The influence of the temperature increase rate on the accuracy of diffusion parameters estimated under non-isothermal conditions

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Summary The accuracy of the diffusion parameters estimated under non-isothermal conditions was studied using computer-generated pseudo-experimental points. The data sets were obtained from Fick's 2nd law and an Arrhenius-type temperature dependence of the diffusivity. A normally distributed error was randomly attributed to the model data. The pseudo-experimental points thus obtained were then fitted to the model equation, with non-linear regression using the Simplex algorithm, yielding the estimates of the pre-exponential factor and activation energy. Several linear temperature profiles were studied, from 0.014 to 16°C min^{-1}. It was concluded that the accuracy of the parameters estimation depends on the temperature increase rate. The effects of the pre-exponential factor, the activation energy, the range of temperature and the magnitude of the experimental error on the value of the temperature increase rate that led to maximum accuracy of the parameters estimates were also studied.

Keywords Arrhenius equation, diffusion coefficient, factorial design, Fick's 2nd law.

Introduction

Mass transfer in food processing can often be described as a diffusion phenomena following Fick's 2nd law (Stahl & Loncin, 1979; Schwartzberg & Chao, 1982; Aguerre *et al.*, 1985; Rodger *et al.*, 1984; McCarthy & Heil, 1988; Oliveira, 1988; Beristain *et al.*, 1990). For an adequate analysis and control of these processes, the diffusion coefficients and their temperature dependence should be determined experimentally. Diffusion coefficients are usually calculated using a two-step isothermal methodology. In the first step several experiments are performed at constant temperatures in a range of interest and diffusion coefficients are estimated for each temperature (Rodger *et al.*, 1984; Garrote *et al.*, 1984; Garrote *et al.*, 1986; Garrote *et al.*, 1988); in the second step the dependence of the diffusion coefficients on temperature is determined by applying an Arrhenius-type equation and estimating the pre-exponential factor and the activation energy as parameters (Rice & Selman, 1984; Tomasula & Kozempel, 1989; Floros & Chinnan, 1990). Unfortunately, if a considerable number of temperatures (and, therefore, experiments) are not covered, the confidence intervals may be larger than the predicted parameters (Labuza & Kamman, 1983). This implies a significant amount of experimental work, thus increasing the costs of the study. A more time and cost effective alternative is to apply a single regression to all isothermal data, estimating the pre-exponential factor and the activation energy in one step. This method provides results which are statistically more reliable because it gives less biased and more precise estimation of the parameters (Cohen & Saguy, 1985), although it requires that an Arrhenius-type temperature dependence is valid

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in all the range of experimental conditions. This approach has been applied for first order kinetic parameters (Arabshahi & Lund, 1985; Haralampu *et al.*, 1985; Cohen & Saguy, 1985) and Moreira *et al.* (1993) first applied this analysis to diffusional data with good results. Alternatively, non-isothermal methods may be used (Moreira *et al.*, 1993). Under variable temperature conditions, the pre-exponential factor and the activation energy may be obtained from a single experiment. Non-isothermal methods were first introduced by Rogers (1963) and have been applied in literature since then. However, the majority of these studies are on first order kinetics (Rhim *et al.*, 1989a,b; Nunes *et al.*, 1991). Non-isothermal methods require the choice of a time–temperature relationship. Several temperature profiles have been suggested (Rogers, 1963; Eriksen & Stelmach, 1965; Zoglio *et al.*, 1968; Maulding & Zoglio, 1970) but linear temperature profiles are the most common because they are very easy to obtain experimentally. The choice of the temperature profiles is often limited by the commercially available time–temperature programmers. Furthermore, linear temperature profiles give the same weight to the different temperatures in the experiment.

Non-isothermal methods also have the advantage of minimizing problems associated with thermal lag effects. Additionally, non-isothermal experiments reproduce a more similar dynamic environment to that found in the food processing industry. The majority of unit operations in food processing involving mass transfer phenomena are performed under non-isothermal conditions. Diffusion parameters determined at constant temperatures are used in the description of those processes, often without any validation. However, the application of a non-isothermal methodology for determination of diffusion parameters raises particular problems. The mathematical mass transfer models are rather complex and non-linear regression schemes and iterative methods are required for fitting non-isothermal data to those models. Sometimes the iterative process does not converge readily to the real solution, as the parameters show a high collinearity (Haralampu *et al.*, 1985; Moreira *et al.*, 1993) and consequently, the regression procedure may fail.

