

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

**IPC TECHNICAL PAPER SERIES
NUMBER 90**

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DANIEL R. TRETTIN AND MAHENDRA R. DOSHI**

JANUARY, 1980

ULTRAFILTRATION IN AN UNSTIRRED BATCH CELL

Daniel R. Trettin and Mahendra R. Doshi*
Environmental Sciences Division
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

ABSTRACT

The ultrafiltration of macromolecular solutions in an unstirred batch cell was investigated to isolate the effect of variable diffusion coefficient from that of variable solution viscosity. Solutions of Bovine Serum Albumin (BSA) in 0.15M NaCl (7.40 pH) and 0.10M sodium acetate (4.70 pH) were used. A technique for minimizing the effect of variable membrane properties, as well as pre-gel (low polarization) region is presented. BSA systems are studied over a wide range of concentrations (0.01-0.10 g/cc) and at higher pressures than previously reported (10.34×10^5 N/m²). Results confirm that BSA solutions do reach a pressure-independent flux region at moderate pressures. A constant property integral method solution was developed which agrees well with the exact solution but not with the film theory. Agreement between acquired BSA data and theoretical predictions is excellent, with the average error less than 3%.

INTRODUCTION

Over the past decade, membrane ultrafiltration has become recognized as a viable process for the concentration or separation of moderate to high molecular weight solutes from solutions. Because of the wide application and simplicity of the process, ultrafiltration is currently being

This paper has been submitted for publication in I & EC Fundamentals

used in many commercial and industrial operations from food processing to waste treatment. As a direct result of this increased interest in ultrafiltration, there have been many investigations regarding the nature of the transport phenomena in ultrafiltration [Michaels (1968), Blatt, et al. (1970), Goldsmith (1971), Kozinski & Lightfoot (1972), Porter (1972), Shen & Probstein (1977), Mitra and Lundblad (1978), Probstein, et al. (1978, 1979)].

Although more rigorous predictive models exist, the mainstay of the ultrafiltration technology continues to center around models based on film theory. Shen & Probstein (1977) and Probstein, et al. (1978, 1979) have taken a more exact approach to the problem and have shown that numerical solutions to their exact model for variable viscosity and diffusion-coefficient can be closely approximated by a modified film theory model where the value of the diffusion coefficient is evaluated at the solute gelling concentration. Agreement with experimental data for the parallel plate system is excellent if the values of the solute gelling concentration and corresponding diffusion coefficient cited by Probstein, et al. (1978, 1979) for bovine serum albumin are employed. Possible limitations of Probstein, et al.'s (1978, 1979) data are that flux measurements were taken over a narrow range of solute concentrations. Trettin & Doshi (1980) have theoretically shown with an integral method solution to the solute mass balance equation that permeate flux does not vary logarithmically with solute concentration, which is characteristic of the film theory model. Since there are substantial differences between the two models, there is a definite need for additional data taken over a wider solute concentration range to test the two theories. Besides, existing data have not been corrected for pre-gel region. We appreciate that the pre-gel region is indeed small.

However, permeate rate in the pre-gel region may not be negligible compared to that in the gel region.

A major obstacle in the comparison of the experimental data with the modified film theory model and more exact solutions is that the proper values of the solute gel concentration and diffusion coefficient are not available. Most previous studies have used forced convection ultrafiltration units where added complications may arise due to variable viscosity. The unstirred batch cell system offers the unique opportunity of studying the ultrafiltration of bovine serum albumin solutions without the interfering effect of variable viscosity. The main objective of this work is to develop the analogous form of the integral method solution derived (for parallel plate system) in Trettin & Doshi (1980), along with the film theory analogy, for the unstirred batch cell. Experimental data taken in the unstirred batch cell ultrafiltration of bovine serum albumin are corrected for pre-gel region and compared with both models. Results are further compared to the values of gel concentration and diffusion coefficient determined by Probstein, et al. (1978, 1979).

THEORETICAL DEVELOPMENT

Consider the unstirred cell geometry as shown in Fig. 1 where the general solute mass balance equation of

$$\partial c / \partial t + v \partial c / \partial y = D \partial^2 c / \partial y^2 \quad (1)$$

applies. It is implicitly assumed in the derivation of Equation (1) that the density of the solute is approximately that of the solvent.

