ELECTRICAL CONDUCTIVITY MEASUREMENT OF FILTER CAKE IN DEAD-END ULTRAFILTRATION OF PROTEIN SOLUTION

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Key Words : Ultrafiltration, Filter Cake, Solid Liquid Separation, Protein, Electrical Conductivity

The dynamic ultrafiltration process of protein solution is experimentally investigated by measuring electrical conductivity within the filter cake. Three pairs of platinum wire electrodes were employed to measure the formation process of the filter cake on the membrane surface. The filter cakes formed from protein solutes behave as highly compressible cakes and shifting of pH from 5 to 4 or 9 results in a decrease in cake compressibility, as well as specific filtration resistance. The experimental results for bovine serum albumin and soy protein solutions coincide favorably with the calculated results based on the compressible cake filtration theory.

Introduction

In order to assess more rationally the process design of crossflow ultrafiltration and centrifugal ultrafiltration, it is essential to clarify the physical properties of filter cake in dead-end ultrafiltration. Many theoretical models (Chudacek and Fane, 1984; Nakao *et al.*, 1982) and experimental measurements (Iritani *et al.*, 1991; Vilker *et al.*, 1981) have been reported to make the fouling phenomena of the membrane during ultrafiltration clear. Iritani *et al.* (1991, 1995) recognized formation of the filter cake on the ultrafiltration membrane surface by using a batchwise filter which had a sudden change in its filtration area. Also, Takahashi *et al.* (1991) developed an ultrasonic measurement technique to measure cake thickness in microfiltration. Few works, however, on the formation process of the filter cake on the membrane surface and the variation of internal structure in the filter cake have been reported.

In this study, the dynamic ultrafiltration process of protein solution is evaluated by measuring electrical conductivity within the filter cake during dead-end ultrafiltration. Furthermore, the dead-end ultrafiltration process is analysed based on the compressible cake filtration theory.

1. Experimental Apparatus and Procedure

The experimental apparatus for batchwise ultrafil-

Fig. 1 Experimental apparatus

tration is schematically illustrated in Fig.1. The filter cell constructed of acrylic resin had an internal diameter of 7.0 mm in the bottom section and 17.0 mm in the upper section. In order to determine the electrical conductivity within the filter cake, three pairs of platinum wire electrodes having diameter of 0.3 mm were mounted in the inside filter wall near the membrane surface. The electrodes had three heights x of 0.2, 0.6 and 1.2 mm from the membrane surface (Nakakura *et al.*, 1992). The electrical resistance was measured by an alternating current resistor (LCR meter)(Sambuichi *et al.*, 1994). The cell constants were previously determined for each electrodes with a 0.01 N KCl electrolyte. After solutions are poured into the filter, dead-end ultrafiltration was carried out by applying nitrogen gas under constant pressure. Solutes used in the present study were bovine serum albumin (BSA Powder, Fraction V, Wako Pure Chemical Ind. Corp.) with a molecular weight of 67,000 daltons, soy protein (Fuji Oil Corp.) composed of 7 S globulin and polystyrene latex particles (Nippon Zeon Corp.) with an average particle diameter of 0.2 μm . Polysulfone membranes (Tosoh Corp.) with a nominal molecular weight cut-off of

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Presented at the 57 th Annual Meeting of the Society of Chemical Engineers, Japan, at Osaka, April, 1992 and at the 58th Annual Meeting of the Society of Chemical Engineers, Japan, at Kagoshima, March, 1993.

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Fig. 2 Relationship between κ , L and v for polystyrene latex suspension

Fig. 3 Relationship between κ , L and v for BSA solution at pH9

50,000 and 100,000, nitrocellulose membranes (Advantec Corp.) with a mean pore diameter of 0.1 μm were employed.

