



Numerical error analysis of mass transfer measurements in batch dialyzer

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ABSTRACT

The overall dialysis coefficient, which is the basic transport characteristic of a dialysis process, can easily be determined from experimental data obtained in a two-compartment dialysis cell. Here, the volume changes and the concentrations of component in both the compartments are recorded as functions of time. Generally, all these input quantities can be loaded with an experimental error. The paper deals with the transformation of concentration and liquid volume errors into the final results under the conditions of constant liquid volumes in both the compartments of the dialyzer. Using the generated precise experimental data, small random errors have been introduced into them and the effect of these errors upon the overall dialysis coefficient has been evaluated. The error analysis has proved that the unfavourable effect of the input quantities is dependent upon intensity of mass transfer. Moreover, in some cases the effect of the input quantities can be eliminated to some extent using reconciled experimental data.

Keywords: Batch dialysis; Mass transfer; Overall dialysis coefficient; Error analysis; Data reconciliation

1. Introduction

In the study of mass transport through ion-exchange polymeric membranes a two-compartment mixed cell is mostly used [1–13]. The dialysis cells are constructed in such a way that either both the liquid volumes are equal [5,7,9–11,13] or the liquid volume in a receiver compartment (V^{II}) is less than that in a feed compartment (V^{I}) [1,3,4,6,12]. A cell characterized by the $V^{\text{I}}/V^{\text{II}}$ ratio less than 1 was also used [5]. The component fluxes, the overall dialysis coefficient, the permeability of the membrane and other transport characteristics are determined from dependences of the component concentration upon time and changes of volume. Generally, each of these input quantities can be loaded with an experimental error, so that it is very important to know the extent,

into which the transport characteristics are affected by these errors.

The aim of this communication is to find the effect of errors of the component concentrations and liquid volumes in both the compartments upon the overall dialysis coefficient. For that purpose, a method of numerical error analysis was suggested as from the chemical engineering point of view it can be considered a useful tool enabling to reveal critical points in the determination of the overall dialysis coefficient.

2. Theory

Consider a two-compartment dialysis cell with the liquid volumes V^{I} and V^{II} (Fig. 1). Moreover, consider the transport of only one component (A) through the membrane in the direction from compartment I to compartment II, i.e., $c_A^{\text{I}} > c_A^{\text{II}}$ (c_A^{I} and c_A^{II} are the molar

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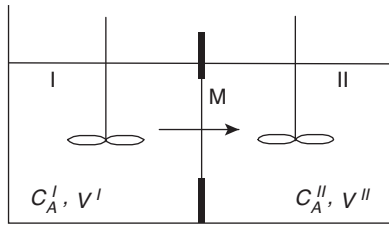


Fig. 1. Scheme of dialysis cell.

concentrations of component A in compartment I and II, respectively). From the balance of component A over compartment I and II during a time period $d\tau$ one can obtain the basic differential Eqs. (1) and (2) describing the dependence of the component concentration upon time in each compartment:

$$\frac{dc_A^I}{d\tau} = -\frac{A}{V^I} K_A (c_A^I - c_A^{II}) - \frac{c_A^I}{V^I} \frac{dV^I}{d\tau} \quad (1)$$

$$\tau = 0 \quad c_A^I = c_{A0}^I$$

$$\frac{dc_A^{II}}{d\tau} = \frac{A}{V^{II}} K_A (c_A^I - c_A^{II}) - \frac{c_A^{II}}{V^{II}} \frac{dV^{II}}{d\tau} \quad (2)$$

$$\tau = 0 \quad c_A^{II} = c_{A0}^{II} = 0$$

In Eqs. (1) and (2) A is the membrane area, K_A is the overall dialysis coefficient and τ is time. If the volumes of liquid during the dialysis process are constant, then analytical solutions to Eqs. (1) and (2) exist. For this purpose, it is necessary to solve Eqs. (1) and (2) simultaneously with the following balance equation:

$$V^I c_{A0}^I - V^I c_A^I - V^{II} c_A^{II} = 0 \quad (3)$$

The solution to the set of Eqs. (1) and (2) is in the form:

$$c_A^I = c_{A0}^I \frac{1}{1 + k_V} \left\{ k_V + \exp \left[- (1 + k_V) \frac{A}{V^I} K_A \tau \right] \right\} \quad (4)$$

$$c_A^{II} = c_{A0}^I \frac{k_V}{1 + k_V} \left\{ 1 - \exp \left[- (1 + k_V) \frac{A}{V^I} K_A \tau \right] \right\} \quad (5)$$

where k_V is the V^I/V^{II} ratio.

If the time dependences of the concentration of component A in both the compartments are known, then it is possible to determine the overall dialysis coefficient using the following methods:

2.1. Method A

This method is based on the linearization of Eq. (4) or (5). In this case, $\ln \frac{c_{A0}^I}{(1 + k_V) c_A^I - k_V c_{A0}^I}$ or

$\ln \frac{c_{A0}^I}{c_{A0}^I - \frac{1 + k_V}{k_V} c_A^{II}}$ is plotted versus time. The overall

dialysis coefficient, $K_{A'}$, is then easily determined from slopes of the straight lines obtained, i.e., from $(1 + k_V) \frac{A}{V^I} K_A$ or $\frac{1 + k_V}{k_V} \frac{A}{V^{II}} K_A$.

2.2. Method B

This method is based on the direct use of Eqs. (4) and (5). In order to determine the overall dialysis coefficient, a one-dimensional optimizing procedure, which searches for a minimum of the objective function Eq. (6), is used:

$$F(K_A) = \sum_{i=1}^n \left[\left(c_{Ai}^{I,exp} - c_{Ai}^{I,calc} \right)^2 + \left(c_{Ai}^{II,exp} - c_{Ai}^{II,calc} \right)^2 \right] \quad (6)$$

In Eq. (6) $c_{Ai}^{k,exp}$ ($k = I, II; i = 1, 2, \dots, n$) are the experimental concentrations and $c_{Ai}^{k,calc}$ ($k = I, II; i = 1, 2, \dots, n$) are the calculated concentrations from Eqs. (4) and (5).

3. Practical part

As the experimental data on dialysis are loaded with errors, it is impossible to use them directly in the numerical error analysis. That is why, it was necessary to calculate the so-called precise "experimental" concentrations of component A in both the compartments as functions of time. These data were calculated from Eqs. (4) and (5).

