

ANALYSIS OF FILTRATION MECHANISM OF DEAD-END ELECTRO-ULTRAFILTRATION FOR PROTEINACEOUS SOLUTIONS

EIJI IRITANI, KATSUHISA OHASHI AND TOSHIRO MURASE
Department of Chemical Engineering, Nagoya University, Nagoya 464-01

Key Words: Membrane Separation, Filtration, Ultrafiltration, Electrofiltration, Electrophoresis, Electro-osmosis, Proteinaceous Solution, Electric Field Strength, Solid-Liquid Separation, Dead-End Filtration

Dead-end ultrafiltration with application of a d.c. electric field to reduce membrane fouling rates was conducted under constant pressure using protein (bovine serum albumin) solution. When electric fields were applied, the filtration rate was significantly increased over that in ordinary dead-end ultrafiltration by both electrophoretic motion of the solutes away from the cake surface and electroosmosis occurring in the filter cake. The improvement in filtration rate becomes more pronounced with increasing electric field strength. In addition, effects of such processing variables as the solution concentration, the pH of solutions and the applied filtration pressure on the performance of dead-end electro-ultrafiltration were examined. A mathematical model was developed to describe the processes occurring during dead-end electro-ultrafiltration, taking both electrophoretic and electroosmotic effects into account. The model accounted well not only for the dynamically balanced filtration rate but also for the variation in filtration rate with time.

Introduction

Ultrafiltration of colloidal and proteinaceous solutions has become increasingly important in recent years in such widely diversified fields as biotechnology, biomedicine, food and beverage processing, and water treatment. One of the major bottlenecks in the application of the ultrafiltration process is the flux decline due to membrane fouling. Such flux decline is mainly attributable to the formation of highly resistant filter cake caused by accumulation of the protein solutes on the membrane surface.⁴⁾ To maintain a high filtration rate for extended periods of time, therefore, it is necessary to prevent a continuous buildup of solutes on the filter surface. For this purpose, ultrafiltration is commonly performed by flowing the feed solution tangentially over the membrane surface (usually called tangential or crossflow filtration³⁾). Many ingenious designs and techniques have been developed, such as the dynamic filter with rotating cylinder,⁷⁾ the upward ultrafilter,²⁾ and the electrically assisted ultrafilter.^{1,5,8,11-20)}

Among them, electro-ultrafiltration is a technique developed to combat residual cake formation at the membrane surface by application of an electric field. This method is particularly attractive for the separation of protein since its charge changes according to the pH of the solution. In electro-ultrafiltration, the accumulation of the solutes on

the membrane surface is limited by electrophoretic migration. In addition, the filtration rate through the filter cake is enhanced due to electroosmosis as a secondary electrokinetic phenomenon. Although there is a growing body of work^{1,5,8,12-14, 16-20)} on the dynamically balanced filtration rate in electro-ultrafiltration in conjunction with the crossflow mode, no study has yet been undertaken concerning a quantitative analysis of the dynamic behavior of electro-ultrafiltration in which both electrophoretic and electroosmotic effects are taken into account.

In the present work, dead-end electro-ultrafiltration is investigated as a basis for clarifying the mechanism of crossflow electro-ultrafiltration, and the effects of the principal process and solution characteristics on not only the dynamically balanced filtration rate but also the time dependence of the filtration rate are examined. Additionally, a method is developed for analyzing the filtration characteristics of dead-end electro-ultrafiltration.

