A study on the accuracy and precision of external mass transfer and diffusion coefficients jointly estimated from pseudo-experimental simulated data

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Abstract

Optimal experimental designs for maximum precision in the estimation of diffusivities (D) and mass transfer coefficients (K_c) for solute transport from/to a solid immersed in a fluid were determined. Diffusion in the solid was considered to take place according to Fick's second law. It was found that the optimal design was dependent on the Biot number. In the range of Biot numbers tested (0.1–200), the first sampling time corresponded to values of fractional loss/uptake between 0.10 and 0.32, and the second sampling time corresponded to values of fractional loss/uptake between 0.67 and 0.82. Pseudo-experimental data were simulated by applying randomly generated sets of errors, taken from a normal distribution with 5% standard deviation, to data calculated using given values of the model parameters. Both optimal and heuristic designs (for which the sampling times corresponded to values of fractional loss/uptake from 0.30 to 0.95) were analyzed. The accuracy and precision of the estimates obtained by non-linear regression were compared. It was confirmed that optimal designs yield best results in terms of precision, although it was concluded that the joint estimation of D and K_c should, in general, be avoided. For intermediate values of the Biot number, reasonably precise and accurate estimates can however be obtained if the experimental error is small. © 1998 IMACS/Elsevier Science B.V.

Keywords: Heuristic experimental design; Mass transfer parameters; Optimal experimental design; Parameter estimation

1. Introduction

When modeling mass transfer of solutes from/to solids immersed in fluids, most authors assume that the resistance of the fluid to mass transfer is negligible [1–4]. For this assumption to be valid, the experiments are often carried out with stirring of the fluid. However, in some cases, the stirring may not be enough to completely destroy the external resistance. Nicolas and Duprat [5] reported that the

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diffusion coefficient (D) of potassium nitrate in agarose depended on the degree of stirring and concluded that with low stirring there was a boundary layer that affected the mass transfer rate. However, they did not measure external mass transfer coefficients. Potts et al. [6] studied the mass transfer of several solutes between cucumbers and brine solutions. They assumed that the major resistance to mass transfer was in a stagnant layer surrounding the cucumber and determined only the external mass transfer coefficient (K_c).

Only a few studies were reported in which both internal and external resistances are taken into account. Azevedo and Oliveira [7] estimated D and K_c in a conventional way: first, D was estimated from experimental data obtained under high stirring, so that the external resistance was confirmed to be negligible; then, experiments were carried out without stirring and K_c was estimated using the value of D obtained from the first set of experiments. One important conclusion from this work was that the model which neglects the external resistance also fits well the data from the static experiments, although leading to inaccurate values of D. Azevedo and Oliveira [8] have also theoretically analyzed the influence of assuming negligible external resistance to mass transfer on the accuracy and precision of the estimated value of D. It was concluded that for very large values of the Biot number (Bi) this assumption is valid, whereas for intermediate values of the Biot number significant errors arise, despite an apparent good fit between the data and the model.

Other studies apply multi-parametric regression to determine simultaneously D and K_c from a single experiment (e.g. [9]). Multiparametric analyses may however be unreliable and the use of an adequate experimental design is very important in order to accurately and precisely estimate the kinetic parameters. In fact, even a very careful analysis of experimental data is unable to recover information that is not present in that data [10]. In general, if the mathematical model is known, optimal experimental designs are very useful to estimate parameters with increased precision. Box and Lucas [11] proposed an optimum design based on determining the sampling conditions that lead to a minimum confidence region for the case where the number of experimental points is equal to the number of parameters. This design, also known as D-optimal design, was applied to different models, such as a first order kinetics [11], diffusional processes [12] and to the Bigelow model [13]. It was further shown that for a number of points larger than the number of parameters, this design often corresponds to r replicates of the optimal p sampling times ($r = N/p$) [14].

However, alternative experimental plans based on common sense are often used instead of optimal designs, because they are much more straightforward and they do not require a full knowledge of the model parameters. The most common heuristic plans used are those corresponding to taking samples at equally spaced values of the fractional loss/uptake of solute, equally spaced values of time, or equally spaced values of the logarithm of time.

The objectives of this work were (i) to define optimal experimental designs for maximum precision in the joint estimation of diffusivities and mass transfer coefficients, (ii) to assess if the parameters estimated with these designs are both accurate and precise, and (iii) to compare the accuracy and precision of these estimates with those obtained by heuristic designs.