In accordance with our experience in dialysis the following values of the overall dialysis coefficients were used: 3×10^{-6} , 1×10^{-6} , 2×10^{-7} , 5×10^{-8} , 2×10^{-8} and $1 \times 10^{-8} \text{ m s}^{-1}$. In the basic calculations, values of A , V^I , V^{II} and c_{A0}^I approached the real conditions, which exist in batch dialysis used in our laboratory, i.e., $A = 62.2 \times 10^{-4} \text{ m}^2$, $V^I = 1.0 \times 10^{-3} \text{ m}^3$, $V^{II} = 1.0 \times 10^{-3} \text{ m}^3$ ($k_V = 1$) and $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$. Moreover, an extended series of calculations was also carried out at various V^I/V^{II} and A/V^I ratios. The number of experimental points was limited by the following requirements: $c_A^I - c_A^{II} \geq 10^{-3} c_{A0}^I \text{ kmol m}^{-3}$ and the total time of one measurement $\leq 200 \text{ h}$. The time interval was always 2h. Under these conditions, the number of experimental points generated was in the range from 27 to 101 depending upon intensity of mass transfer characterized by the overall dialysis coefficient.

4. Error analysis

In order to find the effect of the experimental errors upon the overall dialysis coefficient, small errors were introduced into the precise "experimental" concentration data, so that the real "experimental" data were generated. For this purpose, a random number generator

was used. On the basis of our experimental experience, the maximum relative error of the determination of the component concentration can be mostly estimated to be below 1.0%. Because of the cases, where the experimental errors can be over 1.0%, we carried out three series of calculations characterized by the random error simulated in the limits from -0.5 to + 0.5%, from -1.0 to +1.0% and from -2.0 to + 2.0%. Moreover, using the real "experimental" data the overall dialysis coefficient was also calculated with reconciled real data. In order to find a minimum of the objective function (6), the Golden Section Search procedure was used.

5. Data reconciliation

Since all physical quantities obtained by measurements are subject to errors, it is almost certain that the set of equations included in a mathematical model will not be satisfied exactly. In order to solve this problem, an approach based on the finding corrected physical quantities can be used. These corrected quantities are obtained by adding corrections, which can be obtained by a minimization of a suitable objective function, to the measured quantities. Here, we used the least squares method, which is exact if only random errors with normal distribution exist.

If the liquid volume in each compartment is measured correctly, then only corrections of the component concentrations are needed. In order to simplify the further notation, designate: $c_1 = c_{A0}^I$, $c_{1i} = c_{Ai}^I$ and $c_{2i} = c_{Ai}^{II}$. The task is to find such corrections v_{c1} and v_{cki} ($k = 1, 2; i = 2, 3, \dots, n$), which satisfy a minimum of the objective function [14]

$$F = p_{c1} v_{c1}^2 + \sum_{i=2}^n (p_{c1i} v_{c1i}^2 + p_{c2i} v_{c2i}^2) \tag{7}$$

where p_{c1} and p_{cki} ($k = 1, 2; i = 2, 3, \dots, n$) are the weights of the individual measurements. The objective function (7) has a constraint, which is a sum of the balance equations written for component A over the dialyzer at each time (expressed by the subscript i), i.e.,

$$(n - 1)(c_1 + v_{c1}) - \sum_{i=2}^n \left[(c_{1i} + v_{c1i}) + \frac{1}{k_V}(c_{2i} + v_{c2i}) \right] = 0 \tag{8}$$

This task can be solved by the Lagrange method—the constraint (8) is multiplied by a Lagrange multiplier, L , and added to the original objective functions (7)

$$F^* = p_{c1} v_{c1}^2 + \sum_{i=2}^n (p_{c1i} v_{c1i}^2 + p_{c2i} v_{c2i}^2) - 2L(n - 1)(c_1 + v_{c1}) + 2L \sum_{i=2}^n \left[(c_{1i} + v_{c1i}) + \frac{1}{k_V}(c_{2i} + v_{c2i}) \right] \tag{9}$$

(Note: Instead of multiplying Eq. (8) by L , it is more convenient to use $-2L$ (this case) or $2L$)

The corrections v_{c1} and v_{cki} ($k = 1, 2; i = 2, 3, \dots, n$) can then be obtained by solving the set of Eqs. (10)–(13), which are the necessary conditions for a minimum of the Lagrange function F^*

$$\frac{\partial F^*}{\partial v_{c1}} = 2p_{c1} v_{c1} - 2L(n - 1) = 0 \tag{10}$$

$$\frac{\partial F^*}{\partial v_{c1i}} = 2p_{c1i} v_{c1i} + 2L = 0 \quad i = 2, 3, \dots, n \tag{11}$$

$$\frac{\partial F^*}{\partial v_{c2i}} = 2p_{c2i} v_{c2i} + 2 \frac{L}{k_V} = 0 \quad i = 2, 3, \dots, n \tag{12}$$

$$\frac{\partial F^*}{\partial L} = -2(n - 1)(c_1 + v_{c1}) + 2 \sum_{i=2}^n \left[(c_{1i} + v_{c1i}) + \frac{1}{k_V}(c_{2i} + v_{c2i}) \right] = 0 \tag{13}$$

The solution to the set of Eqs. (10–13) is then in the following form

$$v_{c1} = \frac{(n - 1)L}{p_{c1}} \tag{14}$$

$$v_{c1i} = - \frac{L}{p_{c1i}} \quad i = 2, 3, \dots, n \tag{15}$$

$$v_{c2i} = - \frac{L}{k_V p_{c2i}} \quad i = 2, 3, \dots, n \tag{16}$$

$$L = \frac{\sum_{i=2}^n \left(c_{1i} + \frac{1}{k_V} c_{2i} \right) - (n - 1)c_1}{\frac{(n - 1)^2}{p_{c1}} + \sum_{i=2}^n \left(\frac{1}{p_{c1i}} + \frac{1}{k_V^2 p_{c2i}} \right)} \tag{17}$$

If the liquid volumes $V^I (= V_1)$ and $V^{II} (= V_2)$ are measured with errors, then it is necessary to correct them using corrections v_{V1} and v_{V2} . In this case, the objective function, from which these corrections simultaneously with other corrections are determined, is

$$F = p_{V1} v_{V1}^2 + p_{V2} v_{V2}^2 + p_{c1} v_{c1}^2 + \sum_{i=2}^n (p_{c1i} v_{c1i}^2 + p_{c2i} v_{c2i}^2) \tag{18}$$

The objective function (18) has a constraint, which is a modification of Eq. (8).

$$(n-1)(V_1 + v_{V1})(c_1 + v_{c1}) - (V_1 + v_{V1}) \sum_{i=2}^n (c_{1i} + v_{c1i}) - (V_2 + v_{V2}) \sum_{i=2}^n (c_{2i} + v_{c2i}) = 0 \quad (19)$$

The Lagrange function is then

$$F^* = p_{V1} v_{V1}^2 + p_{V2} v_{V2}^2 + p_{c1} v_{c1}^2 + \sum_{i=2}^n (p_{c1i} v_{c1i}^2 + p_{c2i} v_{c2i}^2) - 2L(n-1)(V_1 + v_{V1})(c_1 + v_{c1}) + 2L \left[(V_1 + v_{V1}) \sum_{i=2}^n (c_{1i} + v_{c1i}) + (V_2 + v_{V2}) \sum_{i=2}^n (c_{2i} + v_{c2i}) \right] \quad (20)$$