2. Results and Discussion

In **Fig. 2**, the experimental results of electrical conductivity of the filter cake κ versus the filtrate volume v per unit membrane area are plotted for polystyrene latex suspension under a constant pressure of 98.1 kPa. The κ value in the nearest electrode ($x=0.2$ mm) to the membrane surface increases at first in the course of the filtration process, followed by the increment of the κ values in the upper parts successively, because the positions of the filter cake surface increase beyond the each electrode heights. This result is similar to the relationship between electrical resistance and filtrate volume for clay slurry (Shirato *et al.*, 1971). The thickness of the filter cake L (the key $\bullet$) is determined from κ -variations, and then the average porosity ϵ_{av} is obtained from the slope of L vs. v plots. Although the porosity depends highly on the physical properties of the particle suspensions and the solution environment, the average porosity of 0.40 shows an appropriate value, compared with the value in the literature (Bridger *et al.*, 1983). Therefore, the accuracy of this

Fig. 4 Relationship between κ , L and v for BSA solution at pH4

Fig. 5 Δ vs. ξ

experimental method is confirmed.

Typical results of the ultrafiltration experiments for BSA solution at pH 9 are shown in **Fig. 3**. The variations of electrical conductivity κ are similar to the case of polystyrene latex suspension. κ_0 is the electrical conductivity at which κ begins to increase rapidly for each height of electrode x . A slight increase in κ_0 -value at the initial period ($v < 1.8 \times 10^{-3}$ m) is caused by the variation of the electric current path (Shirato *et al.*, 1971). The BSA molecule has a net negative charge at pH 9 (Fane, 1986; Iritani *et al.*, 1995). Therefore, it is expected that the protein molecules form a loose filter cake on the membrane surface because of the electrostatic repulsive force acting. The average porosity ϵ_{av} in this case is given as 0.98 with the value of partial specific volume ($\bar{v} = 0.73$ cm³/g).

The same plot for experimental results of BSA solution at pH 4 is also illustrated in **Fig. 4**. Although the BSA molecule has a net positive charge at pH 4, the variations of κ -value are similar to the case of pH 9. Based upon the experimental data of pH 4, electrical conductivity κ is plotted in **Fig. 5**, which shows the normalized electrical conductivity Δ ($\equiv (\kappa - \kappa_0) / (\kappa_\infty - \kappa_0)$) vs. the normalized distance ξ ($\equiv x/L$). κ_∞ is an asymptotic value of electrical conductivity at the electrode height of 0.2 mm. Although κ_∞ is not the value at the true equilibrium con-

Fig. 6 Relationship between κ , L and v for soy protein solution

Fig. 7 Relationship between κ , $d\theta/dv$ and v for interrupted flow experiment

dition, the Λ distributions are a function of position ξ alone, independently of filtration time, and this increases with an increase in applied filtration pressure p . These results can be explained well owing to an increase in the packing density of deposited BSA molecules by compression effect, that is, an increase in the positive charge density of BSA molecules. Therefore, it is suggested that the filter cakes formed from protein solute behave like the particles in compressible filter cake. The experimental results for soy protein are also illustrated in **Fig. 6**. Although soy protein with a mean molecular weight of 200,000 has a net negative charge at pH 6 (isoelectric point pI 4.5), a similar filtration behavior is observed.

The experimental results of electrical conductivity κ for the interrupted flow experiment are shown in **Fig. 7**, where the reciprocal filtration rate ($d\theta/dv$) is also plotted as a function of filtrate volume v per unit membrane area. The initial filtration time before flow interruption is 5 h and the duration of the zero-flow period is 1 h. Although

Fig. 8 Relationship between average porosity and applied filtration pressure

a deviation of electrical conductivity is observed at the instant of repressurization, the conductivities following repressurization gradually lay on an extension of the values prior to flow interruption. This phenomena is similar to the variation of the reciprocal filtration rate ($d\theta/dv$) with filtrate volume v (Reihanian *et al.*, 1983; Iritani *et al.*, 1995). Thus the filter cake during dead-end ultrafiltration behaves like a conventional compressible filter cake.

The experimental values of average porosity ϵ_{av} are plotted in **Fig. 8** as a function of the applied filtration pressure p . The values of solute density ρ_p are 1200 kg/m³ for soy protein, and 1050 kg/m³ for polystyrene latex. In the case of protein solutions, ϵ_{av} decreases with an increase in p , i.e., behaves as a compressible filter cake, while the polystyrene latex particles do not. The BSA filter cake has a compact packing structure at its isoelectric point (pH=5), whereas at opposing pH values, it changes the structure to a relatively loose condition because of the acting electrostatic repulsive force (Fane, 1986; Iritani *et al.*, 1991).

