2) Austin, L. G. and P. T. Luckie: *ibid.*, **252**, 259 (1972).
3) Fujino, K. and H. Taniguchi: *Kagaku Kōgaku*, **24**, 93 (1960).
4) Furuya, M., Y. Nakajima and T. Tanaka: *Ind. Eng. Chem., Process Design and Develop.*, **10**, 449 (1971).
5) Furuya, M., Y. Nakajima and T. Tanaka: *ibid.*, **12**, 18 (1973).
6) Hukki, R. T.: *Trans. AIME*, **238**, 233 (1967).
7) Hukki, R. T. and H. Allenius: *ibid.*, **241**, 482 (1968).
8) Imaizumi, T.: *Sentan*, **12**, 40 (1961).
9) Kelsall, D. F. and K. J. Reid: *AIChE. I. Chem. E. Symp. Series*, **4**, 4: 15 (1965).
10) Kelsall, D. F., K. J. Reid and P. S. B. Stewart: *Inst. Engrs. Australia Elec. Eng. Trans.*, **5**, 173 (1969).
11) Lynch, A. J., W. J. Whiten and N. Draper: *Trans. Inst. Mining Met.*, **76**, C169 (1967).
12) Meloy, T. P. and B. H. Bergstrom: *Trans. Intern. Mineral Processing Congress*, **7**, 19 (1964).
13) Miyawaki, I. and K. Fujisaki: *J. Res. Assoc. Powder Tech.* (Japan), **8**, 482 (1971).

14) Onuma, E., K. Kawabata and T. Furukawa: Proceedings of Annual Meeting on Cement Manufacturing (Japan), **24**, 75 (1967).
15) Onuma, E.: *J. Chem. Eng. Japan*, **6**, 527 (1973).
16) Onuma, E.: *J. Res. Assoc. Powder Tech. (Japan)*, **11**, 7 (1974).
17) Onuma, E., N. Asai and G. Jimbo: Preprint of the 39th Annual Meeting of The Soc. of Chem Engrs , Japan, D209 (1974).
18) Onuma, E.: Preprint of the 39th Annual Meeting of the Soc. of Chem Engrs., Japan, D208 (1974).
19) Reddy, I. G.: *Chem. Age (India)*, **19**, 101 (1968).
20) Reddy, I. G. and M. H. Hasan: *J. of Mines, Metals & Fuels*, **19**, 65 (1971).
21) Schönert, K.: Proc. Intern. Symp. Computer Appl. Res. Mineral Ind., p. 677 (1969).
22) Tanaka, T.: *Kagaku Kōgaku*, **21**, 716 (1957).
23) Usui, K.: *ibid.*, **31**, 295 (1967).

A STUDY OF CAKE FILTRATION
—FORMULATION AS A STEFAN PROBLEM—

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Continuity equations and Darcy's law are utilized to obtain a basic equation for cake filtration. The boundary condition at the moving surface is newly derived, and the cake filtration is formulated in a Stefan problem.

A similarity variable is introduced to transform the governing equation into an ordinary one, which in turn is solved numerically. The moment method is shown to offer good initial values to start the numerical computation.

Satisfactory agreement is observed between experimental data of Shirato *et al.* and computed values of some physical properties.

In studies of the internal flow mechanism within filter cakes, it has been demonstrated that consideration must be given to the liquid flow rate and to solids movement as well[12,13]. The solid movement has greater effect on thick slurries. Basic equations consist of continuity equations of solid and liquid, and an integral equation of the solid compressive pressure. These equations were solved by making use of experimental data from a compression-permeability cell. An iterative approximation method was employed to obtain numerical solutions[10,12,13].

The purpose of this study is to fomulate constant-pressure cake filtration as a Stefan problem by combining Darcy's law with the continuity requirement, and to identify the initial and boundary conditions

relevant to the problem.

The governing equation is solved by two different methods. One is to use the moment technique[5]. The other is to use a similarity transformation to convert the partial differential equation into an ordinary one and solve numerically.

Similar problems have been studied by Smiles[15] and Tiller *et al.*[16], but the solution given by Smiles is applicable only to a limited case owing to its inappropriate boundary condition, whereas Tiller *et al.* did not give a detailed solution.