The necessary conditions for a minimum of the Lagrange function, from which the corrections v_{V1} , v_{V2} , v_{c1} , v_{c1i} and v_{c2i} ($i = 2, 3, \dots, n$) can be obtained, are

$$\frac{\partial F^*}{\partial v_{V1}} = 2p_{V1}v_{V1} - 2L \left[(n-1)(c_1 + v_{c1}) - \sum_{i=2}^n (c_{1i} + v_{c1i}) \right] = 0 \quad (21)$$

$$\frac{\partial F^*}{\partial v_{V2}} = 2p_{V2}v_{V2} + 2L \sum_{i=2}^n (c_{2i} + v_{c2i}) = 0 \quad (22)$$

$$\frac{\partial F^*}{\partial v_{c1}} = 2p_{c1}v_{c1} - 2L(n-1)(V_1 + v_{V1}) = 0 \quad (23)$$

$$\frac{\partial F^*}{\partial v_{c1i}} = 2p_{c1i}v_{c1i} + 2L(V_1 + v_{V1}) = 0 \quad i = 2, 3, \dots, n \quad (24)$$

$$\frac{\partial F^*}{\partial v_{c2i}} = 2p_{c2i}v_{c2i} + 2L(V_2 + v_{V2}) = 0 \quad i = 2, 3, \dots, n \quad (25)$$

$$\frac{\partial F^*}{\partial L} = -2(n-1)(V_1 + v_{V1})(c_1 + v_{c1}) + 2(V_1 + v_{V1}) \sum_{i=2}^n (c_{1i} + v_{c1i}) + 2(V_2 + v_{V2}) \sum_{i=2}^n (c_{2i} + v_{c2i}) = 0 \quad (26)$$

As the non-linearities in Eqs. (21)–(26) exist, this set of equations, whose dimension is $2n + 2$, must be solved numerically, e.g., by the Newton-Raphson procedure.

In order to decrease the dimension of this set, it is necessary to express the corrections v_{c1i} and v_{c2i} from Eqs. (24) and (25), respectively, and substitute them into Eqs. (21), (22) and (26). From this new set of equations, whose dimension is only 4, the corrections v_{V1} , v_{V2} , v_{c1} and the Lagrange multiplier L can be calculated. The remaining corrections, i.e., v_{c1i} and v_{c2i} ($i = 2, 3, \dots, n$) can be obtained from Eqs. (24) and (25).

The weights of the individual measurements p_{V1} , p_{V2} , p_{c1} and p_{cki} ($k = 1, 2; i = 2, 3, \dots, n$) can be calculated from the measured values of V_1 , V_2 , c_1 and c_{ki} ($k = 1, 2; i = 2, 3, \dots, n$) and mean quadratic relative errors, E_V and E_c , which can be determined from repetitional experiments, using the following relations

$$p_{vk} = \frac{1}{E_V V_k^2} \quad k = 1, 2 \quad (27)$$

$$p_{c1} = \frac{1}{E_c c_1^2} \quad (28)$$

$$p_{cki} = \frac{1}{E_c c_{ki}^2} \quad k = 1, 2; \quad i = 2, 3, \dots, n \quad (29)$$

In all the calculations we used $E_V \times 100 = 0.01\%$ and $E_c \times 100 = 0.21\%$ —as determined experimentally.

6. Results and discussion

The effect of random experimental errors of the component concentrations in both the compartments of the dialyzer upon the overall dialysis coefficient was judged on the basis of the mean quadratic relative errors of K_A

$$E_k^j = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{K_{Ai}^{real} - K_{Ai}^{precise}}{K_{Ai}^{precise}} \right)^2} \times 100 \quad j = I, II \quad (30)$$

where subscripts real and precise mean the overall dialysis coefficient calculated from real and precise "experimental" data, respectively. The superscript I and II means that the overall dialysis coefficient was calculated from the concentration data in compartment I and II, respectively. In order to obtain reliable values of E_k^j ($j = I, II$)—they depend upon the number of repetitional experiments under the same conditions—the E_k^j were based on 5000 calculations ($N = 5000$).

6.1. Method A

The application of method A is based on the constant liquid volumes in both the compartments. In practice, two cases can occur: i) The liquid volumes are measured much more precisely than the component concentrations,

so that it is possible to suppose them correct. ii) The measurements of the liquid volumes are loaded with the same errors as those of the component concentrations. Both these cases were analyzed. An important problem, which has to be solved in the connection with method A, is a number of experimental points used, mainly at high intensity of mass transfer, because under these conditions, owing the experimental errors the fraction

$$\frac{c_{A0}^I}{(1 + k_V) c_A^I - k_V c_{A0}^I} \text{ or } \frac{c_{A0}^I}{c_{A0}^I - \frac{1 + k_V}{k_V} c_A^{II}}$$

Figs. 2–5 present the dependences of E_k^j ($j = I, II$) upon the number of experimental points used in the calculation of the overall dialysis coefficient. The parameter of the individual dependences is the overall dialysis coefficient. Figs. 2 and 3 are valid for the maximum errors generated $\pm 0.5\%$, while Figs. 4 and 5 concern the errors $\pm 2.0\%$. Generally, if the higher random errors are introduced into the precise “experimental” concentration data, the higher values of the mean quadratic relative error can be seen. If the calculation of the overall dialysis coefficient is based on the concentration data in compartment I and if a small number of experimental data is used, then at low intensity of mass transfer the mean quadratic relative error, $E_{k'}^I$ is very high, so that the results obtained can be considered practically inapplicable (Figs. 2 and 4). These large errors follow from the incorrectly determined slopes of the straight lines, which are calculated from a small number of near points. The E_k^I decreases with an increasing number of

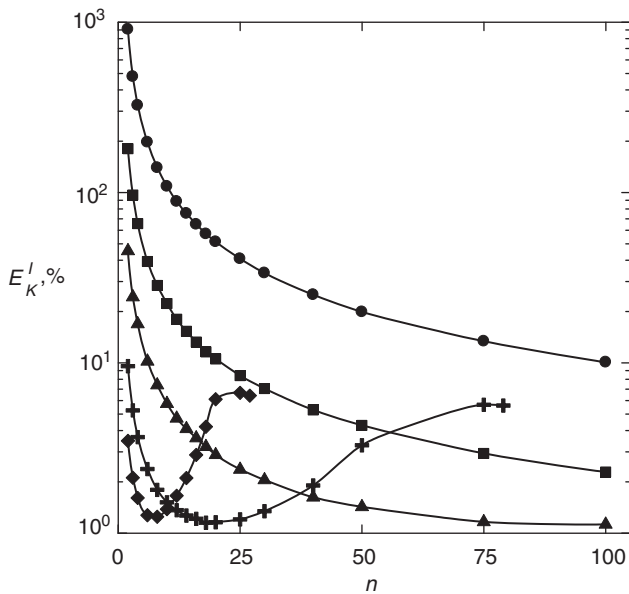


Fig. 2. Dependence of mean quadratic relative error, $E_{k'}^I$, upon number of experimental points. Method A—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $V^I/V^{II} = 1.0$, $A/V^I = 6.22 \text{ m}^{-1}$, $\delta_{\text{max}} = \pm 0.5\%$. K_A [m s^{-1}]: $\bullet - 1 \times 10^{-8}$, $\blacksquare - 5 \times 10^{-8}$, $\blacktriangle - 2 \times 10^{-7}$, $+ - 1 \times 10^{-6}$, $\blacklozenge - 3 \times 10^{-6}$.