The reliability of non-isothermal methods has not yet been studied. Because a large amount of information is extracted from limited data, an analysis of the ability of the method to produce accurate parameters is crucial. In this work a non-isothermal procedure was applied to estimate diffusional parameters of a Fickian mass transfer process. Linear temperature profiles were used with the objective of assessing the effect of the temperature increase rate on the accuracy of the parameters estimated. The influence of intrinsic variables of the system (pre-exponential factor of diffusivity and activation energy), experimental conditions (initial and final temperature) and the magnitude of the experimental error were also studied.

Methods

Data generation

By generating pseudo-experimental data applying a random error to model data, it is possible to quantify the deviation between the estimates and the original parameters used in the simulation. Therefore, all the analysis was based on simulated data sets.

A simple diffusional process following Fick's 2nd law was assumed. Considering a spherical solid immersed in a large well-stirred bath, so that the external resistance to mass transfer is negligible and the solute concentration in the bath remains reasonably constant with time, the concentration of diffusing solute at the solid–liquid interface is also constant with time. However, under non-isothermal experimental conditions the diffusion coefficient is time and temperature dependent and an average value of the diffusivity may be considered in the analytical solution of Fick's 2nd law. For the sake of simplicity it was assumed that the diffusivity was not dependent on the position. In these conditions, the total amount of diffused substance uptake/loss (M_t) by a sphere of radius r at a particular time (t) can be calculated by (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \mathrm{EXP}\left(- \frac{n^2\pi^2}{r^2} \int_0^t D(t')dt' \right) \quad (1)$$

where M_∞ is the content of the diffusing solute in the solid at equilibrium and thus at the solid surface.

The diffusion coefficient, D(t), can be correlated with temperature by an Arrhenius type equation. Considering a linear temperature increase, one obtains:

$$D(t) = D_0\, \mathrm{EXP}\left(-\frac{E_a}{R(T_0 + \beta\, t)}\right) \qquad (2)$$

with D_0 being the pre-exponential factor and E_a the activation energy of the mass transfer process. T_0 is the initial temperature and β is the temperature increase rate. The model of the fractional uptake/loss can be obtained combining the previous equations.

Thirty data points, equally spaced in time, were generated for each set of conditions tested. Errors (e) randomly chosen from a normally distributed population with mean equal to zero and constant variance were then added to the values of M_t/M_∞ calculated from eqn 1:

$$\left(\frac{M_t}{M_\infty}\right)_{exp} = \left(\frac{M_t}{M_\infty}\right)_{Eq\ 1} + e(0, s^2) \qquad (3)$$

These new data were considered as experimental observations and will be called pseudo-experimental data. Two sets of 30 errors were considered with a standard deviation of 5% (e_1) and 6% (e_2), respectively (small plot in Fig. 1). An example of a simulated M_t/M_∞ vs. time curve with pseudo-experimental points is shown in Fig. 1.

Experimental design

A 2^4 factorial design (Box *et al.*, 1978) was applied for each of the two sets of errors used, to assess the effect of (i) pre-exponential factor, (ii) activation energy, (iii) initial temperature and (iv) final temperature on the accuracy of the parameters estimated. The levels of these variables are shown in Table 1. The values of the diffusional parameters D_0 and E_a selected for the simulations will be called reference parameters (or 'true' parameters). These values are in the range of magnitude found for the diffusion of solid/liquid substances in foods (Schwartzberg & Chao, 1982; Garrote *et al.*, 1984; Rice & Selman, 1984; Rodger *et al.*, 1984; Garrote *et al.*, 1986; Garrote *et al.*, 1988; McCarthy & Heil, 1988; Oliveira, 1988; Moreira *et al.*, 1993). For each set of conditions a radius of 10 mm was considered for the sphere and 19 different heating rates were tested, from 0.014 to 16°C min^{-1}. A total of 608 runs was therefore conducted.