Mathematical Treatment

To describe the behavior of cake during filtration the following five values must be determined: the velocity of solid particles relative to a fixed coordinate, v_s,

the velocity of liquid relative to the solid, v_l, the solid compressive pressure, p_s, the hydraulic excess pressure, p_l, and the porosity, ε. Writing in one-dimensional form, we have the following expressions for the continuity equations of liquid and solid in a filter cake:

$$\frac{\partial \varepsilon}{\partial t} = \left\{ \frac{\partial(\varepsilon v_l)}{\partial w} + \varepsilon \frac{\partial v_s}{\partial w} \right\} \frac{\partial w}{\partial x} \qquad (1)$$

and

$$\partial x/\partial w = 1/\rho_s(1-\varepsilon) \qquad (2)$$

where t is time, w the mass of solid per unit filtering area from the medium, ε_0 the porosity of feed slurry, x the distance from the medium, and ρ_s the density of solid particles.

The motion of liquid is assumed to be describable by Darcy's law:

$$\varepsilon v_l = \frac{kg_c\rho_s(1-\varepsilon)}{\mu} \cdot \frac{\partial p_l}{\partial w} \qquad (3)$$

where k is the permeability, μ the viscosity of liquid. The force balance in cake yields

$$p_s(w, t) + p_l(w, t) = p_a(t) \qquad (4)$$

where p_a is applied pressure.

Utilizing the idea of compression-permeability cell, and assuming that the solid network in the cake is purely elastic to stress, we get

$$\varepsilon = \varepsilon(p_s) \qquad (5)$$

Combining Eqs. (1) to (5) yields the governing equation for flow through compressible porous media (or filter cake)[1,9,11],

$$\frac{\partial e}{\partial t} = \frac{\partial}{\partial w} \left\{ C_p \frac{\partial e}{\partial w} \right\} \qquad (6)$$

in which the void ratio, $e = \varepsilon/(1-\varepsilon)$, is used to express the equation in a compact form. C_p is defined as

$$C_p = -\rho_s^2 kg_c / \{\mu(1+e)de/dp_s\} \qquad (7)$$

and is a variable coefficient associated with permeability and compressibility. And in this sense it may be appropriate to call C_p the compression-permeability coefficient. Formally, however, C_p is almost identical to the expression coefficient defined in the literature[1,9,11].

The initial and boundary conditions are

$$w_i(0) = 0 \qquad (8)$$
$$e(w_i(t), t) = e_i \qquad (9)$$
$$e(0, t) = e_1 \qquad (10)$$

where w_i is the value of w from the medium to the cake surface, and e_i is the void ratio at the cake surface; e_1 is the void ratio at equilibrium under applied pressure, and it will be constant for constant-pressure filtration.

As the location of the moving boundary, w_i, is unknown a priori, one more condition is required to solve the problem. The filtrate at time t is expres-

sible as the difference between the volume of slurry which contains the solid of w_i, and the volume of cake at that time. Thus the filtrate volume per unit area, $v(t)$, is written as

$$v(t) = (1+e_0)w_i/\rho_s - x_i(t) \qquad (11)$$

where x_i is the cake thickness.

Utilizing Eqs. (2) and (6) results in

$$\frac{dx_i}{dt} = \frac{1}{\rho_s} \left[C_p \frac{\partial e}{\partial w} \bigg|_{w_i} - C_p \frac{\partial e}{\partial w} \bigg|_0 + (1+e_i) \frac{dw_i}{dt} \right] \qquad (12)$$

Differentiating Eq. (11) with respect to t and combining it with Eq. (12) yields

$$\frac{\partial e}{\partial w} \bigg|_{w_i} = \frac{e_0 - e_i}{C_p(e_i)} \frac{dw_i}{dt} \qquad (13)$$

This is the newly derived boundary condition at the moving boundary. Thus we have now the Stefan problem with the basic equation, Eq. (6), and the boundary and initial conditions, Eqs. (8) to (10), (13).

In filtration, e_i is usually smaller than e_0[13], and the right-hand side of Eq. (13) does not reduce to zero in general.

Smiles[15] set $e_0 = e_i$, which signifies no liquid flux at the cake surface. This indicates the limited applicability of Smiles' work to real systems. In the case of expression, the feed slurry is very concentrated, which causes the difference between e_0 and e_i to be very small, and the right-hand side of Eq. (13) may reduce to zero[1,9]. With regard to this, the expression may be considered as a limiting case of cake filtration.