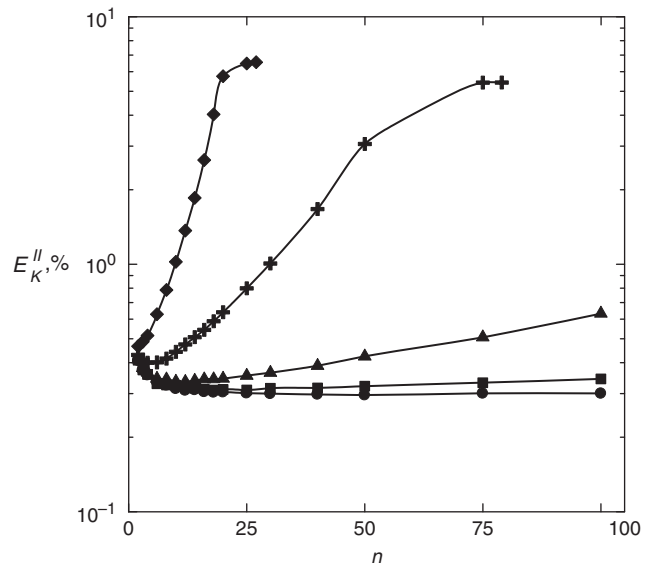


Fig. 3. Dependence of mean quadratic relative error, $E_{K'}^{II}$, upon number of experimental points. Method A—without data reconciliation. For experimental conditions and meaning of symbols, see legend to Fig. 2.

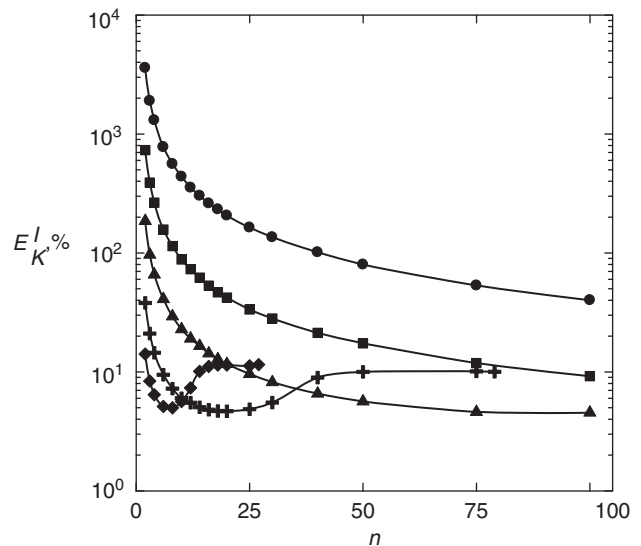


Fig. 4. Dependence of mean quadratic relative error, $E_{k'}^I$, upon number of experimental points. Method A—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $V^I/V^{II} = 1.0$, $A/V^I = 6.22 \text{ m}^{-1}$, $\delta_{\text{max}} = \pm 2.0\%$. For meaning of symbols, see legend to Fig. 2.

experimental points and intensity of mass transfer. At very high intensity of mass transfer characterized by $K_A = 1 \times 10^{-6}$ and $3 \times 10^{-6} \text{ m s}^{-1}$ a minimum on the dependence $E_k^I = f(n)$ can be identified. The existence of the minima has a connection with the denominator of the fraction, which is plotted (in a semilogarithmic scale)

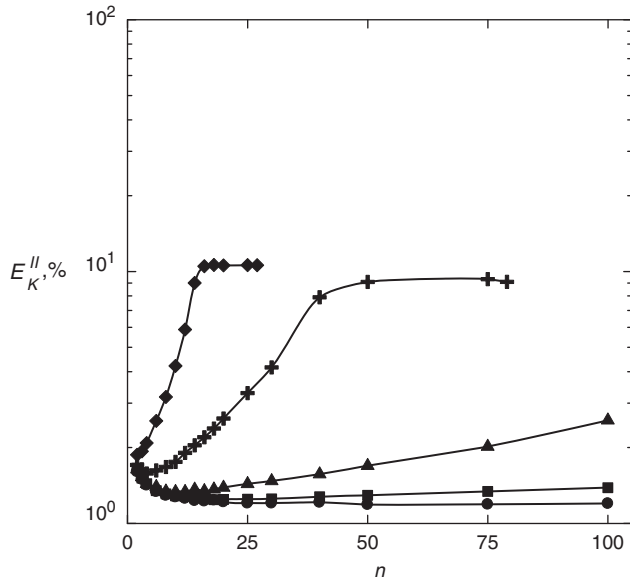


Fig. 5. Dependence of mean quadratic relative error, E_K^{II} , upon number of experimental points. Method A—without data reconciliation. For experimental conditions and meaning of symbols, see legend to Fig. 4.

against time. After a certain time (expressed by the number of points), both the terms in the denominator become comparable, so that the introduced errors start to play very negative role in subtraction, which consequently affects the value of the fraction. On the other hand, if K_A is based on the concentration data in compartment II, more reliable results can be obtained – see Figs. 3 and 5. If the component concentrations are also measured with a small error (i.e., below $\pm 0.5\%$), then at low intensity of mass transfer ($K_A = 1 \times 10^{-8} - 2 \times 10^{-7} \text{ m s}^{-1}$), the calculation of the overall dialysis coefficient is loaded with small errors—even if a small number of experimental points is used. At high intensity of mass transfer, i.e., $K_A = 1 \times 10^{-6}$ and $3 \times 10^{-6} \text{ m s}^{-1}$ the E_K^{II} sharply increases with an increasing number of the experimental points—max. error is approximately 10%.