[Figure 1 here]

The appropriate boundary and initial conditions are the following:

$$c(0,y) = c_o, \quad \text{for } y > 0 \quad (2)$$

$$\left. \begin{aligned} c(t,0) &= c_g \\ c(t,\infty) &= c_o \end{aligned} \right\} \text{for all } t \quad (3)$$

$$v(c_g - c_p) = - |v_w| (c_g - c_p) = D[\partial c / \partial y]_{y=0} \quad (4)$$

Clearly, the model assumes that a solute gel concentration is reached instantaneously at the membrane surface and that the value of the solute diffusion coefficient is constant. Adopting a similarity transformation of the form,

$$\eta = y / (4Dt)^{1/2} \quad (5)$$

Equation (1) may be rewritten as,

$$d^2c/d\eta^2 + [2\eta + v_w] dc/d\eta = 0 \quad (6)$$

where,

$$v_w = \frac{|v_w| (4Dt)^{1/2}}{D} = \text{constant} \quad (7)$$

and the boundary conditions of Equations (2)-(4) reduce to,

$$c(0) = c_g \quad (8)$$

$$c(\infty) = c_o \quad (9)$$

$$dc/d\eta|_{\eta=0} = -v_w (c_g - c_p) \quad (10)$$

Integration of Equation (6) with the substitution of the boundary condition given in Equation (10) yields

$$\theta = \frac{\frac{c}{g} - \frac{c}{g}}{\frac{c}{g} - \frac{c}{g}} \frac{c_o - c_p}{c_g - c_p} = V_w \int_0^\infty \exp [-(\eta^2 + V_w \eta)] d\eta \quad (11)$$

Upon evaluation of the closed integral of Equation (11), the result is

$$\theta = \frac{\sqrt{\pi}}{2} V_w \exp [V_w^2/4] \operatorname{erfc} [V_w/2] \quad (12)$$

For small values of V_w , Equation (12) may be simplified to

$$\theta = \frac{\sqrt{\pi}}{2} V_w - \frac{1}{2} V_w^2 + \frac{\sqrt{\pi}}{8} V_w^3 - \frac{1}{12} V_w^4 + \frac{\sqrt{\pi}}{64} V_w^5 - \frac{1}{120} V_w^6 + \dots \quad (13)$$

Similarly, for large values of V_w , Equation (12) may be written as

$$\theta = 1 - 2 V_w^{-2} + 12 V_w^{-4} - 120 V_w^{-6} + \dots \quad (14)$$

It will be interesting to obtain a solution by the integral method in an analogous manner to the previously solved case of the parallel plate (rectangular flow channel) system (Trettin & Doshi, 1979). Assume a concentration profile of the form,

$$c = c_o + (c_g - c_o) (1-y/\delta)^n \quad (15)$$

Note that at $y=\delta(t)$, $c=c_o$. The solution involves the integration of Equation (1) over the boundary layer thickness, $\delta(t)$, with the substitution of the concentration profile equation. The result may be expressed as

$$d\delta/dt = \frac{n(n+1)}{\delta} D \left[\frac{c_o - c_p}{c_g - c_p} \right] \quad (16)$$

or, integrating Equation (16) with respect to t and noting that at $t=0$, $\delta(t)=0$,

$$\delta = [2n(n+1)]^{1/2} D^{1/2} \left(\frac{c_o - c_p}{c_g - c_p} \right)^{1/2} t^{1/2} \quad (17)$$

Equation (17) may be written in terms of $|v_w|$ using the boundary condition of Equation (4)

$$|v_w| = \begin{bmatrix} c & -c \\ g & o \\ c & -c \\ g & p \end{bmatrix} \begin{bmatrix} c & -c \\ g & p \\ c & -c \\ o & p \end{bmatrix}^{1/2} \left[\frac{nD}{2(n+1)t} \right]^{1/2} \quad (18)$$

Transforming Equation (18) to dimensionless form using Equation (7) yields,

$$V_w = \begin{bmatrix} F & -1 \\ g & \\ F & -F \\ g & p \end{bmatrix} \begin{bmatrix} K & F-F \\ g & p \\ 1-F & \\ p & \end{bmatrix}^{1/2} \quad (19)$$

where

$$K = 2n/n+1 \quad (20)$$

$$F = c/c_o$$

In order to determine the proper value of the coefficient, n, a moment technique was applied by multiplying Equation (1) by y:

$$y \partial c / \partial t - |v_w| y \partial c / \partial y = y D \partial^2 c / \partial y^2 \quad (21)$$

Upon substitution of the assumed concentration profile into Equation (21) and integration over the boundary layer thickness, the result may be expressed as,

$$n^2 (1-F_p) + n (F_p - F_g) + 2(F_p - F_g) = 0 \quad (22)$$

or, since $n > 0$,

$$n = \frac{[F_g - F_p] + [(F_g - F_p)^2 + 8(1-F_p)(F_g - F_p)]^{1/2}}{2(1-F_p)} \quad (23)$$

A comparison of the developed integral method solution was made with the calculated solutions of Equation (12) within a range of F_g values from 2 to 100. The agreement of the predicted values of V_w between the two solutions is excellent with a difference less than 1%. F_p was assumed to be zero in the comparison. In the calculation of permeate flux, the use of Equation (19) is more convenient since Equation (12) must be solved by trial and error.