Let us introduce the following non-dimensional variables:

$$b = w/w^*, \ \theta = C^*t/w^{*2}, \ \eta = (e-e_1)/(e_i-e_1), \ F = C_p/C^* \qquad (14)$$

where C^* and w^* are characteristic values of C_p and w, then Eqs. (6), (8)–(10) and (13) become respectively,

$$\frac{\partial \eta}{\partial \theta} = \frac{\partial}{\partial b} \left\{ F(\eta) \frac{\partial \eta}{\partial b} \right\} \qquad (15)$$

$$b_i(0) = 0 \qquad (16)$$

$$\eta(0, \theta) = 0 \qquad (17)$$

$$\eta(b_i, \theta) = 1 \qquad (18)$$

$$\frac{\partial \eta}{\partial b} \bigg|_{b_i} = \frac{n}{F(1)} \frac{db_i}{d\theta} \qquad (19)$$

where b_i and n are defined as

$$b_i = w_i/w^*, \ n = (e_0 - e_i)/(e_i - e_1) \qquad (20)$$

Solution of the Basic Equation

Many important operations in chemical engineering such as freezing, melting and evaporation are often associated with the moving boundary, and they can be classified as Stefan problems. Due to its non-linearity, which stems from the presence of the moving boundary, only a few exact solutions are available[2-4].

In the case of filtration, one more complication arises because C_p varies over the operating period, or more specifically it is usually expressed as a function of the dependent variable.

To solve Eq. (15) with relevant relations, Eqs. (16)–(19), some simplification is possible by making use of experimental facts. Details are illustrated in the following.

As an alternative form of x_i, we have

$$x_i(t)=(1+e_{av})w_i/\rho_s \qquad (21)$$

where e_{av} is the average void ratio of the entire cake. Substituting this into Eq. (11) results in

$$w_i(t)=\rho_s v(t)/(e_o-e_{av}) \qquad (22)$$

Let us utilize now the well-known experimental facts that, in the case of constant-pressure filtration, the average concentration of cake is independent of time[8], except at the begining of the process[16], and that v is proportional to $t^{1/2}$ when the medium resistance is negligible. And w_i becomes proportional to $t^{1/2}$ so that introducing a similarity variable,

$$\lambda=b/\sqrt{t} \qquad (23)$$

we can transform Eq. (15) into an ordinary differential equation.

$$\frac{d^2\eta}{d\lambda^2}+\frac{d\ln F}{d\eta}\left(\frac{d\eta}{d\lambda}\right)^2+\frac{\lambda}{2F}\frac{d\eta}{d\lambda}=0 \qquad (24)$$

The boundary and initial conditions become

$$\eta(0)=0 \qquad (25)$$

$$\eta(1/\sqrt{\beta})=1 \qquad (26)$$

$$d\eta/d\lambda=n/(2\sqrt{\beta}\,F(1)) \qquad (27)$$

Another form of similarity variable b/b_i, where $b_i=\sqrt{\theta/\beta}$, is frequently used[2,6]. However, this form leaves β in the differential equation and the numerical computation becomes unduly cumbersome.

The numerical computation proceeds as follows: Assume $d\eta/d\lambda$ at $\lambda=0$, then with the boundary condition $\eta(0)=0$, (Eq. (25)), Eq. (24) is integrated till η becomes unity. At this point the independent variable at $\eta=1$ gives $1/\sqrt{\beta}$ and $d\eta/d\lambda$ yields $n/2\sqrt{\beta}/F(1)$, (Eq. (27)). The latter is compared with the experimental value (since n and $F(1)$ are determined experimentally). If these values are not close enough, we pick another value for $d\eta/d\lambda$ at $\lambda=0$ and proceed again as stated above. This scheme is continued till the computed value becomes close enough to the experimentally obtained value. Quasilinearization techniques incorporated with the principle of super-position[7] were also tried but a sharp increase of F with respect to η at near $\eta=0$ (F is nearly an exponential function of η) made the convergence very slow and it turned out to be inadequate. Whereas the value of $d\eta/d\lambda$ at $\lambda=0$ is not too difficult to guess from the solution by the method of moment. This

will be explained later.

As an alternative method to solving Eq. (15) along with the associated boundary and initial conditions, Eqs. (16) to (19), the moment method is employed. Since the mathematical treatment is almost the same as that shown in the previous paper[1], only an outline is presented here.