Another important factors, which can influence the reliability of the results obtained, are the V^I/V^{II} and A/V^I ratios. An increase in both these factors leads to an increase in the component concentration in compartment II, so that higher V^I/V^{II} and A/V^I ratios are used in the cases of low permeability of the membrane. The effect of V^I/V^{II} ratio upon the mean quadratic relative errors of K_A is shown in Figs. 6 and 7. Here, the number of the experimental points equals 100, A/V^I ratio is equal to 6.22 m^{-1} , maximum error generated is $\pm 0.5\%$ and the liquid volumes are precisely measured. From the graphical presentations given in Figs. 6 and 7 it can be seen that an increase in V^I/V^{II} ratio causes an increase in both the errors, i.e., E_K^I and E_K^{II} . Moreover, in the whole

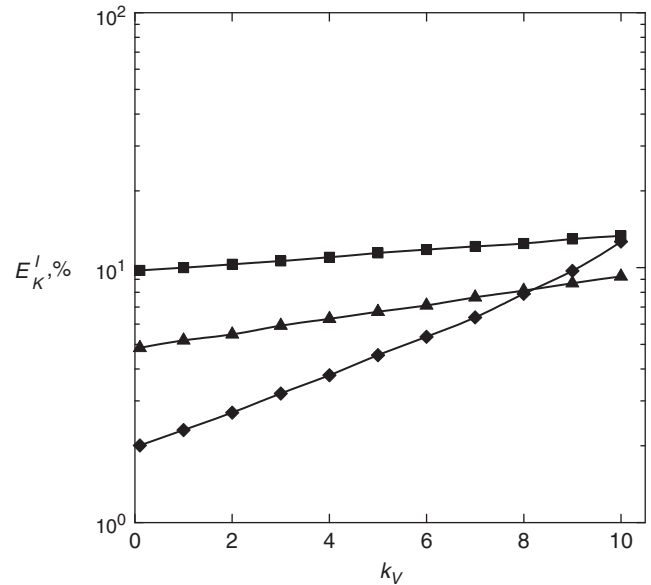


Fig. 6. Dependence of mean quadratic relative error, E_K^I , upon V^I/V^{II} ratio. Method A—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $A/V^I = 6.22 \text{ m}^{-1}$, $n = 100$, $\delta_{\max} = \pm 0.5\%$. $K_A [\text{ms}^{-1}]$: ■— 1×10^{-8} , ▲— 2×10^{-8} , ◆— 5×10^{-8} .

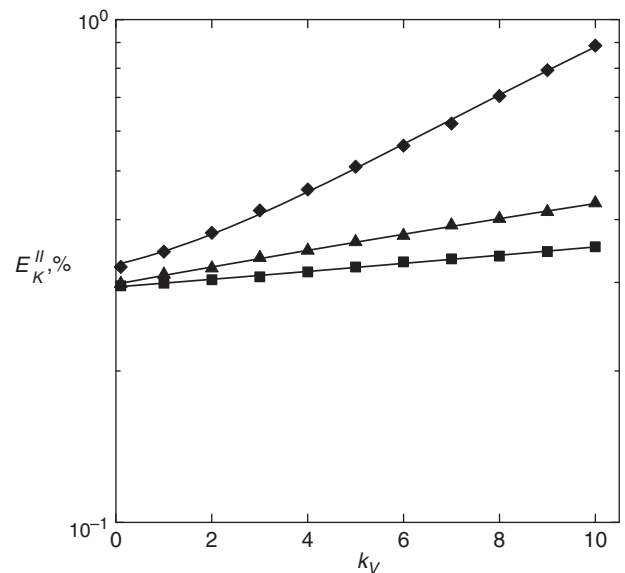


Fig. 7. Dependence of mean quadratic relative error, E_K^{II} , upon V^I/V^{II} ratio. Method A—without data reconciliation. For experimental conditions and meaning of symbols, see legend to Fig. 6.

range of k_V investigated the calculation of K_A based on the concentration data in compartment II is more reliable than that based on the data in compartment I—the error E_K^{II} is less than the error E_K^I . The dependences of the

mean quadratic relative errors of K_A upon the A/V^I ratio at V^I/V^{II} ratio equal to 1 for the case of low intensity of mass transfer are presented in Figs. 8 and 9. If the A/V^I ratio is increased, then the error E_k^I decreases, while an opposite trend can be seen in the case of E_k^{II} .

In all the figures mentioned above, no random errors were introduced into the liquid volumes. The further calculations, where random errors of the same magnitude were introduced also into the liquid volumes, revealed that the addition of these new errors has practically no effect upon the mean quadratic relative error E_k^I , while in the case of E_k^{II} somewhat larger errors were found—this increase was about 25%.

Fortunately, the unfavourable effect of the errors of the component concentrations upon K_A can be eliminated to a large extent if the data reconciliation is used. As an example, the same dependences as in Figs. 2 and 3 are shown in Figs. 10 and 11. Generally, the dependences given in Figs. 10 and 11 have the same trends as those in Figs. 2 and 3. A detailed inspection of the dependences $E_k^I = f(n)$ reveals that the mean quadratic relative errors E_k^I , which exist in the case of data reconciliation, are about one order of magnitude lower than those without data reconciliation. If in the case of low intensity of mass transfer in the calculation of K_A the reconciled data in compartment II are used, then very reliable results can be obtained—the error E_k^{II} is about 0.1% (maximum errors generated 0.5%). On the other hand, if very intensive mass transfer exists, then higher errors of K_A can be expected.

In contrast to the previous case, if random errors are introduced into both the component concentrations and the liquid volumes, then an evaluation of data reconciliation is not straightforward at all. If better results

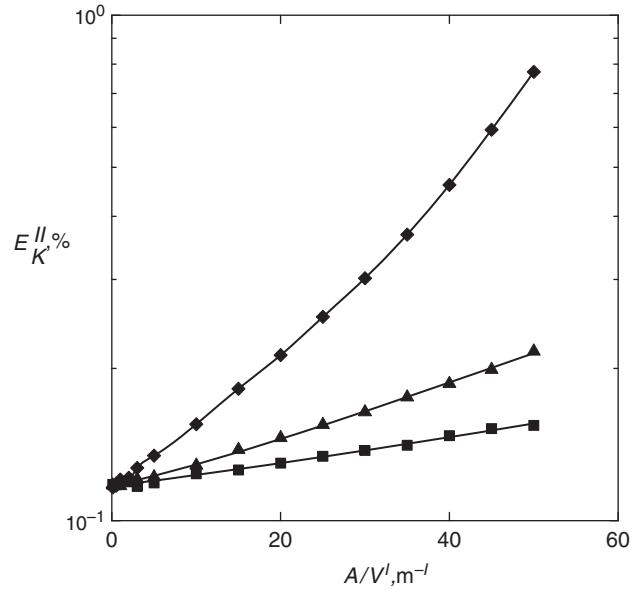


Fig. 9. Dependence of mean quadratic relative error, E_k^{II} , upon A/V^I ratio. Method A—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $V^I/V^{II} = 1.0$, $n = 100$, $\delta_{\max} = \pm 2.0\%$. For meaning of symbols, see legend to Fig. 6.