Parameters estimation

Estimates of the diffusional parameters, D_0* and E_a*, were obtained by fitting the non-isothermal pseudo-experimental data to eqn 1. These will be called the pseudo-experimental parameters, because they minimize the residual between pseudo-experimental and model points. M_∞ was con-

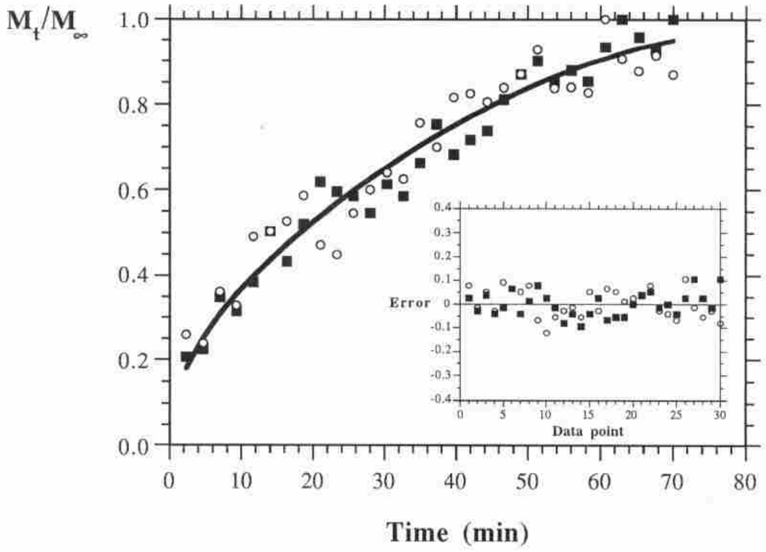


Figure 1 Computer simulated pseudo-experimental data for solute uptake/loss by a 10 mm radius sphere.
T_0 = 40°C; T_f = 100°C;
$D_0 = 1.0 \times 10^{-4}\ m^2s^{-1}$;
$E_a = 28.0\ kJ\ mol^{-1}$;
$\beta = 0.86°C\ min^{-1}$.
—— reference curve;
■ set of errors e_1 (s = 5%);
○ set of errors e_2 (s = 6%)

Table 1 Reference and estimated values of diffusional parameters for optimum conditions

	Reference diffusional parameters		Calculated parameters							
			$\beta_{opt} \times 10^3$ (°C s^{-1})		$\zeta_{min} \times 10^2$		$D_0^* \times 10^5$ (m^2 s^{-1})		E_a^* (kJ mol^{-1})	
Temperature (°C)	$D_0 \times 10^5$ (m^2 s^{-1})	E_a (kJ mol^{-1})	e_1	e_2	e_1	e_2	e_1	e_2	e_1	e_2
40–100	10.0	28.0	14.3	14.3	4.44	8.73	27.47	1.422	30.87	22.58
	1.00	28.0	1.11	1.67	4.26	8.47	0.9266	0.1484	27.91	22.68
	10.0	22.0	100	143	2.22	9.07	14.40	1.317	23.10	16.37
	1.00	22.0	10.8	14.3	2.95	9.06	1.948	0.1319	23.92	16.37
20–100	10.0	28.0	11.5	14.3	3.90	7.68	11.00	2.807	28.37	22.58
	1.00	28.0	1.11	1.48	4.36	7.54	1.010	0.2871	28.15	22.68
	10.0	22.0	103	133	3.04	7.97	11.88	2.694	22.56	16.37
	1.00	22.0	11.5	14.3	3.18	8.05	1.670	0.2653	23.45	16.37
40–80	10.0	28.0	5.75	9.52	2.89	7.62	12.63	0.8449	28.73	21.27
	1.00	28.0	0.556	0.741	3.66	9.57	1.000	0.04591	28.10	19.63
	10.0	22.0	51.3	95.2	2.41	8.42	13.80	0.6588	22.96	14.60
	1.00	22.0	5.75	9.52	3.16	9.82	2.865	0.04179	24.91	13.37
20–80	10.0	28.0	7.19	8.62	3.15	7.99	19.18	1.821	29.78	23.53
	1.00	28.0	0.694	0.833	2.72	8.03	1.667	0.1812	29.42	23.52
	10.0	22.0	66.7	76.9	2.97	8.62	18.75	1.629	23.71	17.26
	1.00	22.0	6.17	8.62	2.34	8.75	1.380	0.1576	22.92	17.16

e_1 – Experimental errors with a standard deviation of 5%.
e_2 – Experimental errors with a standard deviation of 6%.