Assuming that $\eta(b,\ \theta)$ can be expressed, in the range of $0\leq b\leq b_i$, as a cubic equation of b/b_i:

$$\eta=A_1(\theta)(b/b_i)+A_2(\theta)(b/b_i)+A_3(\theta)(b/b_i) \qquad (28)$$

where A_1, A_2 and A_3 are functions of θ, and combining it with the zeroth and the first moments of Eq. (15) with respect to b/b_i, there results

$$\eta=(9/2+15n+3n/4\beta-\alpha\beta)(b/b_i)$$
$$+(-6-30n-2n/\beta+2\alpha\beta)(b/b_i)^2$$
$$+(5/2+15n+5n/4\beta-\alpha\beta)(b/b_i)^3 \qquad (29)$$

where

$$\alpha=30\int_0^1 F(\eta)d\eta \qquad (30)$$

and β is the positive root of the following relationship:

$$24\alpha F(0)\beta^3+(\alpha-360nF(0)-108F(0))\beta^2$$
$$+(3/2-18nF(0)-3n)\beta-n/4=0 \qquad (31)$$

The numerical solution and the solution by the moment method are plotted in **Figs. 1a, b,** and **c.** Wherein $F(\eta)=\exp(a(1-\eta))$ is set and five numbers 0.1, 0.5, 1, 2.303 and 4.606 are given for a, and three numbers 0.1, 1 and 10 for n. This formula and numbers are chosen to cover some experimental work. These figures indicate that when $F(\eta)$ varies within the range of several fold over $0<\eta<1$, the difference between solutions by the two methods remains less than several percent, whereas when $F(\eta)$ varies more than 10-fold, the difference becomes very noticeable. However, the values of $d\eta/d\lambda$ at $\lambda=0$ calculated by these methods are very close to each other even for a 100-fold change of $F(\eta)$ and of n (**Fig. 2**). From this it may be concluded that the moment method is useful in estimating $d\eta/d\lambda$ at $\lambda=0$ to start the numerical computation, but the method itself is not a proper technique to obtain the solution when $F(\eta)$ varies more than 10-fold during filtration.

To check the mathematical analysis against experimental data, the work on ignition plug slurry by Okamura and Shirato[8] was used. The C_p was determined from e vs. p_s relation (from Table 3 in reference 8), and k vs. e relation (from Table 5 in reference 8). Details are shown in **Figs. 3 to 5.** Fig. 5 indicates that C_p can be approximated by the following formula:

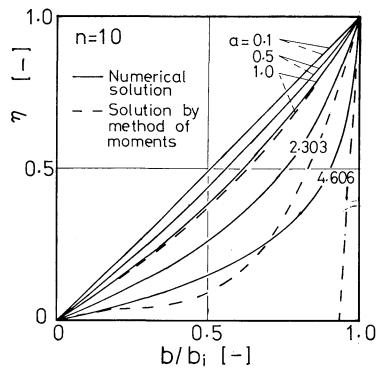$$C_p=C^*\cdot\exp\{1.62(e^*-e)\} \qquad (32)$$

Due to lack of experimental data in the range of low compressive pressure, however, it may not
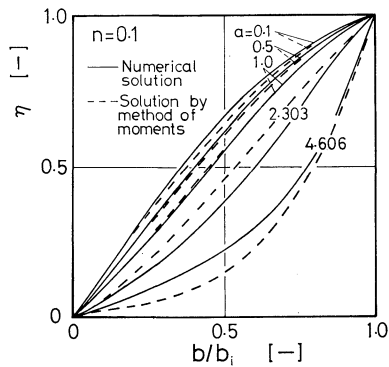
(a) $n=0.1$
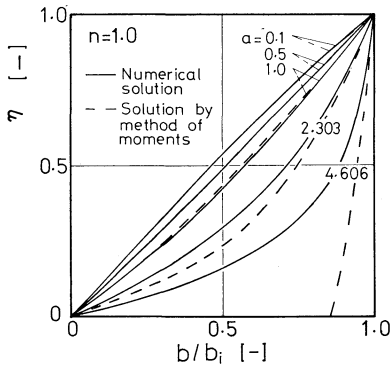
(b) $n=1.0$