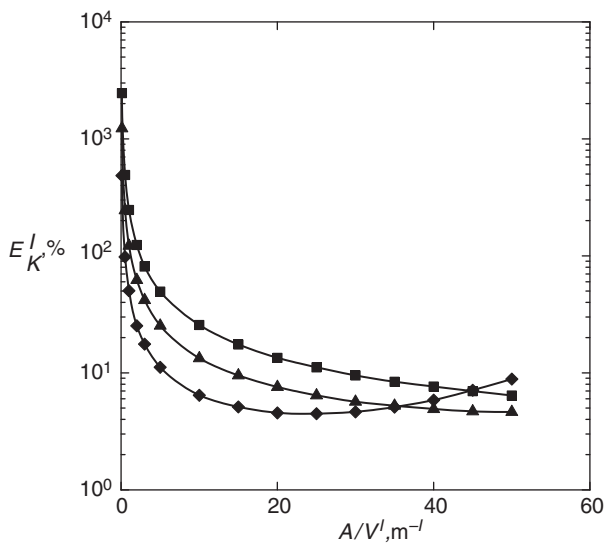


Fig. 8. Dependence of mean quadratic relative error, E_k^I , upon A/V^I ratio. Method A—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $V^I/V^{II} = 1.0$, $n = 100$, $\delta_{\max} = \pm 2.0\%$. For meaning of symbols, see legend to Fig. 6.

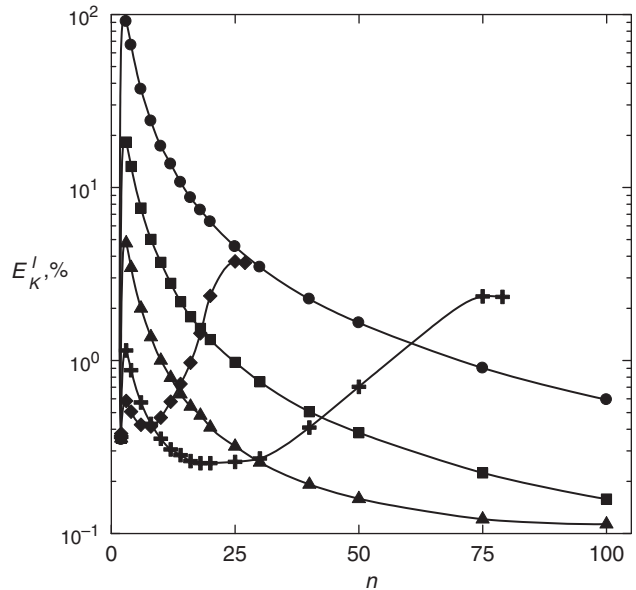


Fig. 10. Dependence of mean quadratic relative error, E_k^I , upon number of experimental points. Method A—with concentration data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $V^I/V^{II} = 1.0$, $A/V^I = 6.22 \text{ m}^{-1}$, $\delta_{\max} = \pm 0.5\%$. K_A [m s^{-1}]: $\bullet - 1 \times 10^{-8}$, $\blacksquare - 5 \times 10^{-8}$, $\blacktriangle - 2 \times 10^{-7}$, $+$ $- 1 \times 10^{-6}$, $\blacklozenge - 3 \times 10^{-6}$.

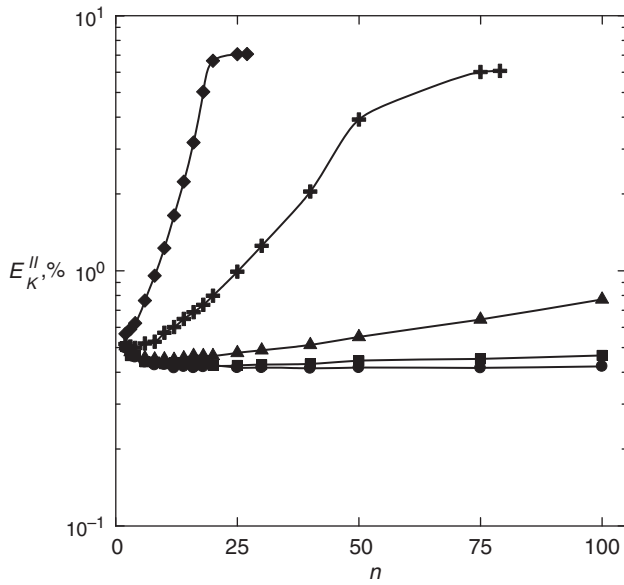


Fig. 11. Dependence of mean quadratic relative error, E_k^{II} , upon number of experimental points. Method A—with concentration data reconciliation. For experimental conditions and meaning of symbols, see legend to Fig. 10.

Table 1
Evaluation of data reconciliation—Method A: $\delta_{max} = \pm 1\%$

Variable changed	E_k^I	E_k^{II}
Number of points	+	No effect
V^I/V^{II} ratio, $n = 100$	+	-
A/V^I ratio, $n = 100$	+	-

+ means better results.
- means worse results.

are obtained or not, it depends upon the criterion used and the variable changed. This situation is schematically illustrated in Table 1.

When analyzing the effect of the number of experimental points upon the mean quadratic relative errors using reconciled data, rather surprising results were obtained for the least number, i.e., for $n = 2$. Under these conditions, one can obtain very reliable results, mainly if both the liquid volumes are measured correctly. Also if random errors are introduced into all the data, relative good results are obtained (Table 2).

6.2. Method B

Similarly as in the case of method A, it is possible to analyze two variants: i) the introduction of random errors into the concentrations only; ii) the introduction of errors into the concentrations and volumes. In analogy to method A, the calculation of the overall dialysis coef-

Table 2

Mean quadratic relative errors calculated from reconciled data—Method A: $V^I/V^{II} = 1$; $A/V^I = 6.22 \text{ m}^{-1}$; $n = 2$

$K_{A'} \text{ m s}^{-1}$	$\delta_{max} = 0.5 \%$		$\delta_{max} = 1.0 \%$		$\delta_{max} = 2.0 \%$	
	$E_k^{I^a}$	$E_k^{I^b}$	$E_k^{I^a}$	$E_k^{I^b}$	$E_k^{I^a}$	$E_k^{I^b}$
3×10^{-6}	0.376	1.589	0.746	3.244	1.506	6.648
1×10^{-6}	0.360	3.474	0.724	6.972	1.487	13.770
2×10^{-7}	0.354	2.473	0.711	5.057	1.424	10.105
5×10^{-8}	0.357	0.821	0.711	1.647	1.434	4.106
1×10^{-8}	0.356	0.475	0.706	0.949	1.412	1.912

Note: ^arandom errors introduced into concentration data only.
^brandom errors introduced into all data; in all cases $E_k^I = E_k^{II}$.

