12} and (\times) t_{\max} . ($L_0 = 0.5\text{ m}, v_x = 0.19\text{ ms}^{-1}$)

linearly dependent on x_0 for a wide range of distances, which supports the notion of segment flow (Fig. 3). Now, that we have found the experimental values of t_{01}, t_{02}, t_{02} and t_{12} we are able to investigate, in detail, the validity of the theoretical predictions. The time of exit (t_{12}) also followed a simple expression. It was previously suggested, in dispersion experiments, that the time of exit coincided approximately with the time of peak maximum, which was confirmed in the present work. In dispersion experiments, the time of exit followed the expression to good precision:

$$t_{12} \cong \frac{x_0 + L_0 + l}{v_x} \quad (5)$$

where the width of the detection cell (l) is introduced. In FIA experiments, however, eq. 5 was only valid for the first peak and had to be extended with a value that corresponded to the time of passage of the loop length. The dispersion experiments are compared with the FIA experiments in Fig. 4 ($L_0 = 1.5\text{ m}$), which shows that the product presumably is contained in the second peak owing to the differences in friction. This result implies that a FIA system, to some degree, exhibits a chromatographic effect. The time predicted by eq. 5 is simply the time required for

the rear point of the segment to travel, at the velocity of linear flow rate, the distance from injection to detection, that is, diffusion, friction and other features of the physical flow dynamics were omitted. This observation simplifies the description considerably and with the notion that the time of peak maximum is generally very close to t_{12} [12-13], i.e., $t_{12} \cong t_{\max}$, the full extent of the FIA trace may be described by eqs. 1-5 where the time values are appropriately approximated by using the flow rate, the physical dimensions of the system, the initial absorbance (A) and the parameter of friction (α_D). Thus, the number of novel parameters introduced as to perform a detailed description of the FIA trace is reduced to the single parameter α_D .

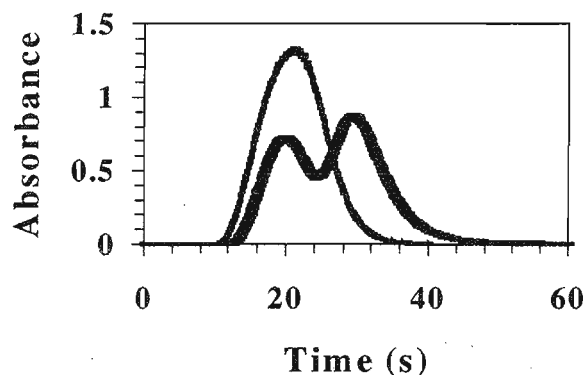


Fig. 4. Comparison of dispersion experiments ($-$, 50 mg/L, 350 nm) with FIA experiments ($-$, 3 mg/L, 548 nm). The solid lines represent the theory, as fitted to the data by eq. 1. $x_0 = 2\text{ m}, L_0 = 1.5\text{ m}$ and $v_x = 0.19\text{ ms}^{-1}$.

When comparing the present model to contemporary models of FIA [3-11, 17], the major differences are found in the significance of diffusion on the shape of the FIA trace. Taylor introduced the convection-diffusion equation and, by that formulation, defined the concept of dispersion, which has been included in many theories [3-11]. In view of the present theory, diffusion is of minor importance in the evolution of the FIA trace but the convection term was not considered. However, convection and diffusion contribute to the flow with relatively small velocities, of the order of cms^{-1} [1-2, 18], but together with the overall Poiseuille-flow rate, the

description of the FIA trace became possible [3, 6, 8-9]. It was found, in the present theory, that it was not possible to obtain reliable information about molecular diffusion owing to the relatively high level of uncertainty on the flow rate, which was induced by the peristaltic pump. The proposition that the dispersion of solute molecules originates predominantly from friction may be further supported by considering the segment residence time, as given by, $\Delta t_R = t_{12} - t_{01}$ (eqs. 3 and 5):

$$\Delta t_R \cong \frac{L_0 + l}{v_x} - \frac{x_0}{v_x} \cdot \frac{\alpha_D \cdot L_0}{2 - \alpha_D \cdot L_0} \quad (6)$$

The first term of eq. 6 corresponds to the time required for the segment to pass the detection cell in the absence of friction while the second term adds to the time value (α_D attains negative values) by a term of friction that depends on x_0 , on L_0 and on α_D . In FIA experiments, eq. 6 was also valid when the α_D -value of the second peak was applied. The dependence on x_0 and L_0 , in particular, signifies that the second term of eq. 6 is a term of friction. It was found that eq. 6 fitted the data of FIA very well, as shown in Fig. 5 where the residence time is depicted as a function of linear-flow rate.