The experimental results of the dead-end ultrafiltration for BSA solution at pH 5 under various filtration pressures are shown in **Fig. 9**. The relationship between reciprocal filtration rate ($d\theta/dv$) and filtrate volume v per unit membrane area indicates a straight line throughout the progress of filtration, and the slope of these plots decreases with increasing p like a conventional filter cake. Consequently, the basic filtration rate equation (known as Ruth's equation) can be applied for analysis of dead-end ultrafiltration.

$$\frac{d\theta}{dv} = \frac{\alpha_{av}\mu\rho s}{p(1-ms)}v + \frac{\mu R_m}{p} \quad (1)$$

where α_{av} is the average specific filtration resistance, μ the viscosity of the filtrate, ρ the density of the filtrate, s

Fig. 9 Relationship between reciprocal filtration rate and filtrate volume per unit membrane area

Fig.10 Relationship between average specific filtration resistance and applied filtration pressure

the mass fraction of solute in solution, m the ratio of wet to dry cake mass, and R_m the membrane resistance. The average specific filtration resistance α_{av} is calculated from the slope of experimental plots in Fig.9 and Eq.(1).

In Fig.10, α_{av} for five kinds of solution is plotted as a function of the applied filtration pressure p . The plots show a linear relationship in accordance with the Sperry-type equation ($\alpha_{av} = \alpha_0 p^n$). The compressibility coefficient of filter cake n , obtained from the slopes of the line is 0.75 for BSA at pH5 and 0.79 for soy protein. It is clear that a shifting of pH from 5 to 4 or 9 results in a decrease in cake compressibility as well as α_{av} -value, because of the electrostatic repulsive effects (Fane, 1986; Iritani *et al.*, 1991).

The variation of α_{av} with p is somewhat different from that of $(1-\epsilon_{av})$ with p at pH 5 illustrated in Fig.8. This is caused by differences in the distributions of local porosity ϵ and specific filtration resistance α within the filter cake. Therefore, it is essential to clarify not only the overall filtration characteristics but also the internal structures of the filter cake.

3. Analysis and Discussion

The basic filtrate flow equation for constant pressure filtration of compressible filter cake can be written as (Shirato *et al.*, 1969)

$$u_\omega = \frac{1}{\mu \alpha p_p} \frac{\partial p_L}{\partial \omega} = - \frac{1}{\mu \alpha p_p} \frac{\partial p_s}{\partial \omega} \quad (2)$$

where α is the local specific filtration resistance and u_ω the apparent relative velocity of the liquid, p_L the hydraulic pressure, p_s the local compressive pressure, and ω the solute volume per unit membrane area lying between the membrane and an arbitrary position in the filter cake.

Variation of the relative filtrate velocity to solutes u_ω is given by

$$\frac{u_\omega}{u_0} = 1 - \frac{(e - e_{av\omega})(m-1)}{e_{av}(1-ms)} s \frac{\omega}{\omega_0} \quad (3)$$

where e ($\equiv \epsilon/(1-\epsilon)$) is the local void ratio of liquid to solutes, e_{av} the average void ratio of liquid to solutes, and $e_{av\omega}$ the average void ratio over the range from 0 to ω . Integrating Eq.(2) over the entire filter cake and rearranging yields

$$\alpha_{av} = \int_0^1 \left(\frac{u_\omega}{u_0} \right) d \left(\frac{\omega}{\omega_0} \right) \frac{p}{\int_0^p \frac{1}{\alpha} dp_s} \quad (4)$$

Although it is very difficult to obtain the compression permeability data (C-P data) for protein solutions, the data of constant pressure filtration, ϵ_{av} and α_{av} vs. p , are converted to ϵ and α vs. p_s by applying a theory (Murase *et al.*, 1989; Iritani *et al.*, 1991). Accordingly, the dead-end ultrafiltration process of protein solutions can be analysed based on both the compressible cake filtration theory mentioned above and the trial-and-error calculation method (Sambuichi *et al.*, 1988). In Fig.11, the predicted distributions of compressive pressure p_s , porosity ϵ and specific filtration resistance α within the filter cake are illustrated for different values of pH, where the filtration pressure and the filtrate volume are the same.