(c) $n=10$

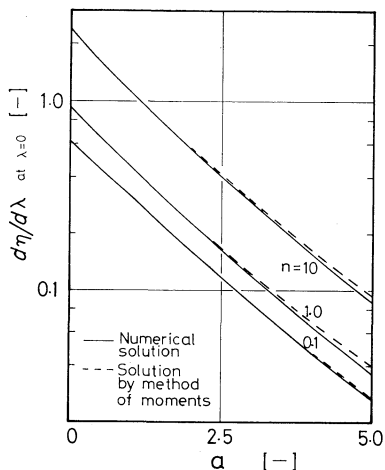Fig. 1 Solutions for $F(\eta)=\exp\ (a(1-\eta))$

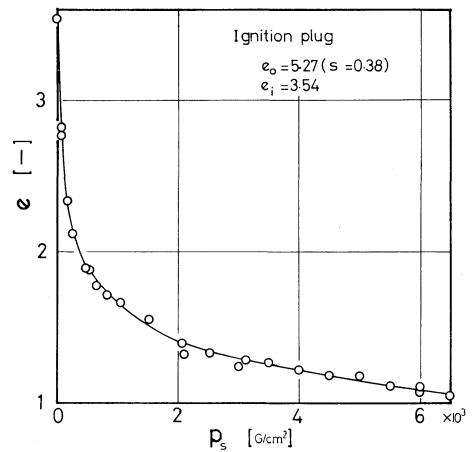Fig. 2 Values of $d\eta/d\lambda$ at $\lambda=0$ for $F(\eta)=\exp(a(1-\eta))$

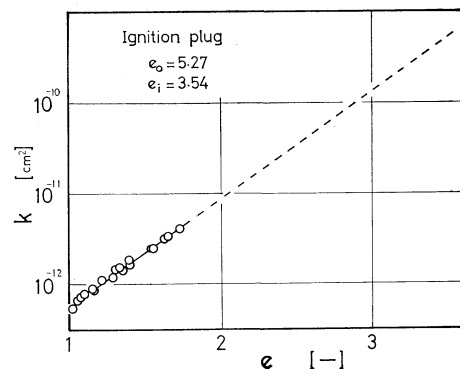Fig. 3 Result of compression experiment by Okamura and Shirato[8]

Fig. 4 Result of permeability experiment by Okamura and Shirato[8]
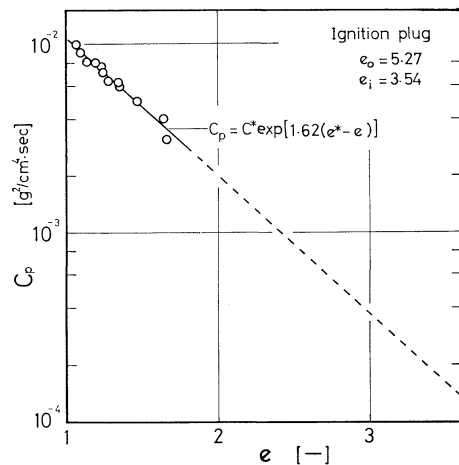

Fig. 5 Compression-permeability coefficient

be proper to use this formula for computations covering low compressive pressure range. Nevertheless, satisfactory results were obtained as shown later.

Now that we have the formula for C_p (Eq. (32)) and e_0, e_i, and e_1 values (**Table 1**), the numerical computation can be done by the Runge-Kutta-Gill method. The normalized distance x/x_i is related to the solution e by the equation

$$x/x_i=(w/w_i+\int_0^{w/w_i} e\,dz)/(1+e) \qquad (33)$$

which is derived by combining Eqs. (2), (14) and (21). The computed results of e vs. x/x_i are plotted in **Fig. 6**.

By using Figs. 3 and 6 and Eq. (4), p_l-distribution was calculated for the slurry concentration $s=0.38$. The results are shown in **Fig. 7**. For the sake of comparison, the experimental data of Okamura and Shirato[8] ($s=0.22-0.367$) are also included in Fig. 7.

The wet-to-dry cake mass ratio, m, and the product of Ruth's coefficient, K, and the solid mass fraction in slurry, s, are obtained by the following relationships:

$$m=\rho e_{av}/\rho_s+1$$

$$K\cdot s=C^*(e_0-e_{av})^2/\{\beta\rho_s(e_0\rho+\rho_s)\}$$

The calculated values from the above relationships and the experimental data of Shirato et al.[8,14] are shown in Table 1.