1. Theoretical Analysis

When solutes migrate in the reverse direction to the filtrate flow due to electrophoresis through application of a d.c. electric field, the growth rate of the filter cake formed on the membrane in dead-end electro-ultrafiltration may be written as

$$\frac{dw}{d\theta} = \frac{\rho s}{1 - ms} \frac{dv}{d\theta} - s\rho_1 u_E \quad (1)$$

where w is the mass of solutes in the filter cake per unit effective membrane area, θ the filtration time, ρ

* Received February 6, 1992. Correspondence concerning this article should be addressed to T. Murase.

the density of the permeate, s the mass fraction of solute in the solution, m the ratio of wet to dry cake mass, v the filtrate volume per unit effective membrane area, ρ_l the density of the solution, and u_E the electrophoretic velocity of the solute. The first and second terms on the right-hand side of Eq. (1) represent, first, the mass flux of the solutes toward the cake surface due to convective transport by the solvent and, second, the mass flux of the solutes away from the cake surface due to electrophoretic transport. The electrophoretic velocity u_E of solutes is determined by the strength E of the d.c. electric field and the electrophoretic mobility k as follows:

$$u_E = kE \quad (2)$$

Substitution of Eq. (2) into Eq. (1) and integration yield

$$w = \rho s(v - k_E E \theta) / (1 - ms) \quad (3)$$

where k_E is a measure of the electrophoretic effect, which is defined by

$$k_E = \rho_l(1 - ms)k/\rho \quad (4)$$

On the assumption of negligible membrane resistance, the electro-ultrafiltration rate q through a filter cake containing the mass w of solutes can be written as

$$\frac{1}{q} = \frac{d\theta}{dv} = \frac{\mu\alpha_{av}w}{p + p_E} \quad (5)$$

where μ is the viscosity of the permeate, α_{av} the average specific filtration resistance, p the applied filtration pressure, and p_E the electroosmotic force per unit effective membrane area under the condition that the Ruth equation^{9,10} can be applied to the electroosmotic flow through the filter cake.¹⁵ Taking the fictitious electroosmotic force into account, the electroosmotic effect can be incorporated into the modified Ruth equation (5). Substituting Eq. (3) derived from the growth rate of the filter cake into Eq. (5), the electro-ultrafiltration rate equation can be given as

$$\frac{1}{q} = \frac{d\theta}{dv} = \frac{2}{K_E}(v - k_E E \theta) \quad (6)$$

where the filtration coefficient K_E of constant pressure electro-ultrafiltration is defined by

$$K_E = 2(p + p_E)(1 - ms) / (\mu\alpha_{av}\rho s) \quad (7)$$

It should be noted that the values of m and α_{av} in Eq. (7) are influenced by p , s and the electroosmotic effect. Although it is very difficult to obtain these values individually because of the extreme thinness of the cake formed in electro-ultrafiltration, the value of K_E , which is a measure of the electroosmotic effect, can be determined experimentally, as mentioned

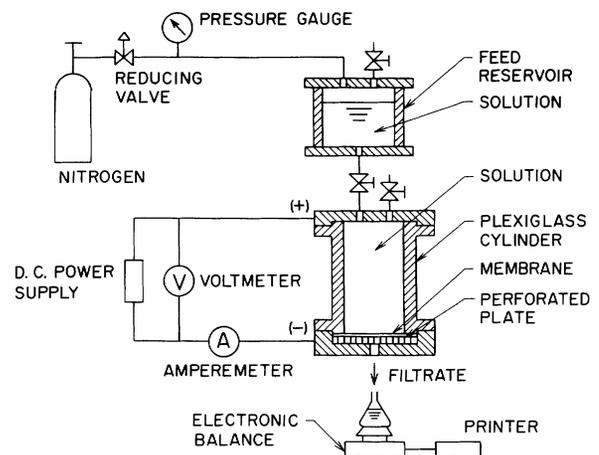


Fig. 1. Schematic diagram of experimental apparatus

later. Solving Eq. (6) under the initial condition of $v=0$ at $\theta=0$, an expression that relates v to time can be written as

$$\theta = \frac{v}{k_E E} + \frac{K_E}{2k_E^2 E^2} \left\{ \exp\left(-\frac{2}{K_E} k_E E v\right) - 1 \right\} \quad (8)$$

Provided both k_E (or k in Eq. (4)) and K_E are given, the variation of v over time can be calculated from Eq. (8). The variation of q over time can be obtained by substituting the relation between v and θ into Eq. (6).