The unstirred batch cell analogy of the film theory model can be obtained by neglecting the accumulation term from Equation (1) and integrating:

$$1-\theta = \exp \left[- \frac{|v_w| \delta}{D} \right] \quad (24)$$

The quantity D/δ is taken to be equal to the unsteady state mass transfer coefficient (assuming constant wall concentration) in the absence of transverse velocity:

$$k = D/\delta = (D/\pi t)^{1/2} \quad (25)$$

Substituting for D/δ in Equation (24) yields

$$1-\theta = \exp \left[- |v_w| (t\pi/D)^{1/2} \right] \quad (26)$$

or, expressed in a more conventional form,

$$|v_w| = (D/\pi t)^{1/2} \ln \left[\frac{c_g - c_p}{c_o - c_p} \right] \quad (27)$$

Transforming to dimensionless variables with the use of Equation (7) yields

$$V_w = \frac{2}{\sqrt{\pi}} \ln \left(\frac{F_g - F_p}{1 - F_p} \right) \quad (28)$$

A comparison of the film theory solution to the integral method solution for the unstirred batch cell is shown in Table 1.

[Table 1 here]

As shown in Table 1, the film theory model consistently underpredicts the integral method model with progressively better agreement as the value of F_g approaches unity. Film theory deviates from the more exact theory by more than 25% for all values of F_g greater than 4.0. Similar results were obtained for the case of parallel plate system (Trettin & Doshi, 1980).

EXPERIMENTAL PROCEDURE

Bovine serum albumin (Cohn fraction V), obtained from Sigma Chemicals Company in granular form, was selected as a macromolecular solute. The justification for this choice of material was twofold. First, BSA is a reasonably well characterized protein with Newtonian rheological properties [Kozinski & Lightfoot (1972)] and a narrow molecular weight distribution of approximately 70,000. Second, BSA has been studied extensively by previous investigators [Blatt, et al. (1970), Kozinski & Lightfoot (1972), Shen & Probstein (1977), and Probstein, et al. (1978, 1979)] so their work provides a comparison with our results. Solutions of BSA prepared in 0.15M NaCl (7.4 pH) and 0.10M sodium acetate (4.7 pH) were used. These buffer solutions are comparable to those studied by Shen & Probstein (1977) and Probstein, et al. (1978, 1979). Sodium azide of 200 ppm concentration was added as a preservative and final solutions were filtered through a 0.8 micron Millipore filter to remove undissolved solute. Solutions were then refrigerated at 10°C prior to use. BSA solutions which had aged more than two weeks were discarded. Solute concentrations were determined by ultraviolet light absorption with a spectrophotometer at the absorption peak of 280 nm.

The literature contains numerous experimental determinations of the mutual diffusion coefficient of BSA in various buffer solutions [Creeth (1952), Charlwood (1953), Keller, et al. (1971), Doherty & Benedek (1974), Phillies, et al. (1976)]. The range of reported diffusion coefficient at low concentration is $D = 5.5 - 7.0 \times 10^{-7} \text{ cm}^2/\text{sec}$. However, values

at higher concentration show considerable scatter as pointed out by Shen & Probst (1977). Phillips, et al. (1976) have studied BSA solution diffusivity in both 0.025M sodium acetate - 0.2M NaCl and 0.15M NaCl buffer systems over the pH range of 4.3-7.6. Their work has shown a negligible concentration dependence of the diffusion coefficient in the acetate buffer system within the 4.6-5.6 pH range. Data taken within the higher pH ranges of the 0.15M NaCl system show considerable scatter and have been interpreted by Probst, et al. (1979) to yield an average value in general agreement with their determination of $6.7 \times 10^{-7} \text{ cm}^2/\text{sec}$.

Ultracentrifuge experiments were performed in our laboratory with the acetate and saline buffered BSA solutions ($\approx 0.007 \text{ g/cc}$) using the optical procedure of Longworth (1952) and Creeth (1955) as outlined by Tostevin (1966). Limitations of this method are that only low concentrations of BSA in solution may be studied due to refraction fringe merging at higher concentrations ($> 0.01 \text{ g/cc}$). Corresponding values of the diffusion coefficient for the 0.10M sodium acetate (4.7 pH) and 0.15M NaCl (7.4 pH) systems are $6.79 \times 10^{-7} \text{ cm}^2/\text{sec}$ and $6.91 \times 10^{-7} \text{ cm}^2/\text{sec}$, respectively. Experiments were performed at 23.5°C . Both Creeth (1952) and Charlwood (1953) have reported the diffusivity of dilute BSA solutions to be within the range of $6.6 \times 10^{-7} \text{ cm}^2/\text{sec}$ to $7.1 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 25°C . Their data also show that the effects of pH value and buffer type upon the diffusion coefficient are negligible. This observation is in agreement with our measurements.