sidered as a known parameter and the residual (Res) between pseudo-experimental and reference values was expressed in terms of the fractional uptake/loss of diffusing solute. This residual was minimized using the Simplex algorithm (Nelder & Mead, 1965):

$$\mathrm{Res} = \sqrt{\sum_{i=1}^{N}\left[\left(\frac{M_t}{M_\infty}\right)_{est} - \left(\frac{M_t}{M_\infty}\right)_{exp}\right]^2} \qquad (4)$$

The diffusivity calculated with the pseudo-experimental values D_0^* and E_a^* (D_{est}) was compared with the reference diffusivity (D_{ref}), calculated with the reference values of D_0 and E_a used in the pseudo-experimental data generation (the 'true' solution). A variable ζ was defined to evaluate the average deviation of the estimated diffusivity relatively to the reference, extended to the temperature range of interest.

$$\zeta = \frac{\displaystyle\int_{T_0}^{T_f} \frac{|D_{ref}(T') - D_{est}(T')|}{D_{ref}(T')}\,dT'}{T_f - T_0} \qquad (5)$$

All data generation and regression analyses were performed with a PC 486 compatible computer, using programs specially written in FORTRAN language (Fortran 5.1, Microsoft Corporation, 1990).

Results and discussion

For all the conditions studied it was observed that the heating rate greatly influences the accuracy of the estimated parameters, expressed by the variable ζ (the average error between pseudo-experimental and reference diffusivity) in the temperature range tested. Figure 2 shows a typical result for the two sets of experimental errors tested. From this plot, the existence of an optimum heating rate that led to maximum accuracy is obvious. Particularly for low heating rates, ζ increases markedly as the heating rate deviates from its optimum value. In the neighbourhood of this optimum the points were well fitted by a parabolic model, as shown in the small plot in Fig. 2.

Optimum heating rates were then calculated for all the conditions tested, by finding the minimum of the parabola fitted to the points in the neighbourhood of the minimum ζ (ζ_{min}). Table 1 shows the optimum heating rates for all conditions test-

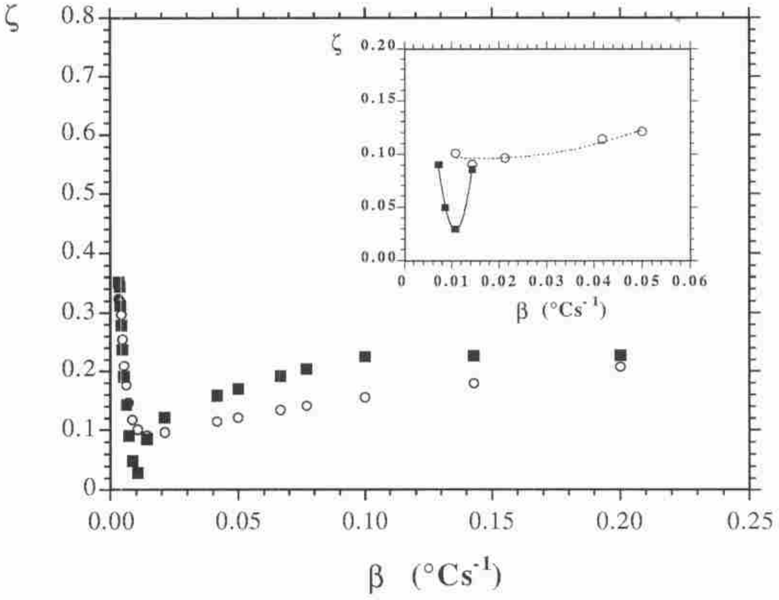


Figure 2 Influence of the heating rate on the accuracy of the estimated diffusivities.
T_0 = 40°C; T_f = 100°C;
$D_0 = 1.0 \times 10^{-4}$ $m^2 s^{-1}$;
E_a = 28.0 kJ mol^{-1}.
■ ζ values calculated from pseudo-experimental data with set of errors e_1 (s = 5%);
○ ζ values calculated from pseudo-experimental data with set of errors e_2 (s = 6%)

ed, together with the corresponding value of ζ_{min} and the estimated diffusional parameters (D_0* and E_a*). The influence of the variables tested and eventual interactive effects on the responses ζ_{min} and optimum heating rate, β_{opt}, were analysed using the Statgraphics Statistics Software (Statgraphics 5.0, Statistical Graphics Corporation, 1991). The analysis of the influence of the magnitude of the standard deviation of the experimental error was not included in this factorial design, because its effect was already very clear. The data in Table 1 show that the ζ_{min} values for the runs with 6% error are on average 2.6 times the values obtained with a 5% error. This means that minimizing experimental errors is most important to assure accuracy in the estimation of the parameters. A positive effect, although much weaker, was also noticed for β_{opt}. On average, for the higher experimental error, optimum heating rates were 40% higher.