As the filtration rate gradually decreases with the growth of the filter cake, the value of the first term on the right-hand side of Eq. (1) decreases with time and eventually becomes equal to the value of the second term on the right-hand side of Eq. (1). Under this condition, the filter cake ceases growing, and thus the filtration rate becomes constant. Equations (1), (2) and (4) under the equilibrium condition of $dw/d\theta=0$ can be combined to obtain the following expression for the dynamically balanced filtration rate q_e :

$$q_e = k_E E \quad (9)$$

2. Experimental Apparatus and Procedure

The experimental setup is shown schematically in Fig. 1. After the solution is fed into an unstirred dead-end filter with an effective membrane area of 24.4 cm², the filter is connected to a feed reservoir. The filter consists of a acrylic cylinder and upper and lower stainless steel plates, which provide electrical contact. The lower plate supports a acrylic perforated plate with a membrane on it. Polysulfone membranes (PTTK, Millipore Corp.) with a nominal molecular-weight cutoff of 30,000 are used. The macromolecular solute used in the experiments is bovine serum albumin (BSA) (Fraction V, Katayama Chemical Ind. Corp.) with a molecular weight of about 67,000 Da. A buffer solution of phosphate of cons-

tant ionic strength for use in electrophoresis⁶⁾ is utilized in order to adjust the pH of the solution. To prevent gas evolution at the electrodes by electrolysis and heat production, the ionic strength of the buffer solution used is relatively low (0.02). The pH of the solution is adjusted upward compared with the isoelectric point (about 4.9 in the case of BSA) so that the solutes are negatively charged. The electric field is applied through the electrodes from a d.c. power supply so that the electrode of the lower plate is the cathode. Thus, the solutes migrate in a direction away from the filter surface. Electro-ultrafiltration experiments are conducted under constant pressure by introducing nitrogen gas into the free space of the reservoir. The variations of filtrate volume over time are continuously measured by an electronic balance. The variations of the electric current over time and the specific electric conductivity of the solution before and after experiments are also measured. Neither the electric current nor the specific electric conductivity varied significantly during the experimental run. The electric field strength E can be calculated from the following equation.

$$E = i / (\kappa A) \quad (10)$$

where i is the electric current, κ the specific electric conductivity, and A the effective membrane area. The applied electric field strength E ranges from 0.80 to 4.11 V/cm, s from 5×10^{-4} to 3×10^{-3} , pH from 6.2 to 7.7, and the filtration pressure p from 24.5 to 147 kPa.

3. Results and Discussion

In Fig. 2, the experimental results for various values of E are plotted in the form of the reciprocal filtration rate ($d\theta/dv$) versus the filtrate volume v per unit effective membrane area. For ordinary dead-end ultrafiltration with no imposed electric field, the plots are virtually linear. This is in accordance with the Ruth filtration rate equation^{9,10)} under constant pressure, which can be obtained by setting E in Eq. (6) as zero. For electro-ultrafiltration, the filtration rate increases substantially compared with that in dead-end ultrafiltration, and tends to approach a dynamically balanced filtration rate as filtration proceeds. This quasi-steady rate increases noticeably with the magnitude of the imposed field strength. A higher electric field strength causes the filtration rate to equilibrate more rapidly. A notable feature is that the filtration rate in electro-ultrafiltration increases from the early stages of filtration compared with that in dead-end ultrafiltration. On the other hand, for crossflow ultrafiltration the plot shows a linear relationship which coincides with that of dead-end ultrafiltration until the filtration rate drops to a critical value.³⁾ This is the distinguishing difference