The gelling concentration of BSA in saline solution (7.4 pH, 25°C) has been independently determined by Kozinski & Lightfoot (1972) to be 0.585 g/cc . As for BSA in acetate solution (4.7 pH), there are no direct determinations of gelling concentration reported in the literature. Probst, et al. (1978) have indirectly determined the value of gelling concentration to be 0.340 g/cc (4.7 pH, acetate buffer system) through their interpretation of parallel plate data using film theory principles.

Batch cell experiments were performed in stainless steel pressure cells manufactured by the Gelman Filter Company. Average membrane area equalled 15.62 cm² and the total cell volume was approximately 230 cm³. The batch cells were affixed to a support integral with the building structure to prevent extraneous vibration and the room temperature was controlled within the range of 21-24°C. Total permeate volume was gravimetrically measured as a function of time for periods as long as 20 hours. The batch cell geometry was such that a volume correction of 2 ml had to be added to the initial permeate volume measurement to account for permeate trapped in the cell. The value of the correction was confirmed experimentally. Cell pressure was varied from 2.76×10^5 - 10.34×10^5 N/m² (40 to 150 psig). A schematic diagram of the batch cell apparatus is shown in Figure 2.

[Figure 2 here]

The majority of the batch cell experiments were done using cellulose acetate membranes (5,000-10,000 MW cutoff) supplied to us through the courtesy of UOP-Fluid Systems. Several experiments were additionally conducted using a noncellulosic (X-117) and polysulfone membrane also from UOP-Fluid Systems. Both noncellulosic membranes performed as well as the cellulose acetate membrane, yielding solute rejections greater than 95%.

ANALYSIS OF DATA

From the integral method analysis of the batch cell it was shown that

$$V_w (D/4)^{1/2} = |v_w| t^{1/2} = \text{constant} \quad (7)$$

Let A = the transport surface area of the membrane, and $B = AV_w (D/4)^{1/2}$;
therefore

$$A |v_w| = Bt^{-1/2} \quad (29)$$

integrating with respect to t from 0 to T yields

$$\int_0^T A |v_w| dt = \Delta V = 2BT^{1/2} \quad (30)$$

where ΔV equals the total permeate collected from $t=0$ to $t=T$. If ΔV_i represents permeate collected between time $t=0$ and $t=T_i$, we have from Equation (30)

$$\frac{\Delta V_2 - \Delta V_1}{\Delta V_3 - \Delta V_1} = \frac{T_2^{1/2} - T_1^{1/2}}{T_3^{1/2} - T_1^{1/2}} \quad (31)$$

In all experiments, permeate collection measurement times were selected so that $T_2 = 2T_1$ and $T_3 = 4T_1$, giving

$$\frac{T_2^{1/2} - T_1^{1/2}}{T_3^{1/2} - T_1^{1/2}} = 0.4142 \quad (32)$$

Acceptability limits of the data were established as $\pm 3\%$ of the 0.4142 value.

It may be noted that 83% of the collected data fell within this range, and over 94% of the collected data fell within the $\pm 4\%$ range limits. Results of the above analysis show that the average time to reach a limiting condition at the membrane surface is indeed less than the first experimental collection time (T_1).

Even though the duration of the pre-gel region is short, the permeate collected during this time may represent a sizable percentage of total permeate collected at longer times. This is particularly true for situations where the bulk solute concentrations (c_o) are high and consequent permeate fluxes are small. Also, because it was not possible to clean the membranes effectively to restore initial pure solvent flux, new membranes were used in each sample run. This fact introduces the additional complication of variable pure solvent flux and rejection coefficients between experiments which in turn affect the rate of accumulation of solute at the membrane surface in the pre-gel region. It is, therefore, necessary to utilize a method of data analysis so that the effects of membrane variation in the pre-gel region may be minimized.

It was observed from experimental data that when values of $2B$ were calculated from a permeate volume difference relationship, a constant value to within 3% was obtained for the various time intervals used $[(T_2, T_1), (T_3, T_1), \text{ or } (T_3, T_2)]$. However, when this same value of $2B$ was used in Equation (30) to back calculate the corresponding values of ΔV_1 , ΔV_2 , and ΔV_3 , differences as great as 20% were found between experimental measurements and the calculated values of ΔV . Also, it is known that pre-gel permeate flux will be greater than the corresponding gel limiting flux since the secondary hydraulic resistance of the gel layer is not present. Therefore,

in a system where both a pre-gel and gel regions are found, collected permeate will be greater than in the equivalent gel polarized system. In view of the cited observations, a correction factor was subtracted from experimentally measured permeate volumes

$$\Delta V = \Delta V_{\text{exp}} - \Delta V_{\text{corr}} \quad (33)$$

Clearly, Equation (33) has no effect upon a permeated volume difference relationship since the correction volume cancels out. However, Equation (30) becomes

$$\Delta V_{\text{exp}} - \Delta V_{\text{corr}} = 2BT^{1/2} \quad (34)$$

Equation (34) can be rewritten as:

$$\frac{\Delta V_{\text{exp}}}{T^{1/2}} = 2B + \Delta V_{\text{corr}} (1/T^{1/2}) \quad (35)$$