2. Methods

A cube geometry was chosen for this work. The mathematical model of a Fickian process considering both internal and external resistance to mass transfer, for a cube immersed in a large

volume of solution, is [15,16]

$$\frac{M_t}{M_\infty} = 1 - \left[\sum_{n=1}^{\infty} \frac{2\text{Bi}^2}{\beta_n^2 (\beta_n^2 + \text{Bi}^2 + \text{Bi})} \exp(-\beta_n^2 Dt/L^2) \right]^3 \tag{1}$$

where M_t is the total amount of solute uptake/loss at time t, M_∞ the total amount of solute uptake/loss at equilibrium, L the half-thickness of the cube, D the diffusion coefficient, Bi the Biot number ($\text{Bi} = LK_c/(K_pD)$), K_c the mass transfer coefficient, K_p the partition coefficient, and β_n the roots of the equation $\beta \tan \beta = \text{Bi}$.

For a specific set of the model parameters, this equation allows the calculation of values of M_t/M_∞ for a given time. The values of time for this calculation were chosen both according to optimal and heuristic designs. A wide range of Biot numbers were considered, from 0.1 to 200. Early studies have shown that the values of D, K_c, K_p and L, on their own, do not influence the accuracy and precision of the diffusivities and mass transfer coefficients estimated. For calculation purposes, the following values were then used, without loss of generality: $D = 1 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$, $K_p = 1$, $L = 0.01$ m. The Biot numbers were then calculated assuming different values of K_c.

2.1. Optimal design

The D-optimal design concept was applied, considering a number of sampling times equal to the number of parameters and five replicates of each sampling time. Minimization of the error region of the parameters corresponds to maximization of the determinant of the derivatives of the model function (f) in order to the parameters [11,14]. For the case of two parameters, the determinant is given by

$$|\Delta_N| = \begin{vmatrix} \sum_{i=1}^{N} \left(\frac{\partial f}{\partial p_1} \right)_i^2 & \sum_{i=1}^{N} \left(\frac{\partial f}{\partial p_1} \cdot \frac{\partial f}{\partial p_2} \right)_i \\ \sum_{i=1}^{N} \left(\frac{\partial f}{\partial p_1} \cdot \frac{\partial f}{\partial p_2} \right)_i & \sum_{i=1}^{N} \left(\frac{\partial f}{\partial p_2} \right)_i^2 \end{vmatrix} \tag{2}$$

where N is the number of points, and p_1 and p_2 are the parameters.

For each Biot number, the two sampling times (and the corresponding values of M_t/M_∞) that maximized the absolute value of the determinant in Eq. (2) were determined; the function f corresponds to Eq. (1) and D and K_c are the parameters of interest. The Simplex method for minimization was used; the objective function was the reciprocal of the determinant. For these calculations, a subroutine was written in FORTRAN 77.

2.2. Heuristic design

In this work, a heuristic design based on equally spaced values of M_t/M_∞ was used. Ten sampling times were considered, for values of M_t/M_∞ ranging from 0.3 to 0.95: for values of M_t/M_∞ smaller than 0.7, the time interval was chosen so that the increase of M_t/M_∞ from one sampling point to the next was 0.1, whereas for larger values of M_t/M_∞ this interval was 0.05.

The efficiency of the heuristic design (ε) was calculated by

$$\varepsilon = \left[\frac{|\Delta_N|^{\text{HD}}}{|\Delta_N|^{\text{OD}}} \right]^{\frac{1}{p}} \tag{3}$$
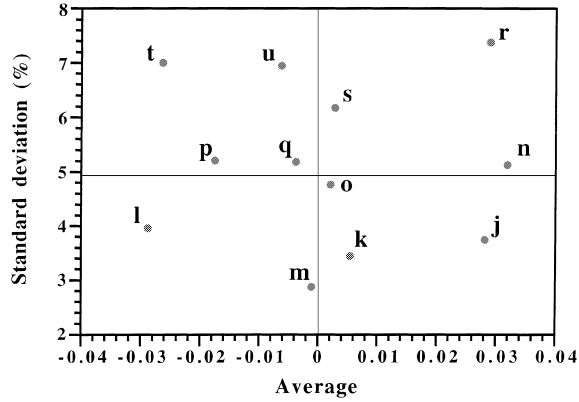
Fig. 1. Standard deviation and average of the 12 sets of errors attributed to the values of M_t/M_∞ obtained by simulation.

where p is the number of parameters (in this case, $p = 2$) and the superscripts HD and OD refer to heuristic design and optimal design, respectively.