The factorial design analysis showed that the variables that have a more important effect on β_{opt} are the intrinsic parameters of the system: the pre-exponential factor D_0 and the activation energy E_a. An interactive effect between these variables was also significant at a 95% level. Lower E_a values led to higher values of β_{opt}, that is, when the process is less temperature sensitive a faster variation in the temperature is required to fully assess its effect. This effect is particularly important at low D_0 values, that is for lower mass transfer rates. However, higher D_0 values, particularly for high activation energies, led to the need for a higher β_{opt}, i.e. for fast diffusion and a low heating rate most of the process would take place in a range of temperature too limited to allow an accurate estimation of the parameters. The value ζ_{min} was only affected by the initial temperature at a 95% significance level, with higher initial temperatures producing a larger error. Experiments should therefore commence at the lowest possible temperature, independently of the values of the diffusional parameters.

Figure 3 shows an example of the dependence of diffusivity on temperature, for the reference parameters and for pseudo-experimental parameters obtained, both for optimum and non-optimum heating rates. From this plot it may be concluded that when non-optimum conditions are used the errors between estimated and reference parameters may be very high, increasing with temperature. It is curious to note that this error would not be noticed by the analysis of the fit between the model equation and the pseudo-experimental data. Figure 4 shows this fit for optimum (Fig. 4b) and non-optimum (Figs 4a, 4c) heating rates. The sum of squares of the residuals is 6.23×10^{-2} for optimum conditions (β_{opt} = 0.86°C min^{-1}) and 4.76×10^{-2} and 5.10×10^{-2} for non-optimum conditions

Figure 3 Dependence of the diffusion coefficient on temperature
$T_0 = 40°C$; $T_f = 100°C$;
$D_0 = 1.0 \times 10^{-4}\ m^2s^{-1}$;
$E_a = 28.0$ kJ mol^{-1}
Set of errors e_1 ($s = 5\%$).
———— reference curve;
- - - - - - - estimated from pseudo-experimental data for the optimum β (0.86°C min^{-1});
— — — estimated from pseudo-experimental data for a non-optimum β (1.28°C min^{-1});
— - — - estimated from pseudo-experimental data for a non-optimum β (0.43°C min^{-1})