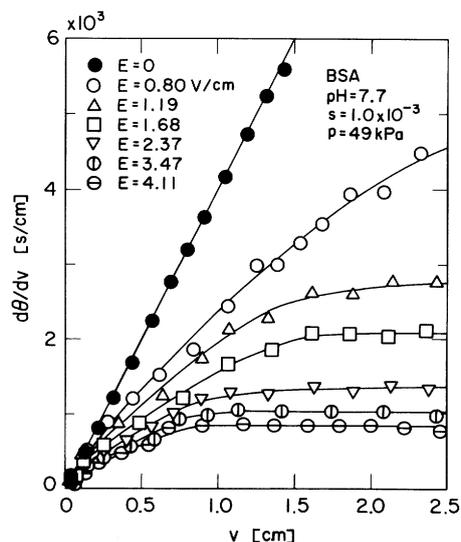


Fig. 2. Effects of electric field strength on filtration rate

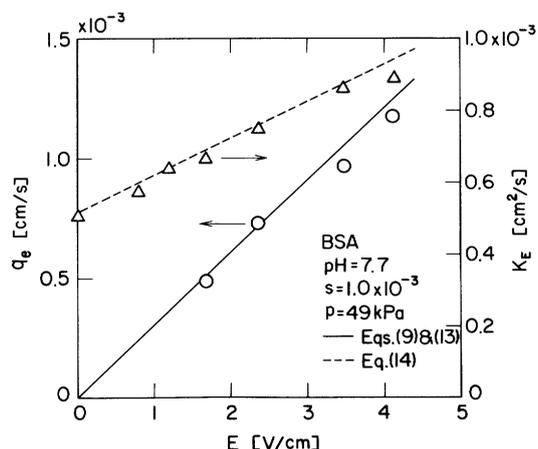


Fig. 3. Effects of electric field strength on q_e and K_E

between the two processes.

In Fig. 3, the dynamically balanced filtration rate q_e , which is a measure of the electrophoretic effect, and the electrofiltration coefficient K_E , which is a measure of the electroosmotic effect, are plotted against E on the basis of the results in Fig. 2. The plot of q_e versus E shows a linear relationship through the origin in accordance with Eq. (9). The value for k_E is therefore taken from the slope. The value of k_E being known, the value of K_E can be determined by fitting the experimental data of ($d\theta/dv$) versus v to Eq. (6). The relationship between K_E and E can be represented by the following empirical equation.

$$K_E = K_{E0} + aE \quad (11)$$

where K_{E0} is the value of K_E in the absence of the electrical field, which represents the Ruth filtration coefficient.^{9,10)} The results imply that both electrophoretic and electroosmotic effects become more marked as E increases.

Figure 4 shows the influence of increasing solution concentration on both q_e and K_E . A plot of q_e versus s shows a linear relationship. Combining Eq. (4) with Eq. (9), one obtains

$$q_e = \rho_i(1 - ms)kE/\rho \quad (12)$$

The electrophoretic mobility k decreases because of interactions of the charged BSA molecules as s increases. Furthermore, the value of $(1 - ms)$ in Eq. (12) decreases as s increases. For these reasons, it can be deduced that q_e decreases as s increases. The filtration coefficient K_E decreases with s , as predicted by Eq. (7).

The effect of surface charge is investigated by altering the pH of solutions. **Figure 5** shows how q_e and K_E vary with pH. It may be expected that both electrophoretic and electroosmotic effects become more conspicuous at higher pH levels since BSA molecules have a higher net negative charge. The value of q_e , which is a measure of the electrophoretic effect, increases linearly with pH. However, K_E , which is a measure of the electroosmotic effect, is notably insensitive to pH. This is an unexpected result that requires further consideration.

The dependence of q_e and K_E on the applied filtration pressure p is shown in **Fig. 6**. Increasing the pressure does not necessarily lead to an increase in q_e , which has also been shown in the case of crossflow ultrafiltration,³⁾ whereas K_E increases linearly with p . It can be inferred from Eq. (7) that the average specific filtration resistance α_{av} of the filter cake in electro-ultrafiltration increases minimally with p .