2.3. Pseudo-experimental data generation

Pseudo-experimental data were calculated by applying to the values of M_t/M_∞ a set of random errors taken from a population with normal distribution with zero mean and 5% standard deviation. Twelve different sets of random errors were tested. The average and standard deviation of each set of errors are shown in Fig. 1.

For the optimal design, five replicates of each M_t/M_∞ were considered, giving a total of 10 points, the same number of points used for the heuristic design. The pseudo-experimental data were generated in the same manner for both designs, using the same sets of errors.

Fig. 2 shows typical simulated curves and pseudo-experimental data, for both optimal and heuristic designs. The pseudo-experimental data shown in this figure were generated using a set of errors with -0.00114 average and 2.8839% standard deviation (set m in Fig. 1).
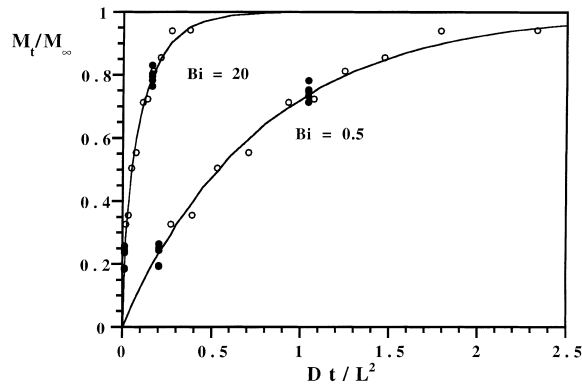

Fig. 2. Simulated curves (solid curves) and pseudo-experimental data (considering the set of errors m), for the fractional uptake/loss of solute by a cube, for Biot numbers of 0.5 and 20. ○ heuristic design; ● optimal design.

2.4. Estimation of parameters

The parameters D and K_c were estimated by non-linear regression using the Simplex method to minimize the residual (Res) between pseudo-experimental and theoretical data. The residual was calculated by

$$\text{Res} = \sum_{i=1}^{N} \left[\left(\frac{M_t}{M_\infty} \right)_{\text{p.exp.}} - \left(\frac{M_t}{M_\infty} \right)_{\text{theo.}} \right]^2 \tag{4}$$

A subroutine was also written in FORTRAN 77 for these calculations. A total of 720 runs were done.

The precision of each estimated parameter was calculated by a standardized half-width (SHW), defined as half of the confidence interval, at a 95% level, divided by the estimated value of the parameter. The accuracy was expressed by the absolute value of the fractional error of the estimated parameter relative to its 'true' value.

Joint confidence regions for D and K_c were calculated at a 90% confidence level, as described by Box et al. [17]

$$\text{Res}_{90\%} = \text{Res}_{\text{min}} \left[1 + \frac{p}{N-p} F_{0.10}(p, N-p) \right] \tag{5}$$

where Res_{min} is the minimum value of the residual defined by Eq. (4); $\text{Res}_{90\%}$ is the residual for the 90% joint confidence region; and $F_{0.10}$ is the F value at a 90% confidence level.

3. Results and discussion

3.1. Optimal and heuristic designs

Fig. 3 shows the effect of M_t/M_∞ (and, thus, the effect of the corresponding sampling times) on the value of the determinant, for $\text{Bi} = 20$. Similar results were obtained in the whole range of Biot numbers tested, although the values of M_t/M_∞ that maximize the determinant were dependent on the Biot number, as shown in Fig. 4. These values ranged from 0.10 to 0.32 for the first sampling time, and from 0.67 to 0.82 for the second sampling time. Additional calculations have shown that as the Biot number tends to zero, one of the values of M_t/M_∞ tends to zero and the other to 0.632; this is the result expected for the case of negligible internal resistance to mass transfer ($M_t/M_\infty = 1 - 1/e$ [11]). On the other hand, for very large Biot numbers, one of the values of M_t/M_∞ tends to zero and the other to 0.704; additional calculations have shown that this is the result obtained when the model for negligible external resistance to mass transfer is used.