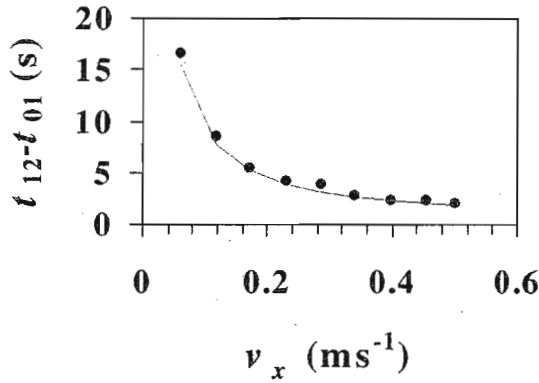


Fig. 5. The residence time (solid line) of eq. 6 depicted as a function of v_x . (●) The time differences as obtained by eqs. 1 and 4. $x_0 = 1.0m$ and $L_0 = 0.5m$.

The residence time of eq. 6 does not represent the total-peak width, i.e., the baseline-to-baseline time [7, 14] that is measured experimentally but it represents the residence time of the segment as it appears at the time of onset. Because the segment expands during the measurement, the total-peak-

residence time, t_{TPR} , can be found from eq. 3 and eq. 2 in [12]:

$$t_{TPR} \cong \frac{L_0 + l}{v_x} \cdot \exp \left[-2 \cdot x_0 \cdot \frac{\alpha_D}{2 - \alpha_D \cdot L_0} \right] \quad (7)$$

where the cell width (l) was added to the length of the segment, which then accounts for the finite width of the detection cell. The total-peak residence time corresponds to the baseline-to-baseline time of other investigations. In Fig. 6 is shown the total-peak-residence time as a function of L_0 where a satisfactory correspondence was found between experiment and the calculations of eq. 7, which strongly supports the model of segment flow.

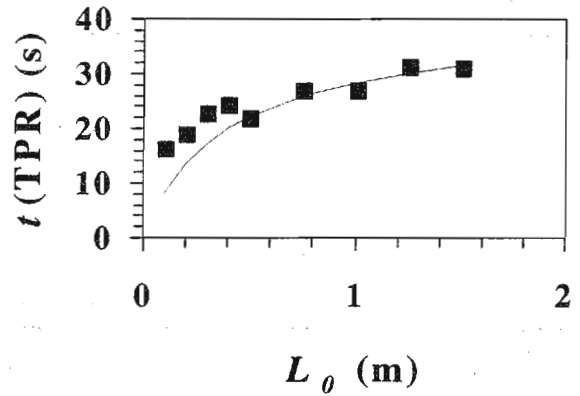


Fig. 6. The total-peak-residence time of FIA measurements, as defined by eq. 7, depicted as a function of loop length. (■) Experiment (—) Theory. $x_0 = 2.0m$ and $v_x = 0.19ms^{-1}$.

The total-peak-residence time leads to the maximum sampling frequency, S_{max} , as given by the reciprocal value of eq. 7:

$$S_{max} = \frac{v_x}{L_0 + l} \cdot \exp \left[2 \cdot x_0 \cdot \frac{\alpha_D}{2 - \alpha_D \cdot L_0} \right] \quad (8)$$

In this manner, it is not necessary to consider the noise level in the calculation of the maximum sampling frequency, as proposed earlier [13]. The maximum-sampling frequency (eq. 8) is proportional to the linear-flow rate, in agreement with other results [14]. Because the exponent is negative in eq. 8, at large distances (x_0), the maximum sampling frequency decreases, which also holds true for a numerically large value of α_D , which agrees intuitively with the notion that

friction is proportional to the magnitude of $(-\alpha_D)$. Since the results were generated on the basis of both dispersion experiments and FIA experiments, the method might constitute a general method of estimating friction. The velocity of the rear of the segment, as investigated as a function of L_0 at constant flow rate, decreased by a constant factor for all values of L_0 . It was found by extrapolation to zero L_0 , that the velocity of the rear of the segment, as determined to be $0.12 \pm 0.01 \text{ ms}^{-1}$, was considerably lower than the linear-flow rate, $v_x = 0.19 \text{ ms}^{-1}$. The overall decrease in velocity was determined to be $-0.028 \pm 0.04 \text{ s}^{-1}$, as found from the fit of a straight line (not shown) to the time-of-exit values (t_{12}) of both dispersion results and FIA results. This dependence on L_0 , showed that the rate of expansion of the moving segment decreased by 0.028 ms^{-1} at $v_x = 0.19 \text{ ms}^{-1}$ for every meter of increment in L_0 . Although the investigation of the characteristic time values of the flow provides useful information about the fluid dynamics, it does not seem to constitute the proper tool for investigating chemical kinetics. The results above demonstrate that only minor differences in time values may be identified when comparing dispersion experiments with FIA experiments. Accordingly, it is necessary to explore some of the other features of the model, and with respect to chemical kinetics, the areas and the peak heights are potential indicators that may be used to characterise a chemical reaction. With the absorbance constants of each peak defined by A_1 and A_2 , it may be shown that the peak maximum attains the approximate value:

$$A_{\max} \cong A_1 \cdot \frac{1 - \exp(t_{11} - t_{01})}{1 + \exp(t_{11} - t_{01})} + A_2 \cdot \frac{1 - \exp(t_{12} - t_{02})}{1 + \exp(t_{12} - t_{02})} \quad (9)$$

which is valid at relatively short loop lengths where single peaks are prevailing but at long loop lengths, the peak splits into two peaks with individual peak heights that corresponds to the first and second term of eq. 9, respectively. With a loop length of 0.5 m, a single peak was observed in both dispersion experiments and in FIA experiments and, thus, a single term of eq. 9 was valid.

Subsequently, it proved very useful to apply eq. 9 to the investigation of chemical reactions as shown in Figs. 7a and 7b, where the peak heights were examined as a function of v_x .

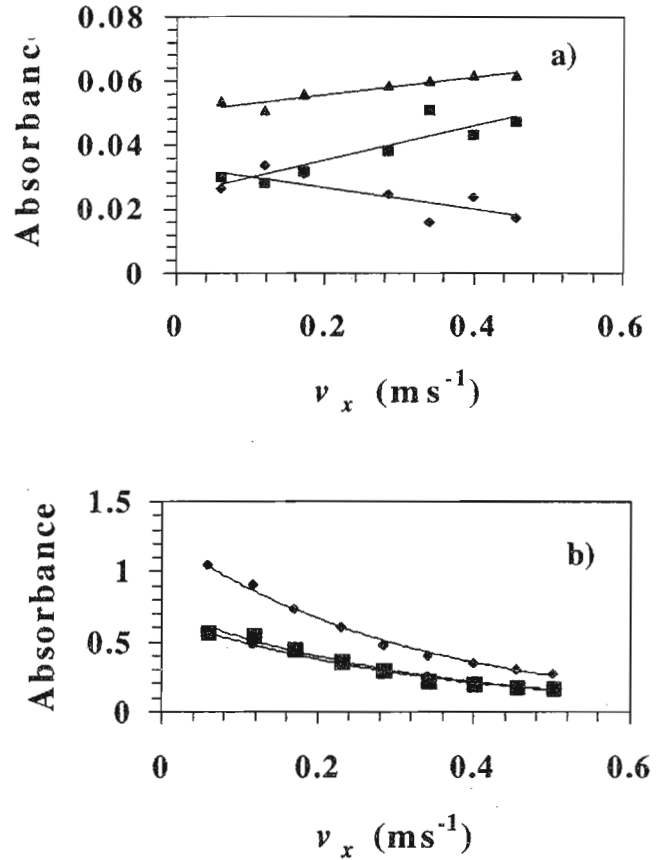


Fig. 7. The peak heights depicted as a function of linear-flow rate in a) Dispersion experiments (\blacktriangle) Total peak height (\blacklozenge) Front peak and (\blacksquare) Rear peak. b) FIA experiments (\blacklozenge) Total peak height (\blacksquare) Front peak and (\bullet) Rear peak. $x_0 = 1.0 \text{ m}$ and $L_0 = 0.5 \text{ m}$.

The peak height of dispersion experiments was found to depend weakly on v_x (Fig. 7a), in correspondence with earlier results [12-13], but the two single peaks that constitute the single major peak depended more strongly on v_x . In the dispersion experiments, the front peak decreased linearly as a function of v_x , while the second peak (the rear peak) increased linearly with v_x (Fig. 7a). This result shows that significant amounts of material is transferred from the front to the rear of the segment during the flow. Since the amount of

solute removed from the front corresponds exactly to the amount of solute gained by the rear segment, the mechanism must be related to friction. It may thus be suggested that more solute is forced to the walls of the tubes when v_x is high. The amount of material transferred from the front to the back of the segment may then be expressed as the difference in absolute slope values of the straight lines, which corresponds exactly to the slope of the increasing peak heights (Fig. 7a). By taking into account the level of uncertainty, the difference in slope values becomes:

$$\Delta A \equiv \alpha_A \cdot v_x = (0.024 \pm 0.05) \cdot v_x \quad (10)$$

(in units of absorbance). The slope of friction, as given by α_A , is measured in units of $\text{Abs}/\text{ms}^{-1}$ or, by using Beer-Lamberts law ($A = \epsilon \cdot l \cdot c$), in units of $\text{moles}/(\text{Lms}^{-1})$. The straight line of the front peak (Fig. 7a) intersects the abscissa at $v_x \cong 1.0 \text{ms}^{-1}$, which is a high flow rate that is difficult to realise experimentally but it shows that the double-peak structure may be reduced to a single peak by using high flow rates, thus simplifying the calculations. When a chemical reaction proceeds, of course, the reaction must be affected by the transfer of sample solute from the front to the rear of the segment. Indeed, this was also found, as shown by the results of Fig. 7b where the peak heights of the FIA experiments are depicted as a function of distance. More product was formed at the rear of the segment, as compared to the front of the segment, owing to the transport of sample molecules from the front to the back (Fig. 7b). In Fig. 7b, the peak heights decrease when v_x increases, which is opposite to the dispersion results of Fig. 7a. This result shows that the chemical reaction has not reached equilibrium even at low flow rates (Fig. 7b), except for the front peak, where the peak height levelled at low flow rates. Because the peak heights of dispersion experiments were almost independent of v_x but

strongly dependent on v_x in FIA experiments it may be suggested that the data of Fig. 7b can be used to derive directly the rate of chemical reaction. An exponential function fit very well the data of Fig. 7b. Accordingly, the absorbance may be expressed as a function of time through the relation:

$$A(v_x) = A_\infty \cdot \exp(k_v \cdot v_x) \quad (11)$$

where A_∞ is the absorbance of the product, when the reaction is completed, and k_v is the rate constant, expressed by reciprocal velocity. The rate constant may be transformed into the conventional rate constant of first order reactions by:

$$k = \frac{1}{x_0 \cdot k_v} \quad (12)$$

and, by using the data of Fig. 7b, it was found that $k = 0.17 \text{ s}^{-1}$, which is a realistic value of first order reactions [14].

5. Conclusion

A theory has been developed and it was shown that it was applicable to dispersion experiments as well as to FIA experiments. The theory evidence the presence of segment flow and the comparison of experimental data to parameters of the theory shows that the segment expands exponentially as a function of time thus providing an exponential decay of the FIA signal. At any given moment the shape of the absorbance profile is approximately rectangular, which allows a detailed description of the measured FIA trace. The model is schematically visualised in Fig. 8, which shows that the injected segment expands by dilution at the front of the segment and at the rear of the segment.

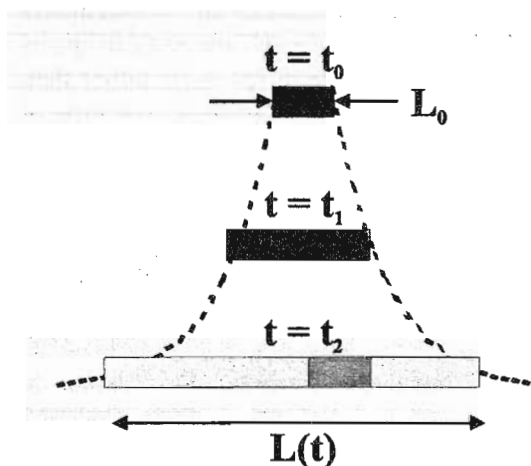


Fig. 8. Schematic representation of the exponential expansion of the segment $L(t)$ subsequent to injection (L_0). The direction of flow is from left to right in the figure. $t_2 > t_1 > t_0$.

The result is an exponential expansion of the segment as a function of time, which may be expressed by a differential equation of friction:

$$\frac{dL(t)}{dt} = -\alpha_D \cdot v_x \cdot L(t) \quad (13)$$

which suggests that α_D is a constant of friction measured in units of reciprocal meters. In the present description the α_D -value controls the shape of the FIA peak and it was found that, in principle, all FIA peaks exhibited a double-peaked structure originating from dilution at both ends of the segment. However, the absorbance of the front peak decreases at a higher rate than the absorbance of the rear peak owing to a continuous transport of material from the front to the rear of the segment imposed by friction to the walls.

In summary, dilution of the segment from both ends of the segment results in a double-peaked structure, which is symmetric, but the symmetry is destroyed by solute-to-wall friction. In the Poiseuille model, the asymmetry of the peak is also caused by friction but dilution of the segment proceeds only from the rear of the segment. The origin of the experimentally observed non-symmetric-absorbance profile is therefore explained as being a consequence of the method of measurement. The total extension of the segment did not depend on chemical reactions while it was found that a chemical reaction influenced the distribution of molecules within the segment and, thus, resulted in a large influence on the magnitude of the peak height. Accordingly, the peak height is used to characterise chemical reactions rather than using time values such as time of onset and time of exit.

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(Received November 24, 2000)

(Accepted December 18, 2000)