Within the experimental conditions tested in this study, k_E , which is related to q_e by Eq. (9), and K_E are correlated to E , s , pH and p by the following equations (13) and (14), respectively.

$$k_E = 2.83 \times 10^{-6}(4.84 \times 10^{-3} - s)(\text{pH} - 4.90) \quad (13)$$

$$K_E = 7.72 \times 10^{-14}(4.74 \times 10^{-3} - s)(p + 3.07 \times 10^5) \times (E + 5.06 \times 10^2) \quad (14)$$

The solid lines and the broken lines in Figs. 3–6 show the calculations by Eqs. (9), (13) and (14).

Figure 7 represents some typical results of v versus θ . The solid lines show the results obtained using Eq. (8) in conjunction with Eqs. (13) and (14), and compares favorably with the experimental data.

In **Fig. 8**, $d\theta/dv$ versus v , replotted using the previous data, is compared with the results based upon Eqs. (6) and (8) with the aid of Eqs. (13) and (14), and good agreement is obtained.

In **Fig. 9**, the dynamically-balanced filtration rate q_e is compared with the values based upon Eqs. (9) and (13).

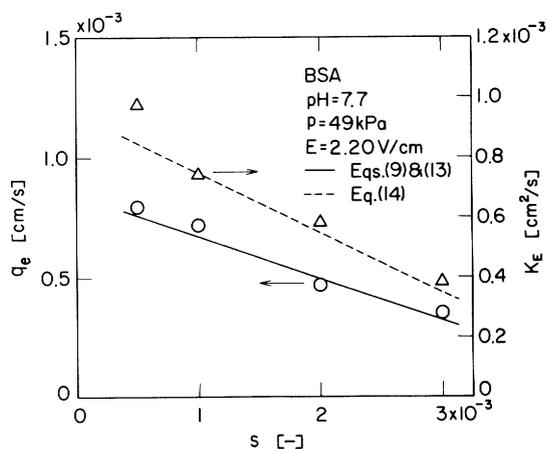


Fig. 4. Effects of solution concentration on q_e and K_E

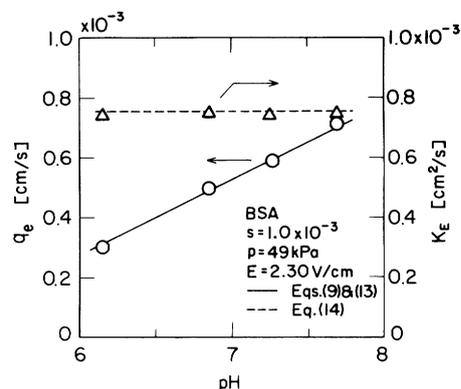


Fig. 5. Effects of pH of solutions on q_e and K_E

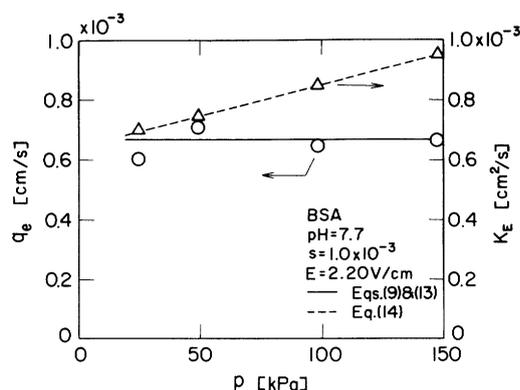


Fig. 6. Effects of filtration pressure on q_e and K_E

Conclusion

The characteristics of electrically enhanced dead-end ultrafiltration were examined by using proteinaceous solutions. Electro-ultrafiltration produced filtration rates higher than those attainable with dead-end ultrafiltration. It was shown that the dynamically-balanced filtration rate q_e is directly proportional to the electric field strength E . The filtration rate is affected by such parameters as the solution concentration s , the pH of solutions and the applied filtration pressure p . It has been found that