The efficiency of the heuristic design was assessed using the true values of the parameters to calculate the determinants of both heuristic and optimal designs. As expected, the values of the efficiency were always smaller than one (Fig. 5), meaning that the optimal design is more precise than the heuristic design. The values of the efficiency lie between 0.43 and 0.80, showing a maximum for a Biot number of 3.5. Optimal designs are specially useful for small efficiency values; in this situation that would be, in principle, the case for very small or large Biot numbers.
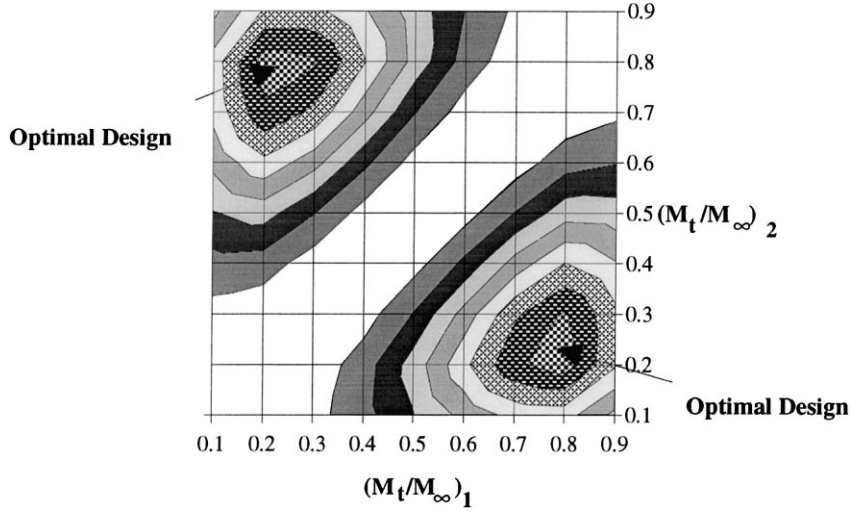
Fig. 3. Effect of the values of $(M_t/M_\infty)_1$ and $(M_t/M_\infty)_2$ on the value of the determinant, for $Bi = 20$. (Optimal design corresponds to $(M_t/M_\infty)_1 = 0.23$ and $(M_t/M_\infty)_2 = 0.79$ or $(M_t/M_\infty)_1 = 0.79$ and $(M_t/M_\infty)_2 = 0.23$).
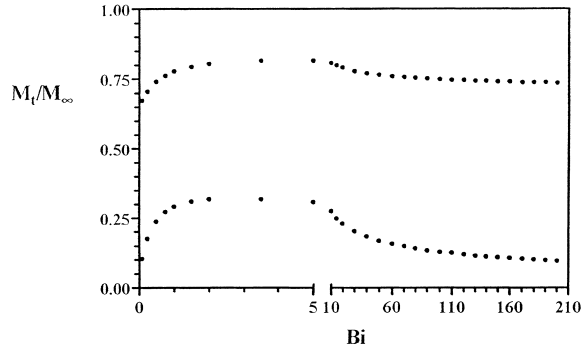

Fig. 4. Optimal values of $(M_t/M_\infty)_1$ and $(M_t/M_\infty)_2$ for all Biot numbers studied.

3.2. Estimation of parameters

The results shown in Table 1 and Fig. 6 were obtained using pseudo-experimental data generated by applying a set of errors with -0.00114 average and 2.8839% standard deviation (set m in Fig. 1). Table 1 shows the results obtained in terms of precision and accuracy of the estimated parameters. For small values of the Biot number, the joint estimation of D and K_c should be avoided, as even the application of optimal designs is unable to generate accurate and precise estimates (it should be noted that the higher the values shown in Table 1, the worse the accuracy or precision of the estimated parameters). When estimating the parameters D and K_c for very small Biot numbers, it was noticed that the correlation coefficients (ρ) obtained for both optimal and heuristic designs were very large ($|\rho| > 0.96$ for $Bi < 2$). Thus, the estimated values of the parameters are not very reliable [18]. This is confirmed by the size and shape of the joint confidence regions shown in Fig. 6(a), which were
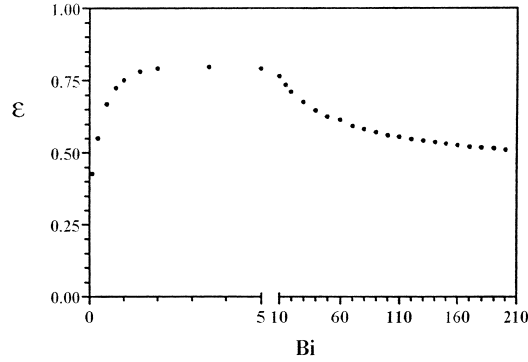
Fig. 5. Influence of the Biot number on the efficiency of the heuristic design.