By plotting $\Delta V_{\text{exp}}/T^{1/2}$ versus $1/T^{1/2}$ and extrapolating to infinite time (T), it is possible to minimize the effects of the pre-gel region (ΔV_{corr}) and determine the appropriate value of 2B. The value of ΔV_{corr} may also be determined from the slope. The true value of $\Delta V/T^{1/2}$ resulting from the pre-gel region correction is referred to as

$$\lim_{T \rightarrow \infty} \left[\frac{\Delta V}{T^{1/2}} \right] = 2B \quad (36)$$

Results of the BSA batch cell experiments are given in Tables 2 and 3. Data are also displayed on Graphs 3 and 4. The noted correlation factors represent the accuracy of the data fit to a straight line. Calculations were performed using a linear regression analysis program and a factor of 1 represents a perfect correlation. The sample scheme represents the times at which the collected permeate volume was measured, where

<u>Sample Scheme</u>	<u>Times of Measurement</u>
A	2,4,8 hours
B	3,6,12 hours
C	5,10,20 hours

[Tables 1 & 2 and Graphs 3 & 4 here]

Average values of bulk concentration and corresponding extrapolated values of $\Delta V_{\text{exp}}/T^{1/2}$ (or $\Delta V/T_{\text{lim}}^{1/2}$) are plotted in Graphs 5 and 6 for the two solvent systems. The dashed line in Graph 5 represents the theoretically calculated values of $\Delta V/T^{1/2}$ from the integral method solution using Kozinski & Lightfoot's (1972) value of 0.585 g/cc for c_g . The value at the diffusion coefficient was taken as 6.91×10^{-7} cm²/sec from our ultracentrifuge experiments. In comparison, the values of c_g and D used by Probst, *et al.* (1978, 1979) for BSA in the saline solvent system (7.4 pH) were 0.580 g/cc and 6.7×10^{-7} cm²/sec, respectively. Correspondingly, the dashed line in Graph 6 represents the integral method solution where the value of the diffusion coefficient was taken as 6.79×10^{-7} cm²/cm. Since an independent measurement of c_g for the acetate BSA system is not available, the value of c_g was interpreted to be 0.385 g/cc from fit of data to the integral method solution. The solid lines in Graphs 5 and 6 represent the film theory predictions of $\Delta V/T^{1/2}$ using the respective values of c_g and D cited above for each solvent system. In comparison, the values of c_g and D determined by Probst, *et al.* (1978, 1979) for BSA in the acetate solvent system (4.7 pH) were 0.340 g/cc and 5.6×10^{-7} cm²/sec, respectively. Since their values for the acetate system vary considerably from ours, plots of the integral method model and the film theory model using their values of c_g and D are also shown in Graph 6. Both

Graphs 5 and 6 indicate that the integral method model fits data well with an average variance of $\pm 4\%$, while the film theory consistently underpredicts experimental flux measurements. If a straight line approximation is fit to the experimental data in an attempt to satisfy the film theory model, the result would necessitate an unrealistically high diffusion coefficient value of $6.1-9.7 \times 10^{-6} \text{ cm}^2/\text{sec}$. This range of values represents an order of magnitude difference from published values.

[Graphs 5 and 6 here]

Graph 7 is an interesting plot showing that the variable c_g/c_o (or F_g) is the independent variable in the integral method model. This explains the experimental observation of two different permeation rates for the same value of c_o in the saline and acetate systems. This is due to the fact that even though c_o is the same, the values of c_g are different in each solvent system and therefore, c_g/c_o has different values.

[Graph 7 here]

Several of the solutions listed in Tables 2 and 3 were studied at lower cell pressures, namely, $2.76 \times 10^5 \text{ N/m}^2$ and $4.14 \times 10^5 \text{ N/m}^2$. The analysis of these systems yielded values of $[\Delta V/T^{1/2}]_{\text{lim}}$ approximately 10 to 15% less than the values at identical concentration and higher pressure. Also, the extrapolated lines of the $\Delta V_{\text{exp}}/T^{1/2}$ versus $1/T^{1/2}$ plots for various low pressures and constant concentration did not intersect at the same point on the y-axis as they did in the case of higher pressures. These results may mean that, at the lower pressures, a gel layer was not formed at the wall, but rather, the system was limited by the osmotic pressure of the BSA solution itself.

CONCLUSIONS

The primary conclusion of this work is that the logarithmic permeate flux behavior predicted by the widely accepted film theory model is not encountered in the unstirred batch cell system. Rather, flux rates are accurately predicted by a more exact theory. Values of the gel concentration and diffusion coefficient for the saline solvent system do, however, agree well with those determined by Shen & Probstein (1977) and Probstein, et al. (1978, 1979) for their parallel plate system. In the acetate solvent system, there exists a discrepancy between Probstein's, et al. (1978) determinations of c_g and D and ours. Accurate analysis of data in terms of the integral method solution, which assumes a constant value of the diffusion coefficient, confirms negligible concentration dependence of the diffusion coefficient for BSA.