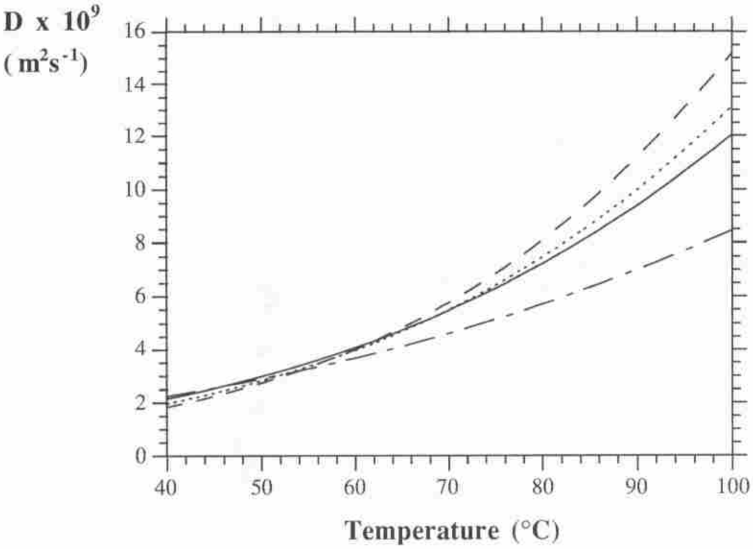
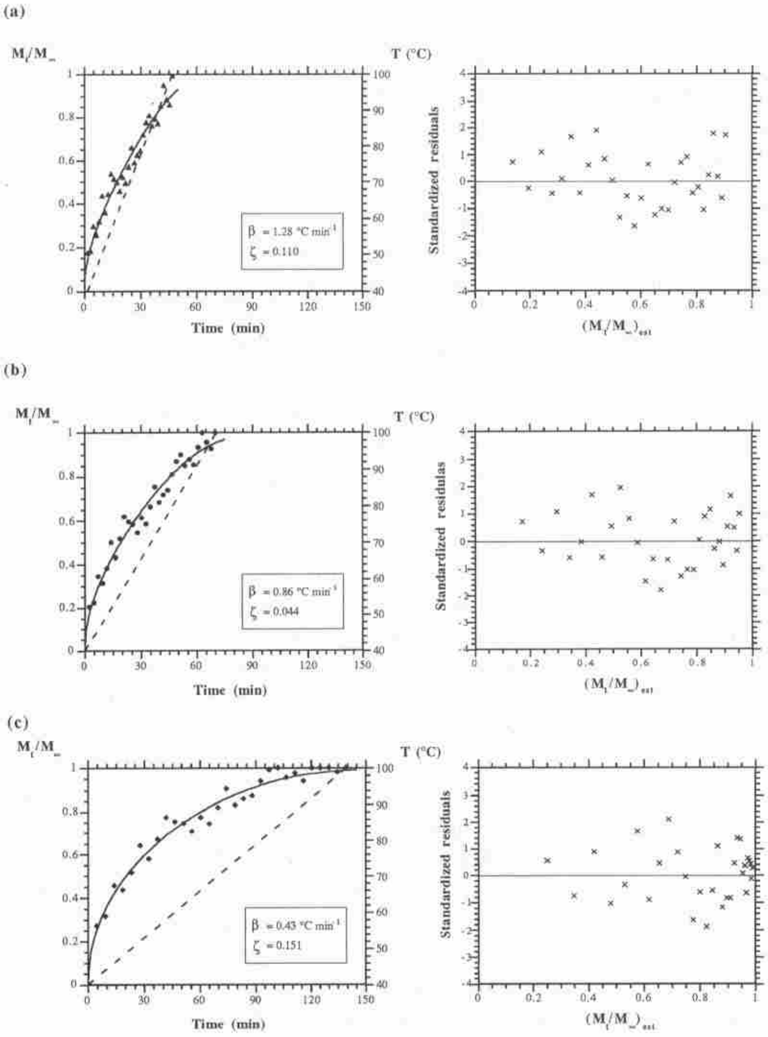


Figure 4 Analysis of the fit of the model to the pseudo-experimental points for different heating rates (the dashed lines represent the temperature profile).
$T_0 = 40°C$; $T_f = 100°C$;
$D_0 = 1.0 \times 10^{-4}\ m^2s^{-1}$;
$E_a = 28.0$ kJ mol^{-1}
Set of errors e_1 ($s = 5\%$)
(a) $\beta > \beta_{opt}$
(b) $\beta = \beta_{opt}$
(c) $\beta < \beta_{opt}$



(β = 0.43 and 1.28°C min^{-1}, respectively). The standardized residuals tend to fall between +2 and −2 and are randomly distributed around zero, showing no distinct pattern of variation. This analysis is considered a way of ensuring that the assumptions of least squares theory are valid, proving the adequacy of the model (Chatterjee & Price, 1991). Therefore, one reaches the very important conclusion that under non-isothermal conditions a good fit between experimental and estimated data does not provide a guarantee that the parameters are being estimated accurately.

Optimum conditions may depend not only on the selected heating rate but also on sampling rate. A high sampling frequency was chosen in this study in order to decrease the influence of the experimental design on the accuracy of the estimated parameters. Nevertheless, to analyse the extent of this effect, histograms of the number of samples collected for a given range of fractional uptake/loss of diffusing solute were plotted, for all the conditions tested. Ten categories of fractional uptake/loss were considered: [0–0.1[; [0.1–0.2[; [0.2–0.3[; [0.3–0.4[; [0.4–0.5[; [0.5–0.6[; [0.6–0.7[; [0.7–0.8[; [0.8–0.9[; [0.9–1[. Figure 5 shows these plots for optimum and non-optimum heating rates. For the optimum situation, the frequency of sampling increases linearly with the fractional uptake/loss (Fig. 5b) and curiously the optimum slopes for the different conditions tested were not statistically different (7.1 ± 0.93 for the 5% error