obtained for $Bi = 1$. It can also be seen that the joint confidence regions for the optimal and heuristic designs are very similar. The shape of these curves for very large values of D can be explained as follows: when the diffusivity is very large, the internal resistance to mass transfer is negligible, meaning that the process is controlled by the external resistance; therefore, an increase in D does not change the estimated value of K_c.

For $Bi \geq 3.5$, the higher the Biot number the better the precision and the accuracy of the estimated value of D; the opposite happens in terms of K_c, with accuracy and precision decreasing with the increase of the Biot number (Table 1). These results were observed both for heuristic and optimal experimental designs; as expected, regarding precision, the optimal design leads to more precise estimates of D and K_c. Curiously it was found that, although the accuracy of K_c is better for the optimal design, the opposite happens in terms of D. The latter differences, while marginal, show that optimal designs aiming at maximum precision do not necessarily give the best results in terms of accuracy.

For very large values of the Biot number, the estimation of D is feasible whereas the estimation of K_c leads to inaccurate values with large confidence intervals (Table 1). This conclusion is also confirmed by an analysis of Fig. 6(b), which shows the joint confidence regions for $Bi = 100$. As was verified in Fig. 6(a), the shape of the confidence regions for the optimal and heuristic designs are also very similar. For very large values of K_c, the external resistance to mass transfer is negligible, so that an increase in K_c does not change the estimated value of D.

Fig. 6(c) shows the joint confidence regions for an intermediate value of the Biot number ($Bi = 10$). As was verified in Fig. 6(a) and (b), the shape of the joint confidence regions for the optimal and heuristic designs are similar. Because optimal designs lead to maximum precision, the joint confidence region for the optimal design is smaller than that for the heuristic design. This is clearly seen in Fig. 6(c). One important conclusion from Fig. 6(c) is that, opposite to the cases for $Bi = 1$ and $Bi = 100$, the joint estimation of D and K_c for $Bi = 10$ might be considered feasible, although the confidence regions are still large.

As mentioned before, the results shown in Table 1 and Fig. 6 were obtained using a particular set of errors, but all sets of errors shown in Fig. 1 were tested. It was verified that the accuracy and precision of the estimated values of D and K_c depend on the particular set of errors used to generate the pseudo-experimental data but the trends observed with the results shown in Table 1 were also observed with the results obtained for all the other sets of errors.

Table 1
Accuracy and precision of D and K_c for optimal and heuristic designs (considering the set of errors m with -0.00114 average and 2.8839% standard deviation)

Biot number	Optimal design				Heuristic design			
	Accuracy[a]		Precision[b]		Accuracy[a]		Precision[b]	
	D	K_c	D	K_c	D	K_c	D	K_c
0.1	0.0730	0.00700	37.7	1.14	0.0630	0.0131	102	3.07
0.25	0.0670	0.00	8.65	0.612	0.0520	0.0152	17.2	1.25
0.5	2.13	0.0888	21.8	0.991	0.751	0.0710	13.5	1.10
0.75	1.35	0.105	6.99	0.589	0.710	0.0924	6.64	0.781
1	0.800	0.101	3.08	0.424	0.598	0.103	3.89	0.619
1.5	0.472	0.101	1.49	0.343	0.495	0.123	2.14	0.497
2	0.330	0.0970	1.02	0.322	0.400	0.130	1.46	0.449
3.5	0.204	0.103	0.612	0.321	0.260	0.143	0.834	0.426
5	0.156	0.107	0.479	0.338	0.205	0.156	0.646	0.445
10	0.107	0.126	0.336	0.406	0.124	0.179	0.446	0.552
15	0.0910	0.147	0.289	0.471	0.0960	0.202	0.385	0.663
20	0.0830	0.165	0.264	0.532	0.0810	0.220	0.354	0.774
30	0.0730	0.193	0.237	0.644	0.0670	0.262	0.324	0.974
40	0.0690	0.222	0.223	0.743	0.0600	0.297	0.309	1.16
50	0.0660	0.247	0.214	0.835	0.0560	0.330	0.300	1.32
60	0.0650	0.278	0.208	0.912	0.0510	0.354	0.294	1.49
70	0.0620	0.296	0.203	0.994	0.0490	0.383	0.290	1.62
80	0.0620	0.318	0.199	1.06	0.0460	0.397	0.286	1.78
90	0.0580	0.328	0.196	1.14	0.0470	0.433	0.284	1.86
100	0.0590	0.350	0.194	1.20	0.0440	0.440	0.282	2.02
110	0.0560	0.361	0.192	1.27	0.0450	0.470	0.281	2.09
120	0.0600	0.386	0.190	1.32	0.0410	0.480	0.279	2.22
130	0.0580	0.396	0.189	1.38	0.0420	0.503	0.278	2.29
140	0.0570	0.408	0.187	1.44	0.0410	0.518	0.277	2.38
150	0.0560	0.424	0.186	1.49	0.0420	0.534	0.277	2.45
160	0.0550	0.436	0.185	1.54	0.0410	0.542	0.276	2.56
170	0.0550	0.449	0.185	1.58	0.0410	0.559	0.275	2.61
180	0.0550	0.457	0.184	1.63	0.0400	0.571	0.274	2.68
190	0.0560	0.468	0.183	1.68	0.0390	0.578	0.274	2.78
200	0.0540	0.477	0.182	1.72	0.0380	0.591	0.274	2.83