From Fig. 7 and Table 1, it is seen that the analytical treatment in this study agrees well with the experimental work despite the lack of accurate C_p-data for higher e-values.

As further work, for deeper understanding of the cake filtration mechanism, it is desirable to obtain accurate data of C_p in the range of low compressive pressure.

Conclusion

An attempt has been made to formulate constant-pressure cake filtration as a Stefan problem. The boundary condition at the moving surface is also derived. By using the fact that the mass of solid per unit area measured from the medium to the moving surface is proportional to the square root of time, the governing partial differential equation is transformed to an ordinary differential equation, which in turn is solved numerically with experimentally determined compression-permeability coefficient. Computed values $p_l(x/x_i)$, m, and $K\cdot s$ agreed well with the experimental results of ignition plug slurry of Shirato et al.[8,14].

The moment technique was tried as an alternative method to solve the problem, and was found to be useful in estimating the initial values to start the numerical computation.

Nomenclature

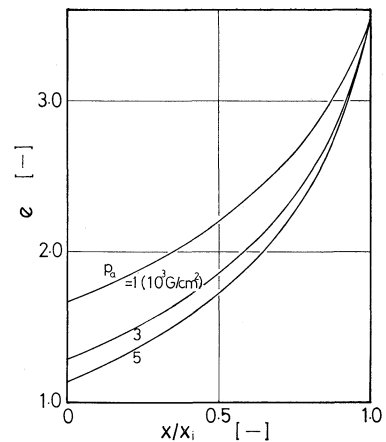|		
A_1, A_2, A_3	= variable coefficient, see Eq. (28)	[—]
b	= non-dimensional value of w ($=w/w^*$)	[—]
b_i	= non-dimensional value of w_i ($=w_i/w^*$)	[—]
C_p	= compression-permeability coefficient	[g²/cm⁴·sec]
C^*	= characteristic value of C_p ($=C_p(e_i)$)	[g²/cm⁴·sec]
e	= void ratio	[—]
e_0,e_i,e_1	= e-values of feed, at cake surface, and at medium	[—]

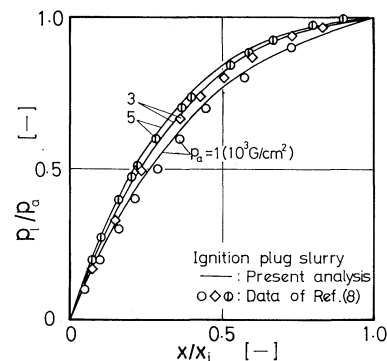**Fig. 6** Void ratio vs. x/x_i for $p_a=1$, 3 and 5[$\times10^3$G/cm²]

Fig. 7 Hydraulic pressure distribution in cake

Table 1 Results of constant-pressure filtration

p_a [10^3G/cm²]	e_1 [—] Exp.*	e_{av} [—] Calc.**	β [—] Calc.	m [—] Exp.	m [—] Calc.	$K\cdot s$ [10^{-3}cm²/sec] Exp.	$K\cdot s$ [10^{-3}cm²/sec] Calc.
1.0	1.67	2.24	0.114	1.67	1.69	0.53	0.58
3.0	1.29	1.90	0.0644	1.58	1.59	1.0	1.1
5.0	1.14	1.77	0.0537	1.54	1.55	1.3	1.4

$e_0=5.27$, $e_i=3.54$, $\rho_s=3.23$
$C^*=C_p(e_i)=1.4\times10^{-4}$ [g²/cm⁴·sec]

* Experimental results of Shirato et al.[8]
** Calculated results by the present analysis

$F(\eta)$	= non-dimensional compression-permeability coefficient ($=C_p/C^*$)	[—]
g_c	= gravitational conversion factor	[g·cm/G·sec²]
K	= Ruth's coefficient per unit area	[cm²/sec]
k	= permeability coefficient	[cm²]
m	= ratio of wet-to-dry cake mass	[—]
n	= $(e_0-e_i)/(e_i-e_1)$	[—]
p_a,p_l,p_s	= applied, local hydraulic excess, and local solid compressive pressure	[G/cm²]
s	= mass fraction of solid in slurry	[—]
t	= time	[sec]
v	= filtrate volume per unit area	[cm]
v_l	= velocity of liquid with respect to surrounding solid	[cm/sec]
v_s	= velocity of solid with respect to fixed coordinate	[cm/sec]