ficient can be based on the component concentrations in compartment I (the second term on the right hand side of the objective function (6) is omitted) or it can be based on the component concentrations in compartment II (the first term is omitted). In addition to these cases, the component concentrations in both the compartments can be used in the calculation of $K_{A'}$. Thus, the corresponding mean quadratic relative errors are E_k^I , E_k^{II} and E_k . They are plotted against the number of experimental points in Figs. 12–14. Here, the experimental conditions are the same as those used in Figs. 4 and 5. A mutual comparison of the dependences presented in Figs. 4 and 12 and in Figs. 5 and 13 reveals that in the cases of low or medium intensity of mass transfer method B gives the same results as method A. But in the case of high intensity of mass transfer, method B is more reliable than method A. The main advantage of method B is the fact that all the component concentrations in compartment I or compartment II can be used and the sign of the fraction, which is plotted against time in a logarithmic scale, need not be checked. Moreover, method B eliminates errors arising from the subtraction of the terms in

$$\frac{c_{A0}^I}{(1 + k_V) c_A^I - k_V c_{A0}^I}$$

and $\frac{c_{A0}^I}{c_{A0}^I - \frac{1 + k_V}{k_V} c_A^I}$ at the end of the experiment, when

both the terms are comparable. If all the experimental concentrations are used in the calculation of $K_{A'}$, the dependences $E_k = f(n)$ have nearly the same course as dependences $E_k^I = f(n)$ but the mean quadratic error E_k is much lower (Figs. 12 and 14).

If no random errors were introduced into the liquid volumes, the calculations revealed that also in the case of other dependences, i.e., $E_k^j = f(V^I/V^{II})$ and $E_k^j = f(A/V^I)$ ($j = I, II$) methods A and B give—in many cases—practically the same results. Larger differences between the corresponding dependences were found at very

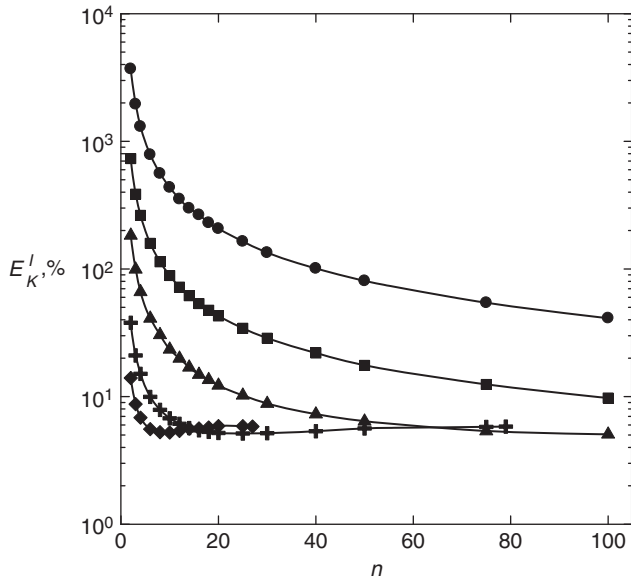


Fig. 12. Dependence of mean quadratic relative error, E_K^I , upon number of experimental points. Method B—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $V^I/V^{II} = 1.0$, $A/V^I = 6.22 \text{ m}^{-1}$, $\delta_{\max} = \pm 2.0\%$. K_A [m s^{-1}]: $\bullet - 1 \times 10^{-8}$, $\blacksquare - 5 \times 10^{-8}$, $\blacktriangle - 2 \times 10^{-7}$, $+ - 1 \times 10^{-6}$, $\blacklozenge - 3 \times 10^{-6}$.

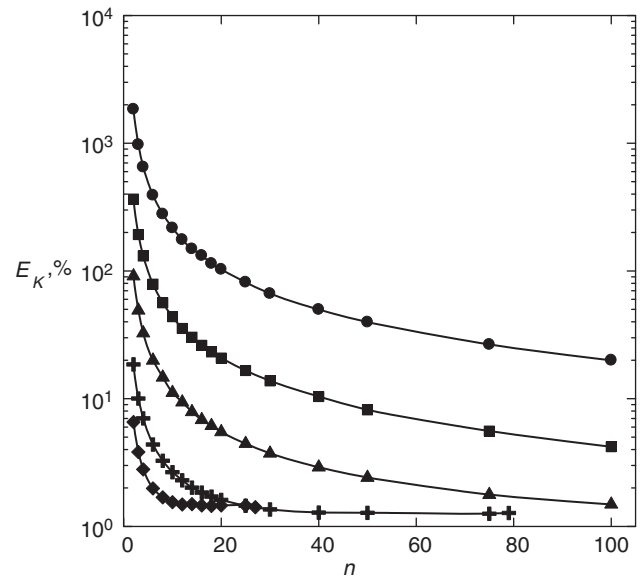


Fig. 14. Dependence of mean quadratic relative error, E_K , upon number of experimental points. Method B—without data reconciliation. For experimental conditions and meaning of symbols (Fig. 12).

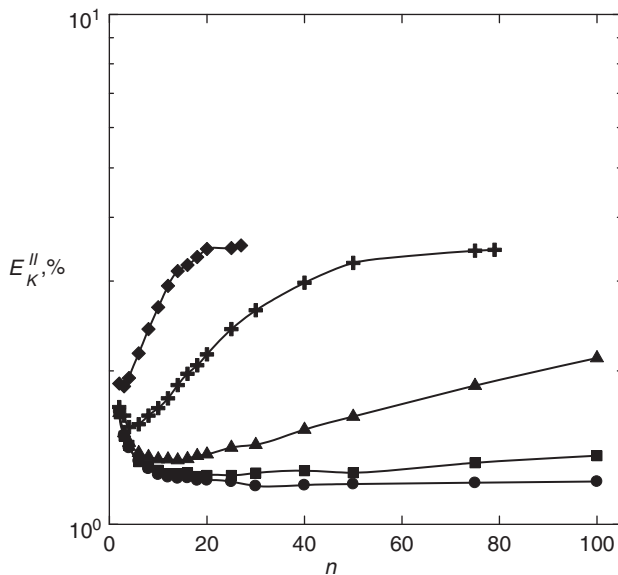


Fig. 13. Dependence of mean quadratic relative error, E_K^{II} , upon number of experimental points. Method B—without data reconciliation. For experimental conditions and meaning of symbols, see legend to Fig. 12.