[a]Accuracy was defined by the absolute value of the fractional error of the estimated parameter relative to its 'true' value.
[b]Precision was calculated by a standardized half-width defined as half of the confidence interval at a 95% level divided by the estimated value of the parameter.

Under real experimental conditions, one expects that the average and the standard deviation of the errors may change from one experiment to another. To analyze the effect of these changes, a different set of errors (randomly chosen) was considered for each Biot number. This study focused only on the optimal design. The results are shown in Fig. 7 (It should be noted that the higher the value in the vertical axis, the worse the accuracy or precision of the estimated parameter). Fig. 7(a) and (c) clearly show that the higher the Biot number, the better the accuracy and the precision of the estimated value of D. This is in total agreement with the conclusions withdrawn from Table 1. The results shown in
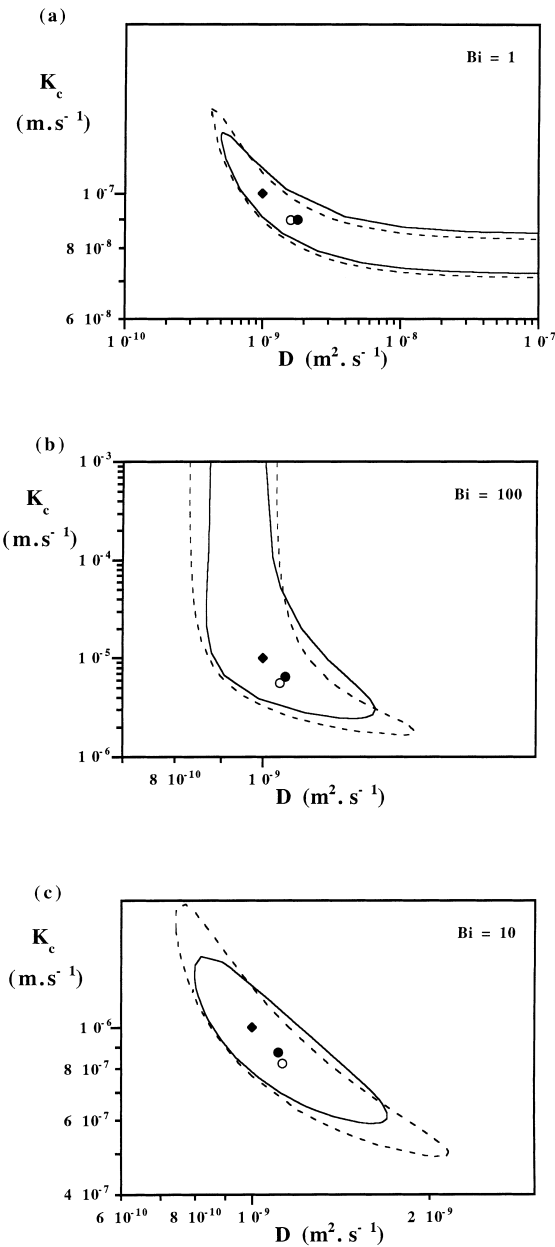
Fig. 6. 90% joint confidence regions for the estimates of D and K_c (considering the set of errors m), calculated by the heuristic (dashed curve) and optimal (solid curve) designs for: (a) Bi = 1; (b) Bi = 100; (c) Bi = 10. The 'true' and estimated values of the parameters are also shown: ◆ 'true' value; ◯ estimate of the heuristic design; ● estimate of the optimal design.