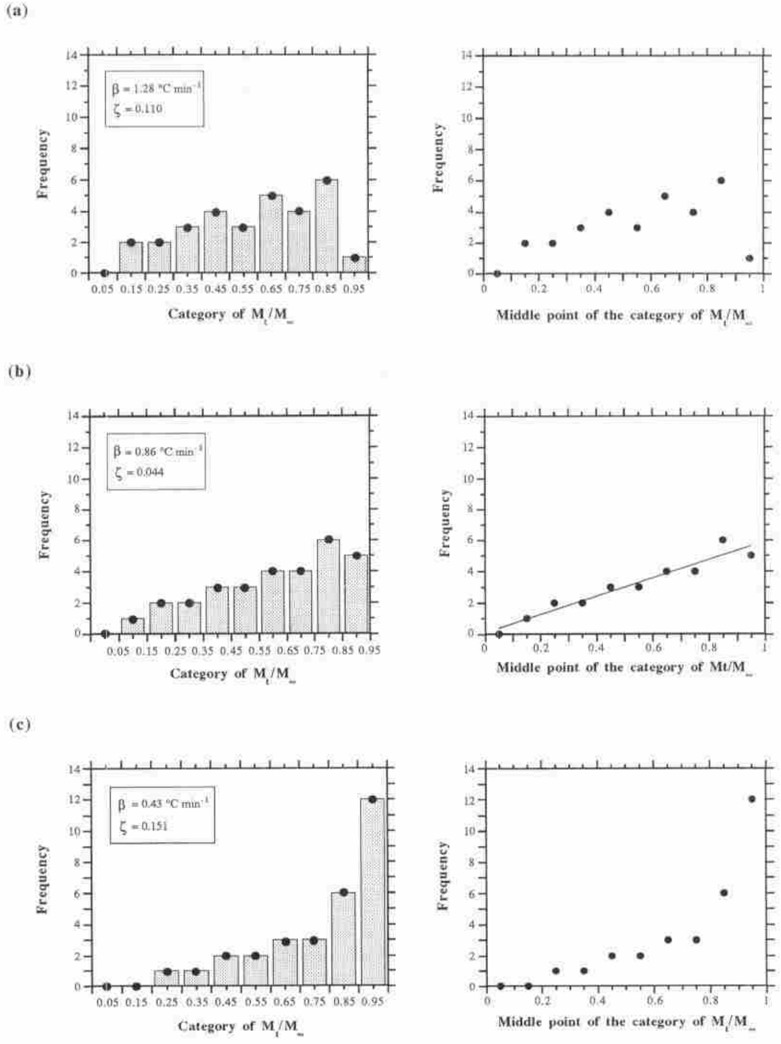


Figure 5 Frequency of sampling times expressed in terms of the fractional uptake/loss of the diffusing solute by the solid. T_0 = 40°C; T_f = 100°C; $D_0 = 1.0 \times 10^{-4}$ m^2s^{-1}; E_a = 28.0 kJ mol^{-1} *Set of errors* e_i *(s* = 5%)
(a) $\beta > \beta_{opt}$
(b) $\beta = \beta_{opt}$
(c) $\beta < \beta_{opt}$

and 6.2 ± 1.4 for the 6% error). For heating rates lower than the optimum, much lower sampling frequencies were taken for the lower M_t/M_∞ values (Fig. 5c), compared to those at high heating rates (Fig. 5a). This means that a significant amount of experimental data was obtained near the equilibrium, where the influence of the mass transfer rate becomes less clear (Fig. 4c). On the other hand for higher heating rates, the sampling frequency at higher M_t/M_∞ values was too low (see example in Figs 5a and 4a). This behaviour was detected in all the conditions tested, stressing that even if a high number of samples is taken, their choice will probably have a significant effect on the reliability of non-isothermal methods.