The low pressure observations of linear $\Delta V/T^{1/2}$ versus $1/T^{1/2}$ plots and nonintersecting values of $[\Delta V/T^{1/2}]_{lim}$ below those for higher system pressures indicate constant solute concentrations at the wall which are less than the corresponding BSA gel concentration.

Ideally, the values of C_g and D should be measured independently. The presented model is intended to be used to predict permeate variation with time. As shown in Fig. 8, a 5% error in the measured value of ΔV can give 8 to 10% error in the calculated value of C_g . We do not recommend the use of batch cell ultrafiltration to determine both C_g and D .

[Figure 8 here]

NOTATION

B = dimensionless constant [Equation (29)]

c = solute concentration (g/cm^3)

D = solute diffusion coefficient (cm^2/sec)

$F = c/c_o$

k = mass transfer coefficient (cm/sec)

$K = \frac{2n}{n+1}$

L = solution level in batch cell (cm)

n = power law coefficient [Equation (15)]

P = pressure (N/m^2)

t = time (sec)

T = permeate measurement time interval (sec)

v = transverse velocity (cm/sec)

V_w = dimensionless permeate constant [Equation (7)]

y = transverse distance coordinate (cm)

Greek Letters

$\delta(t)$ = concentration boundary layer thickness (cm)

η = similarity variable [Equation (15)]

ΔP = total pressure gradient (N/m^2)

ΔV = permeate volume collected in time T (cm^3)

$\theta = (c_g - c_o) / (c_g - c_p)$

Subscripts

a = at the ambient condition

$cell$ = inside the cell condition

$corr$ = correction

exp = experimental

g = at the gelling condition

i = at measurement i

lim = limiting

o = at the bulk solution condition

p = at the permeate condition

w = at the membrane surface condition

$1,2,3$ = at measurement 1,2,3

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Table 1. Comparison of Film Theory Model
with Integral Method Solution

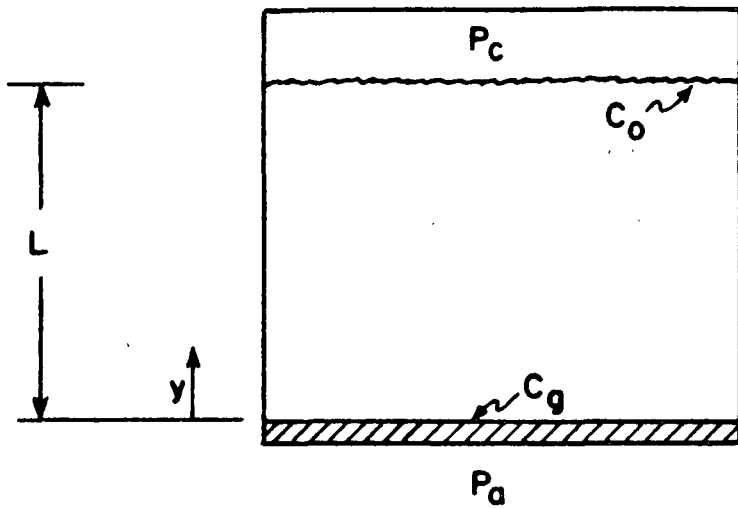
F_g	V_w Film Theory	V_w Integral Method	$\frac{V_w \text{ (I.M.)}}{V_w \text{ (F.T.)}}$
100	5.20	13.93	2.68
75	4.87	12.01	2.46
50	4.41	9.71	2.20
25	3.63	6.67	1.84
15	5.06	4.97	1.63
10	2.60	3.86	1.49
5	1.82	2.36	1.30
4	1.56	1.95	1.25
2	0.78	0.87	1.12
1.5	0.46	0.49	1.07

Table 2. BSA, 0.15M NaCl, 7.4 pH

c_o [g/cc]	$\Delta P \times 10^{-5}$ [N/m ²]	$\left[\frac{\Delta V}{T^{1/2}} \right]_{lim}$ [mL·sec ^{-1/2}]	Correlation Factor	Sample Scheme	ΔV_{corr} [mL]	$\frac{\Delta V_{corr}}{\Delta V_1}$	Corresponding Line on Graph 2
0.0051	10.34	0.2014	0.99	B	1.6180	0.07	
0.0098	10.34	0.1434	0.99	A	1.8210	0.13	1
0.0098	10.34	0.1446	1.00	A	1.8623	0.13	2
0.0103	6.89	0.1355	1.00	B	2.4433	0.15	3
0.0103	10.34	0.1362	1.00	B	2.1286	0.13	4
0.0217	4.14	0.0879	1.00	A	1.8621	0.20	5
0.0217	6.89	0.0885	1.00	A	0.9221	0.11	6
0.0219	6.89	0.0879	1.00	A	1.3360	0.15	7
0.0215	10.34	0.0877	1.00	A	0.4945	0.06	8
0.0515	6.89	0.0532	1.00	C	2.1417	0.23	9
0.0510	10.34	0.0529	1.00	C	0.9142	0.11	10
0.0973	6.89	0.0343	1.00	C	0.1065	0.02	11
0.0973	10.34	0.0345	--	C	0.0313	0.01	12