Fig. 7(b) and (d), regarding the accuracy and precision of K_c, are more scattered than the results regarding the accuracy and precision of D, indicating a higher effect of the experimental error in K_c than in D. It should be mentioned that the results obtained for three values of the Biot number (140, 150
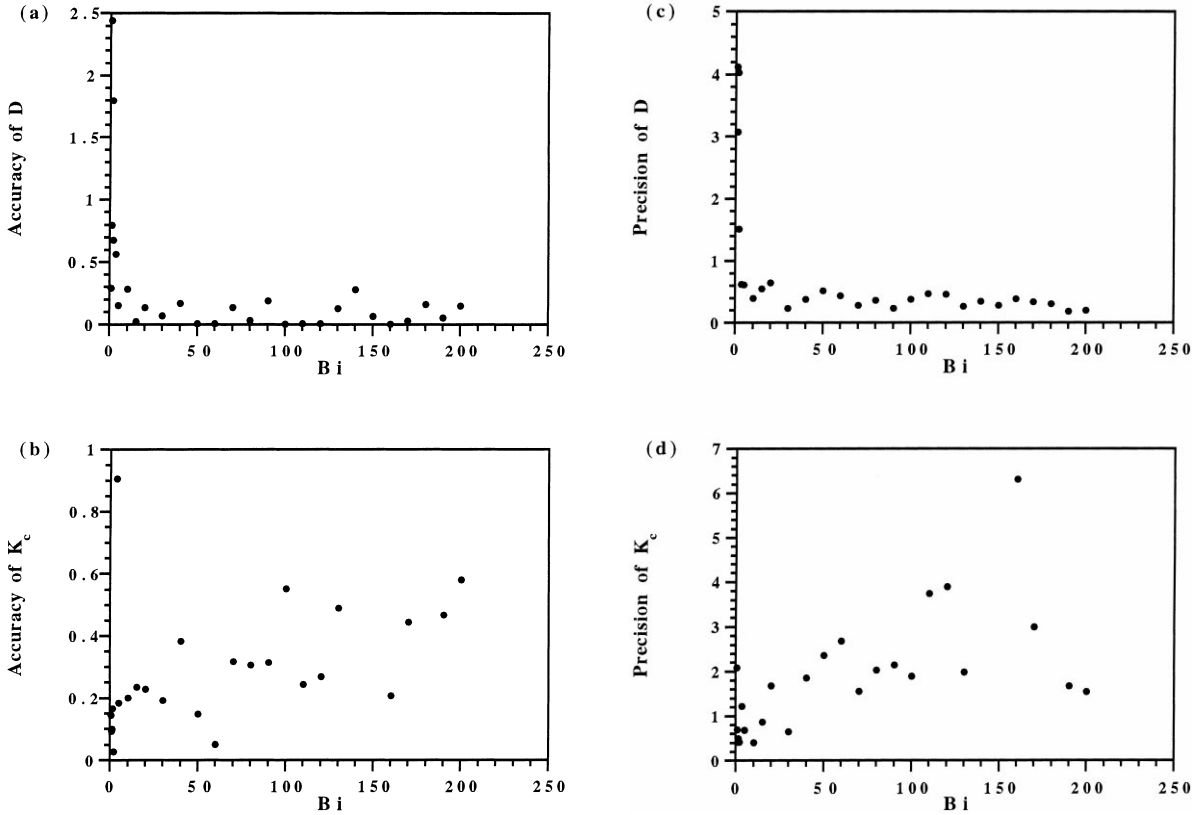
Fig. 7. Accuracy and precision of D and K_c, for optimal design, using a different set of errors (randomly chosen) for each Biot number. (a) accuracy of D; (b) accuracy of K_c; (c) precision of D; (d) precision of K_c.