w	= mass of solid per unit area measured from medium	[g/cm²]
w_i, w^*	= value of w at cake surface and total mass of solid per unit area	[g/cm²]
x	= distance from medium	[cm]
x_i	= thickness of cake	[cm]
α	= defined by Eq. (30)	[—]
β	= θ/b_i^2	[—]
ε	= porosity	[—]
η	= defined by Eq. (14)	[—]
θ	= non-dimensional time, defined by Eq. (14)	[—]
λ	= $b/\sqrt{\theta}$	[—]
μ	= viscosity of filtrate	[g/cm–sec]
ρ, ρ_s	= density of filtrate and of solid	[g/cm³]

Literature Cited

1) Atsumi, K., T. Akiyama and M. Miyagawa: *J. Chem. Eng. Japan*, **6**, 236 (1973).
2) Bankoff, S. G.: *Adv. Chem. Eng.*, **5**, 75 (1964).
3) Carslaw, H. S. and J. C. Jaeger: "Conduction of Heat in Solids", 2nd ed , p. 285, Oxford Univ. Press (1959).
4) Crank, J.: "The Mathematics of Diffusion", Oxford Univ. Press (1956).
5) Fujita, H.: *J. Chem. Phys.*, **21**, 700 (1953).
6) Hamill, T. D. and S. G. Bankoff: *Ind. Eng. Chem. Fundamentals*, **3**, 177 (1964).
7) Lee, E. S. and L. T. Fan: *Can. J. Chem. Eng.*, **46**, 200 (1968).
8) Okamura, S. and M. Shirato: *Kagaku Kōgaku*, **19**, 104, 111 (1955).
9) Satoh, T. and K. Atsumi: *J. Chem. Eng. Japan*, **3**, 92 (1970).
10) Shirato, M. and T. Aragaki: *Advanced Chemical Engineering* (Japan), **8**, 121 (1974).
11) Shirato, M. and T. Murase: *ibid*, **8**, 153 (1974).
12) Shirato, M., M. Sambuichi, T. Aragaki and H. Kato: *Kagaku Kōgaku*, **31**, 359 (1967).
13) idem: *AIChE J.*, **15**, 405 (1969).
14) Shirato, M. and M. Sambuichi: *Kagaku Kōgaku*, **27**, 470 (1963).
15) Smiles, D. E.: *Chem. Eng. Sci.*, **25**, 985 (1970).
16) Tiller, F. M. and H. R. Cooper: *AIChE J.*, **6**, 595 (1960).

Short Communications

TERNARY LIQUID-LIQUID EQUILIBRIA FOR THE SYSTEMS OF AQUEOUS METHANOL SOLUTIONS AND PROPANE OR n-BUTANE

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Introduction

Liquid-liquid equilibrium data are essential for the selection of solvent and for the design of separation processes. Many investigators have reported on liquid-liquid equilibria including ternary aqueous methanol solutions and n-paraffin systems. Stephen and Stephen[7] have compiled comprehensive tables of liquid-liquid equilibrium data. Mutual solubilities for methanol-n-paraffin systems including n-pentane to n-decane have been reported by Kiser[3]. As the mutual solubilities for systems of n-paraffin and water are small and measurements of the solubilities for these systems are very difficult, only a few data have been reported. Kobayashi[4] and Mannheimer[5] have reported the mutual solubilities for the propane-water system and Reamer[6] for the n-butane-water system. This paper presents the mutual solubility data for the methanol-n-butane system and the liquid-liquid equilibrium data for the ternary methanol-water-propane and methanol-water-n-butane systems at 0°C and 20°C.

1. Experimental

Mutual solubilities for the methanol-n-butane system were determined by the cloud point method. Ternary liquid-liquid equilibrium data for the methanol-water-propane and methanol-water-n-butane systems were determined by the same method reported in the previous paper[1] except for the determination of compositions by using gas chromatographic analysis. A column of 3 mm diameter and 3 meter length is filled with Porapak R as a packing material for gas chromatograph and hydrogen is used as a carrier gas.

The sample was injected several times into a gas chromatograph and was analyzed by the total amounts of the sample. The composition of each component was determined by the total areas of the gas chromatogram. As the amount of water in the hydro-