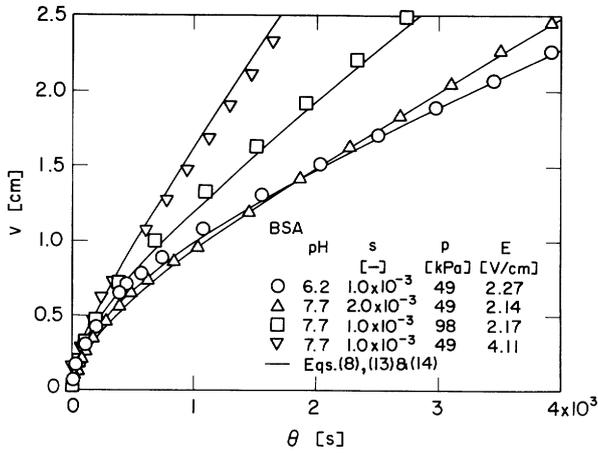


Fig. 7. Relation between v and θ under various conditions

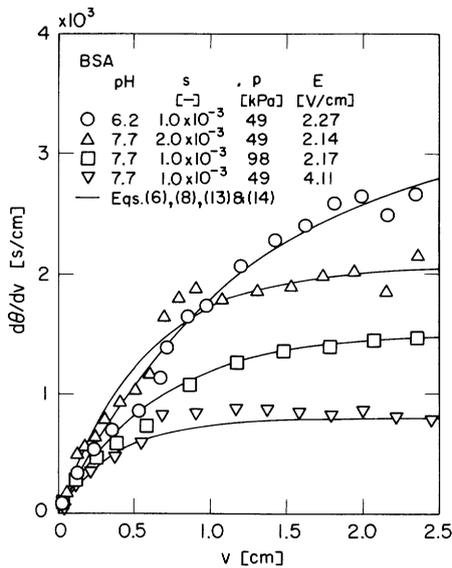


Fig. 8. Relation between $d\theta/dv$ and v under various conditions

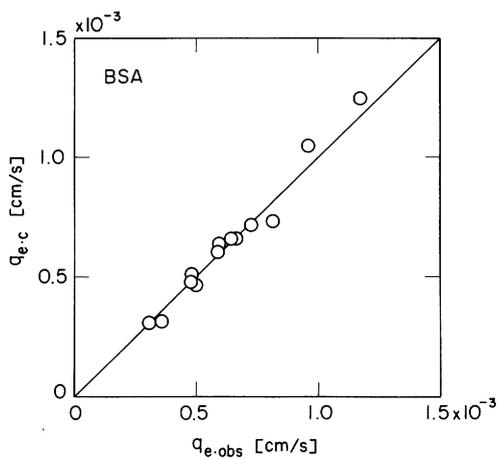


Fig. 9. Dynamically balanced filtration rate

the electrophoretic effects become more conspicuous at lower s and higher pH levels. Taking both electrophoretic and electroosmotic effects into account,

a method has been developed for analyzing the filtration flux rate in dead-end electro-ultrafiltration. If the sweeping performance of the filter cake by crossflow is evaluated, the transient behavior in crossflow electro-ultrafiltration may be analyzed by this method, taking the crossflow effect into account.

Acknowledgement

This work is supported by the Ministry of Education, Japan (Grant No. 03805089).