and 180) are not shown in these figures because they would be out of scale. The results shown in Table 1 indicate that the precision of K_c is maximum for Bi around 3.5. (slightly different values were observed for the other sets of errors tested, but within the same range). However, due to the scatter of the results, the existence of a maximum precision of K_c in the range of small Biot numbers cannot be clearly inferred from Fig. 7(d). Anyway, it should be reminded that the results obtained in this range of Biot numbers are not very reliable because of the high correlation coefficients. For higher Biot numbers, Fig. 7(d) shows that the precision of K_c becomes worse as the Biot number increases, which is in agreement with the conclusions taken from Table 1. Regarding the accuracy of K_c, the results shown in Fig. 7(b) are in agreement with those shown in Table 1, that is, the higher the Biot number the worse the accuracy of K_c.

At this point it should be stressed that any set of experiments aimed at determining D and K_c must be carefully carried out. In fact, it is not possible to obtain accurate and precise estimates of these parameters if the experimental values are not reasonably accurate and precise themselves. Considering only the results obtained using the sets of errors with standard deviations $\leq 5\%$, the following was verified: if a standardized half-width (SHW) of 1 is considered acceptable, then the parameters can in general be estimated for Biot numbers ranging from ~ 3.5 to ~ 20; if a SHW of 0.5 is considered acceptable, then the
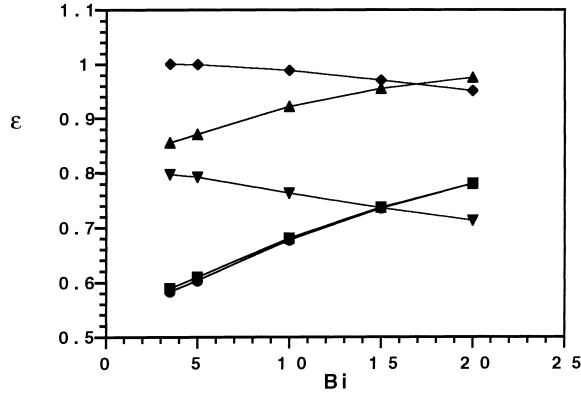
Fig. 8. Comparison between the efficiency of the heuristic design and the efficiencies of four different designs, each considering five replicates of two values of M_t/M_∞: ● - Design 1 (0.104 and 0.673); ■ - Design 2 (0.0957 and 0.736); ◆ - Design 3 (0.317 and 0.815); ▲ - Design 4 (0.181 and 0.759); ▼ - heuristic design.

range of Biot numbers is smaller ($\sim$5 to $\sim$15); if only a SHW of 0.1 is considered acceptable, then there is no range of Biot numbers for which the joint estimation of D and K_c is possible.

As suggested from the results shown in Table 1 and Fig. 6, as well as from the observations stated in the previous paragraph, the joint estimation of D and K_c might only be feasible for intermediate values of the Biot number. The results also clearly suggest that it is better to plan the experiments using the optimal design. However, this would only be possible if the Biot number was known 'a priori', which is generally not the case. With this in mind, additional calculations were done aimed at comparing the efficiency of the heuristic design with the efficiency of four different designs, each considering five replicates of two different values of M_t/M_∞. In three of these designs, the values of M_t/M_∞ corresponded to values earlier determined for the optimal design for Bi $= 0.1$ (Design 1), Bi $= 200$ (Design 2) and Bi $= 3.5$ (Design 3). The values of M_t/M_∞ used in Design 4 corresponded to the average values for all the Biot numbers tested in this work. Fig. 8 compares the efficiency of these four designs with that of the heuristic design, in the range of Biot numbers where estimation of D and K_c might be feasible. It can be seen that Designs 3 and 4 have higher efficiencies than the heuristic design. In particular, the use of Design 3 is recommended because its efficiency is always very close to unity. As shown in the legend of Fig. 8, the values of M_t/M_∞ for this design are 0.317 and 0.815. These values of M_t/M_∞ are particularly attractive because they are neither close to the begining of the experiment nor close to equilibrium.

4. Conclusions

Overall, it can be concluded that the joint estimation of D and K_c should, in general, be avoided. For intermediate values of the Biot number, reasonably precise and accurate estimates can only be obtained if the experimental error is small.

Optimal designs should be applied, although this implies the knowledge of the Biot number. If the Biot number is not known, as usually happens, it was found that a design with replicates of two values of M_t/M_∞ (0.317 and 0.815) is a better option than the heuristic design considered in this work.

Acknowledgements

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