In the case of BSA at isoelectric point (pH=5), a pronounced variation of α can be seen in the vicinity of the membrane, whereas the α distributions of BSA at pH 4 and 9 are substantially flat over the entire range of filter cake. Furthermore, the ϵ value of BSA at pH 5 is relatively small compared with that of BSA at pH 4 and 9,

Fig.11 Predicted distributions of compressive pressure p_s , porosity ε , specific filtration resistance α and mass fraction of solute c in filter cake at pH 4, 5 and 9

because of the difference in internal structure of the filter cake. That is to say, the BSA filter cake has a compact structure at pH 5, whereas at pH 4 and 9 it changes its structure to a relatively loose condition because of the acting electrostatic repulsive force and the decrease in cake compressibility.

The mass fraction of solute c in the filter cake is also illustrated in **Fig.11**. The value of c is given with the assumption of additive property by

$$c = \frac{\rho_p(1-\varepsilon)}{\rho_p(1-\varepsilon) + \rho\varepsilon} \quad (5)$$

In **Fig.12**, the experimental results of the filtrate volume V vs. time θ for BSA and soy protein solutions are plotted under various operating conditions. The solid lines in **Fig.12** represent the calculated results based on the theory and the C-P data mentioned above. They show good agreement with the experimental results over the entire filtration period. Thus it is also confirmed that the compressible cake filtration theory is applicable to the analysis of the dead-end ultrafiltration process for protein solutions.

Conclusion

The dynamic ultrafiltration process of protein solution was experimentally investigated by measuring the electrical conductivity within the filter cake. The following results and conclusions were obtained.

(1) The platinum wire electrodes method can be employed satisfactorily to measure the formation process of the filter cake on the membrane surface.

(2) It was shown that the filter cakes formed from protein solutes are highly compressible and a shifting of pH from 5 to 4 or 9 results in a decrease in cake compress-

Fig.12 Comparison of experimental and predicted results for V vs. θ (BSA and soy protein)

ibility as well as average specific filtration resistance.

(3) The experimental results for bovine serum albumin and soy protein solutions coincide favorably with the calculated results based on the compressible cake filtration theory.

Acknowledgments

The authors wish to thanks Tosoh Co., Ltd., Fuji Oil Co., Ltd. and Nippon Zeon Co., Ltd. for donation of the membrane and the materials used in the experiments. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan, Grant No.06650883.

Nomenclature

c	= mass fraction of solute in filter cake	[—]
e	= local void ratio $\equiv \varepsilon/(1-\varepsilon)$	[—]
e_{av}	= average void ratio	[—]
$e_{av.\omega}$	= average void ratio over the range from 0 to ω	[—]
L	= thickness of filter cake	[—]
m	= ratio of wet to dry cake mass	[—]
n	= compressibility coefficient of filter cake	[—]
p	= applied filtration pressure	[Pa]
p_L	= hydraulic pressure	[Pa]
p_s	= compressive pressure	[Pa]
R_m	= resistance of membrane	[1/m]
s	= mass fraction of solute in solution	[—]
u_0	= superficial velocity of filtrate at membrane	[m/s]
u_ω	= apparent solvent velocity relative to solute	[m/s]
V	= total volume of filtrate	[m³]
v	= volume of filtrate per unit membrane area	[m]
x	= distance from membrane surface	[m]
α	= local specific filtration resistance	[m/kg]
α_{av}	= average specific filtration resistance	[m/kg]
ε	= local porosity	[—]
ε_{av}	= average porosity	[—]
θ	= filtration time	[s]
κ	= electrical conductivity	[S/m]
Λ	= dimensionless electric conductivity	[—]
	$\equiv (\kappa - \kappa_0)/(\kappa_\infty - \kappa_0)$	[—]

μ	= viscosity of filtrate	[Pa·s]
ξ	= relative position in filter cake	[—]
ρ	= density of filtrate	[kg/m ³]
ρ_p	= density of solute	[kg/m ³]
ω	= solute volume per unit membrane area lying between the membrane and an arbitrary position in filter cake	[m]
ω_0	= total solute volume per unit membrane area	[m]

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