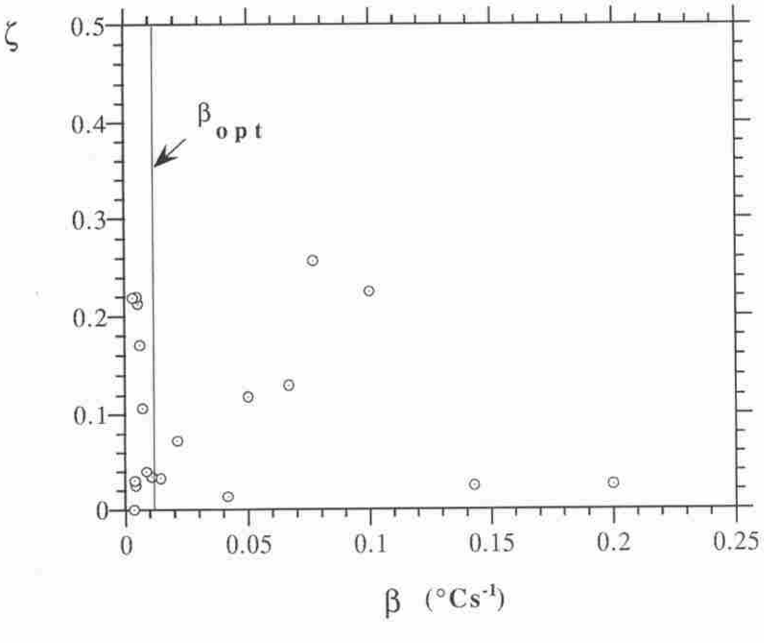
Under real experimental conditions it is also expected that the standard deviation of the errors may vary from experiment to experiment, masking the conclusions derived from this work. To assess this effect, a similar study was made using a different set of errors for each run. These errors were from a large population with an average equal to zero and a standard deviation of 5%. However, the average value and the standard deviation evaluated from a given set of errors randomly chosen from a large population, will often be slightly different. Figure 6 shows a typical example of the influence of the heating rate on the variable ζ, when using different sets of errors from run to run. The optimum heating rate, calculated from the previous analysis when the error was 5%, is also shown. This plot shows that if the error distribution varies from experiment to experiment, the effect of the heating rate is not so smooth. The steep drop of ζ in the low heating rate range is still visible, but in this situation higher heating rates may also cause significant deviations. Values around the previous optimum β are therefore the only ones that ensure a low ζ (good accuracy).

Conclusions

It was concluded that there is an optimum heating rate that allows the estimation of diffusional parameters under non-isothermal conditions with maximum accuracy. This optimum rate depends on the diffusional parameters themselves and varies with the magnitude of the experimental errors. Optimum conditions also appear to depend on sampling times, indicating the need for developing optimum experimental designs for non-isothermal methods.

It should be stressed that for non-isothermal conditions a good fit between experimental results and model predictions does not indicate necessarily that the parameters estimated are accurate.

Figure 6 Influence of the rate of temperature increase on the accuracy of the estimated diffusivity, assuming different error distributions for each set of data.
$T_0 = 40°C$; $T_f = 100°C$;
$D_0 = 1.0 \times 10^{-5}\ m^2s^{-1}$;
$E_a = 22.0\ kJ\ mol^{-1}$.
⊙ ζ values calculated from pseudo-experimental data with random errors ($3.7\% < s < 7\%$)



Acknowledgements

The first author acknowledges *Junta Nacional de Investigação Científica e Tecnológica* for financial support. The authors acknowledge financial support from EU project AIR1-CT92–0746.

Nomenclature

D	Diffusivity ($m^2\ s^{-1}$)
D_0	Pre-exponential factor in the Arrhenius relationship between diffusivity and temperature ($m^2\ s^{-1}$)
e	Set of errors randomly chosen from a normally distributed population with mean equal to zero and constant variance
e_1	Set of errors with standard deviation of 5%
e_2	Set of errors with standard deviation of 6%
E_a	Activation energy (J mol^{-1})
i	Index that varies from 1 to the total number of points used in the regression
M_t	Diffusing solute loss/uptake by the sphere at time t (mol)
M_∞	Diffusing solute loss/uptake by the sphere at equilibrium (mol)
N	Number of pseudo-experimental points
R	Ideal gas constant (8.314 J $mol^{-1}\ K^{-1}$)
r	Radius of the sphere (m)
Res	Residual between pseudo-experimental and estimated values (Eqn 4)
s	Standard deviation of the error
T	Temperature (K)
T_0	Initial temperature (K)
T_f	Final temperature (K)
t	Time (s)
β	Rate of temperature increase (K s^{-1})
ζ	Variable that evaluates the average error between the reference and the estimated diffusivity, in the range of temperature tested (eqn 5)

Subscripts

est	Estimated value
exp	Pseudo-experimental value
min	Minimum value
opt	Optimum value
ref	Reference value

Superscripts

*	Obtained by regression of pseudo-experimental data

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