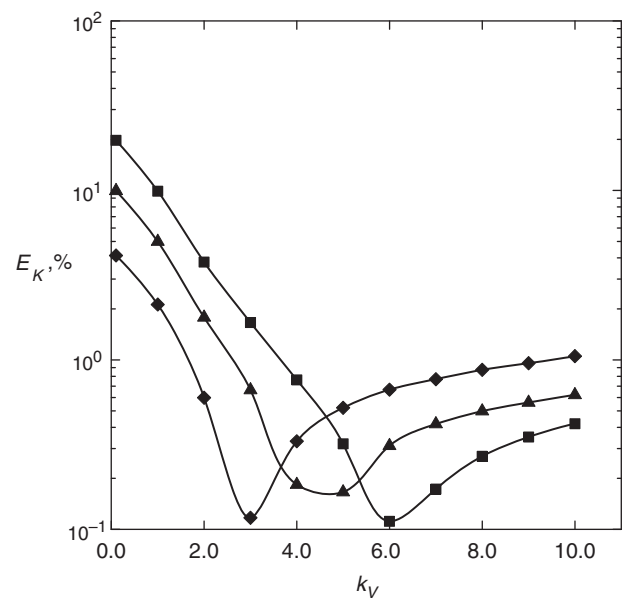


Fig. 15. Dependence of mean quadratic relative error, E_K , upon V^I/V^{II} ratio. Method B—without data reconciliation. Experimental conditions: $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $V^I = 1 \times 10^{-3} \text{ m}^3$, $A/V^I = 6.22 \text{ m}^{-1}$, $n = 100$, $\delta_{\max} = \pm 1.0\%$. K_A [m s^{-1}]: $\blacksquare - 1 \times 10^{-8}$, $\blacktriangle - 2 \times 10^{-8}$, $\blacklozenge - 5 \times 10^{-8}$.

low intensity of mass transfer ($K_A = 1.0 \times 10^{-8} \text{ m s}^{-1}$). Even though no extremes exist on the dependences $E_k^j = f(V^I/V^{II})$ ($j = I, II$), a minimum can be identified on the dependence $E_k = f(V^I/V^{II})$ (Fig. 15). It is not affected by the maximum error generated but it is shifted

to higher values of the V^I/V^{II} ratio with decreasing intensity of mass transfer. Similarly as in the case of method A, if only random errors of the component concentrations exist and if data are reconciled then very

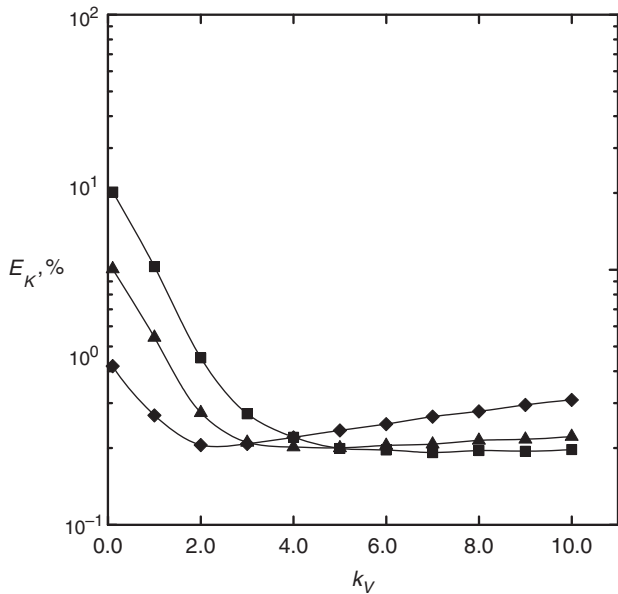


Fig. 16. Dependence of mean quadratic relative error, E_k , upon V^I/V^{II} ratio. Method B—with concentration data reconciliation. For experimental conditions and meaning of symbols, see legend to Fig. 15.

Table 3
Evaluation of data reconciliation—Method B: $\delta_{max} = \pm 1\%$

Variable changed	E_k^I	E_k^{II}	E_k
Number of points	+	–	+
V^I/V^{II} ratio, $n = 100$	+	–, + only at low ratio	–, + only at low ratio
A/V^I ratio, $n = 100$	+	–	No effect

+ means better results

– means worse results

reliable results are obtained—compare e.g., the corresponding dependences in Figs. 15 and 16.

Reconciliation of all the data (the component concentrations and liquid volumes) using Eqs. (21)–(26) produces nearly the same results as found by method A. The evaluation of this procedure is given in Table 3.

Similarly as method A, method B gives the same surprising results for the least number of the experimental points. These results are very closely to those presented in Table 2.

7. Conclusion

The method of numerical error analysis was used to find the effect of random errors of the component concentration in both the compartments of a batch dialyzer upon the overall dialysis coefficient. This method was based on a generation of precise “experimental” concentration

data, into which small random errors were introduced. Two methods for the calculation of the overall dialysis coefficient were evaluated: i) method A, which is based on the linearization of the equation describing the dependence of the component concentration in compartment I or compartment II upon time; ii) method B, which is based on the direct use of the same equation as in (i). The numerical error analysis revealed that:

1. Both the methods give practically the same results.
2. The main advantage of method B is the fact that all the experimental points can be used in the calculation of the overall dialysis coefficient without checking the sign of the fraction, which is plotted against time in a logarithmic scale.
3. The unfavourable effect of the input quantities, which is dependent upon intensity of mass transfer, V^I/V^{II} and A/V^I ratios, can be eliminated to a some extent using reconciled experimental data.

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Symbols

A	—	membrane area, m^2
c	—	molar concentration, $kmol \cdot m^{-3}$
E_c	—	mean quadratic relative error of measurement of component concentration, %
E_k^j	—	($j = I, II$) mean quadratic relative error of calculation of $K_{A'}$, %
E_V	—	mean quadratic relative error of measurement of liquid volume, %
F	—	objective function, (in Eq. (6)) $kmol^2 m^{-6}$
F^*	—	Lagrange function
K_A	—	overall dialysis coefficient, $m s^{-1}$
k_V	—	V^I/V^{II} ratio
L	—	Lagrange multiplier, $m^3 kmol^{-1}$, $kmol^{-1}$ (in Eq. 20)
N	—	number of calculations
n	—	number of experimental points
p_{c1}, p_{cki}	—	($k = 1, 2; i = 2, 3, \dots, n$) weights of individual measurements of component concentration, $m^6 kmol^{-2}$
p_{Vk}	—	($k = 1, 2$) weights of measurements of liquid volumes, m^{-6}
V	—	volume, m^3
v_{V1}, v_{V2}	—	corrections of volumes, m^3
v_{c1}, v_{cki}	—	($k = 1, 2; i = 2, 3, \dots, n$) corrections of concentrations, $kmol m^{-3}$
δ_{max}	—	maximum random error generated, %
τ	—	time, s

Superscripts and subscripts

<i>A</i>	—	referred to component A
<i>c</i>	—	referred to concentration
<i>calc</i>	—	calculated
<i>exp</i>	—	experimental
<i>I</i>	—	referred to compartment I
<i>II</i>	—	referred to compartment II
<i>real</i>	—	real experimental data
<i>precise</i>	—	precise experimental data
<i>V</i>	—	referred to volume
0	—	initial

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