Nomenclature

A	= effective membrane area	[m ²]
a	= empirical constant in Eq. (11)	[m ³ /(V·s)]
E	= electric field strength	[V/m]
i	= electric current	[A]
K_E	= filtration coefficient of constant-pressure electro-ultrafiltration	[m ² /s]
K_{EO}	= Ruth filtration coefficient	[m ² /s]
k	= electrophoretic mobility	[m ² /(V·s)]
k_E	= value defined by Eq. (4)	[m ² /(V·s)]
m	= ratio of wet to dry cake mass	[—]
p	= filtration pressure	[Pa]
p_E	= electroosmotic force per unit effective membrane area	[Pa]
q	= filtration rate	[m/s]
q_e	= dynamically balanced filtration rate	[m/s]
q_{e-c}	= value of q_e obtained using Eqs. (9) and (13)	[m/s]
q_{e-obs}	= observed value of q_e	[m/s]
s	= mass fraction of solute in solution	[—]
u_E	= electrophoretic velocity of solute	[m/s]
v	= filtrate volume per unit effective membrane area	[m ³ /m ²]
w	= mass of solute in filter cake per unit effective membrane area	[kg/m ²]
α_{av}	= average specific filtration resistance	[m/kg]
θ	= filtration time	[s]
κ	= specific electric conductivity	[A/(V·m)]
μ	= viscosity of permeate	[Pa·s]
ρ	= density of permeate	[kg/m ³]
ρ_l	= density of solution	[kg/m ³]

Literature Cited

- 1) Bowen, W. R. and H. A. M. Sabuni: *Ind. Eng. Chem. Res.*, **30**, 1573 (1991).
- 2) Iritani, E., T. Watanabe and T. Murase: *Kagaku Kogaku Ronbunshu*, **17**, 206 (1991).
- 3) Iritani, E., T. Hayashi and T. Murase: *J. Chem. Eng. Japan*, **24**, 39 (1991).
- 4) Iritani, E., S. Nakatsuka, H. Aoki and T. Murase: *J. Chem. Eng. Japan*, **24**, 177 (1991).
- 5) Kimura, S. and T. Nomura: *Maku*, **7**, 245 (1982).
- 6) Miller, G. L. and R. H. Golder: *Arch. Biochem.*, **29**, 420 (1950).
- 7) Murase, T., E. Iritani, P. Chidphong and K. Kano: *Kagaku Kogaku Ronbunshu*, **15**, 1179 (1989).
- 8) Radovich, J. M., B. Behnam and C. Mullon: *Sep. Sci. Technol.*, **20**, 315 (1985).
- 9) Ruth, B. F.: *Ind. Eng. Chem.*, **27**, 708 (1935).
- 10) Ruth, B. F.: *Ind. Eng. Chem.*, **27**, 564 (1946).
- 11) Tarleton, E. S.: *Filtr. Sep.*, **30**, 402 (1988).
- 12) Turkson, A. K., J. A. Mikhlin and M. E. Weber: *Sep. Sci.*

- Technol.*, **24**, 1261 (1990).
- 13) Visvanathan, C. and R. Ben Aim: *Sep. Sci. Technol.*, **24**, 383 (1989).
 - 14) Wakeman, R. J. and E. S. Tarleton: *Trans. IChemE.*, **69**, 386 (1991).
 - 15) Yukawa, H., K. Kobayashi, Y. Tsukui, S. Yamano and M. Iwata: *J. Chem. Eng. Japan*, **9**, 396 (1976).
 - 16) Yukawa, H., H. Obuchi and K. Kobayashi: *Kagaku Kogaku Ronbunshu*, **6**, 288 (1980).
 - 17) Yukawa, H., H. Obuchi and K. Kobayashi: *Kagaku Kogaku Ronbunshu*, **6**, 323 (1980).
 - 18) Yukawa, H., K. Shimura, A. Suda and A. Maniwa: *J. Chem. Eng. Japan*, **16**, 246 (1983).
 - 19) Yukawa, H., K. Shimura, A. Suda and A. Maniwa: *J. Chem. Eng. Japan*, **16**, 305 (1983).
 - 20) Yukawa, H., K. Kobayashi and M. Iwata: *Kagaku Kogaku Ronbunshu*, **15**, 31 (1989).
- (Presented at the 24th Autumn Meeting of The Society of Chemical Engineers, Japan, at Nagoya, October 1991.)