Table 3. BSA, 0.10M Sodium Acetate, 4.7 pH

c_o [g/cc]	$\Delta P \times 10^{-5}$ [N/m ²]	$\frac{\Delta V}{T^{1/2}}$ lim [mL·sec ^{-1/2}]	Correlation Factor	Sample Scheme	ΔV_{corr} [mL]	$\frac{\Delta V_{corr}}{\Delta V_1}$	Corresponding Line on Graph 3
0.0051	6.89	0.1553	--	A	0.1383	0.01	1
0.0050	10.34	0.1564	0.99	B	1.0245	0.06	2
0.0093	6.89	0.1096	1.00	B	2.6298	0.19	3
0.0093	10.34	0.1092	0.99	B	1.4968	0.12	4
0.0213	6.89	0.0680	1.00	A	0.6917	0.11	5
0.0209	10.34	0.0694	0.95	C	0.5202	0.05	6
0.0492	6.89	0.0398	1.00	C	0.9081	0.15	7
0.0493	10.34	0.0404	0.98	C	0.4479	0.08	8
0.0952	6.89	0.0267	1.00	C	0.2411	0.06	9
0.0958	10.34	0.0255	0.99	C	0.2723	0.07	10



where:
 $t > 0$
 $P_c > P_a$
 $L \gg \delta(t)$

Figure 1. Batch cell geometry

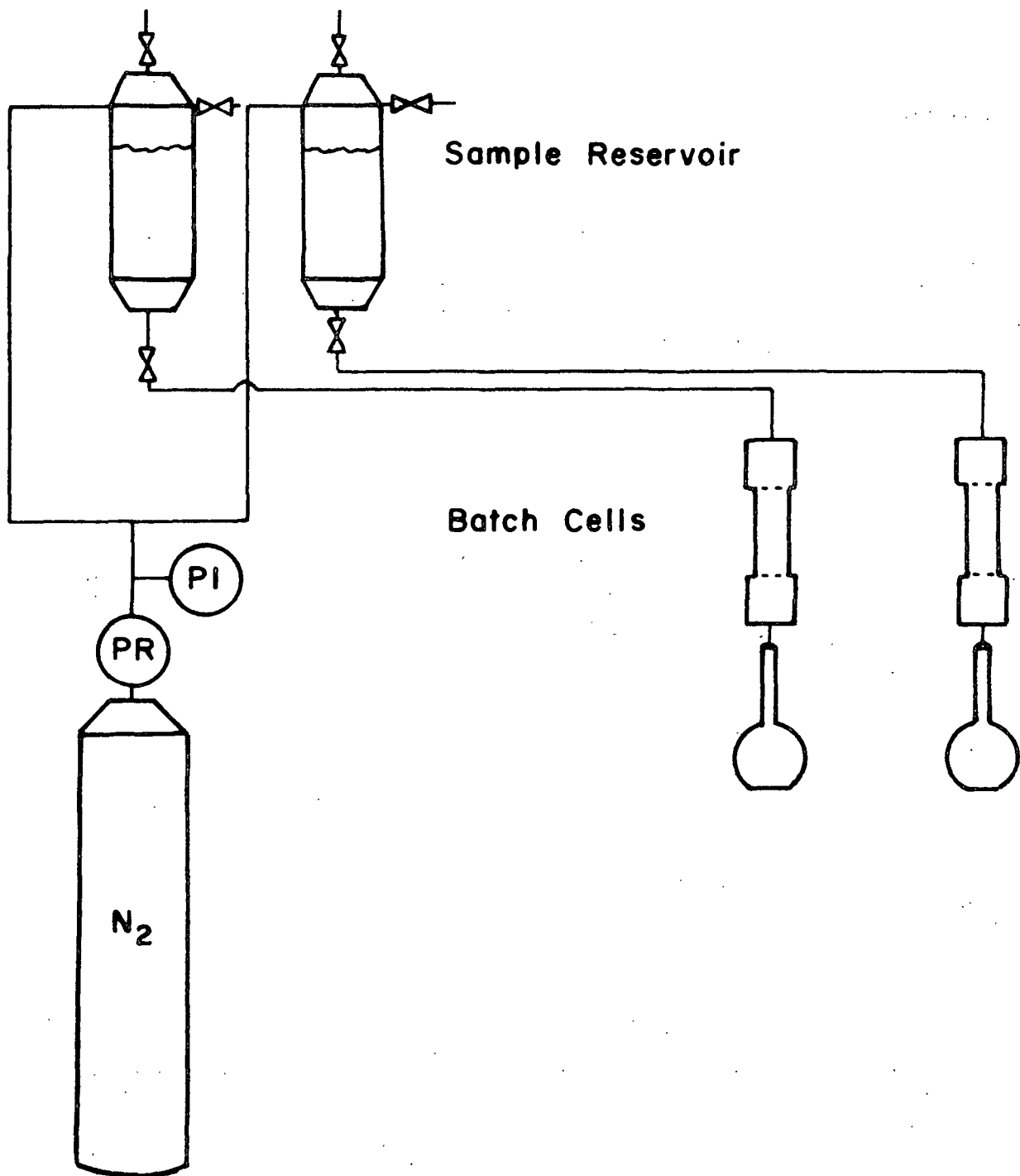


Figure 2. Batch cell arrangement

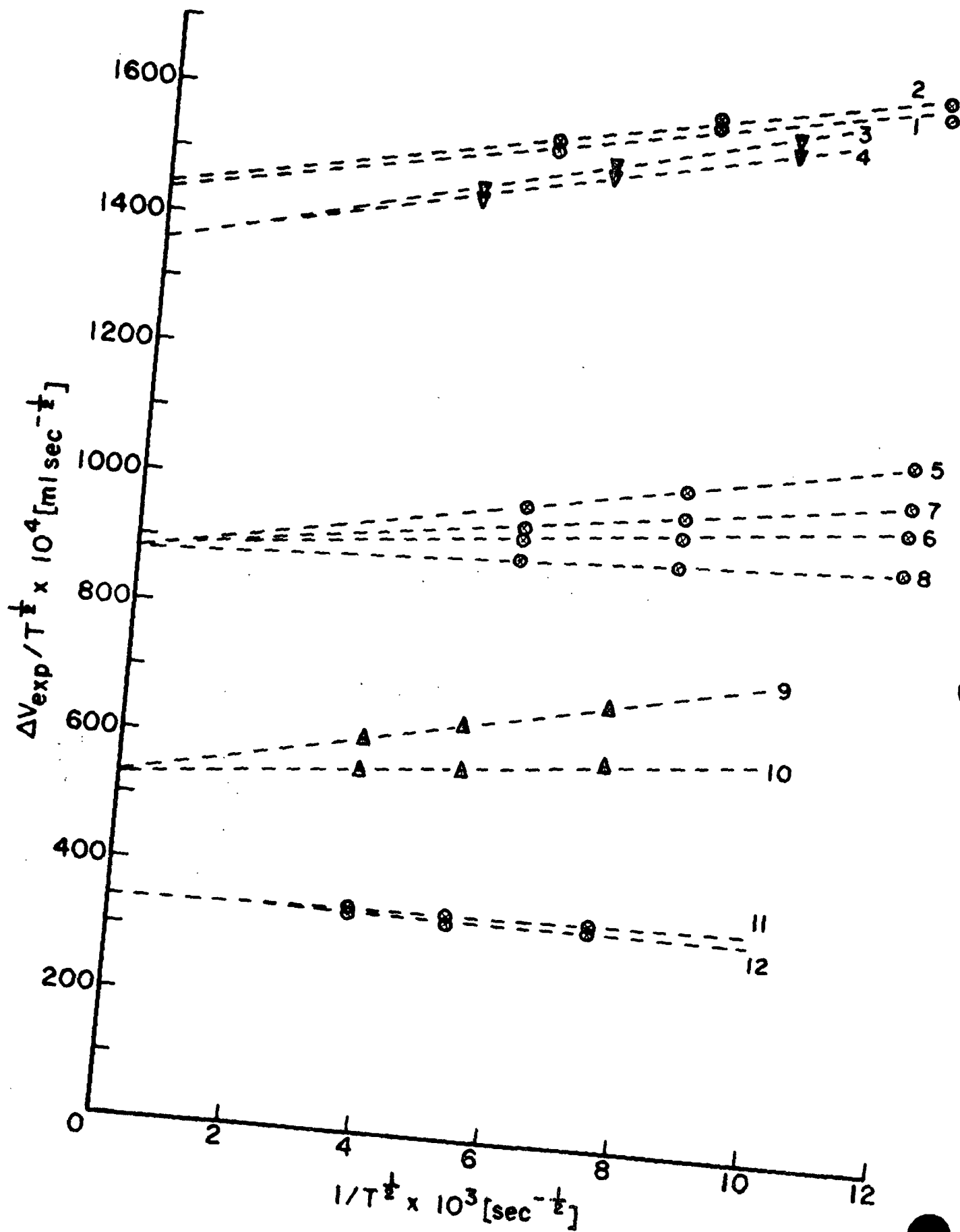


Figure 3. BSA 0.15M NaCl, 7.4 pH

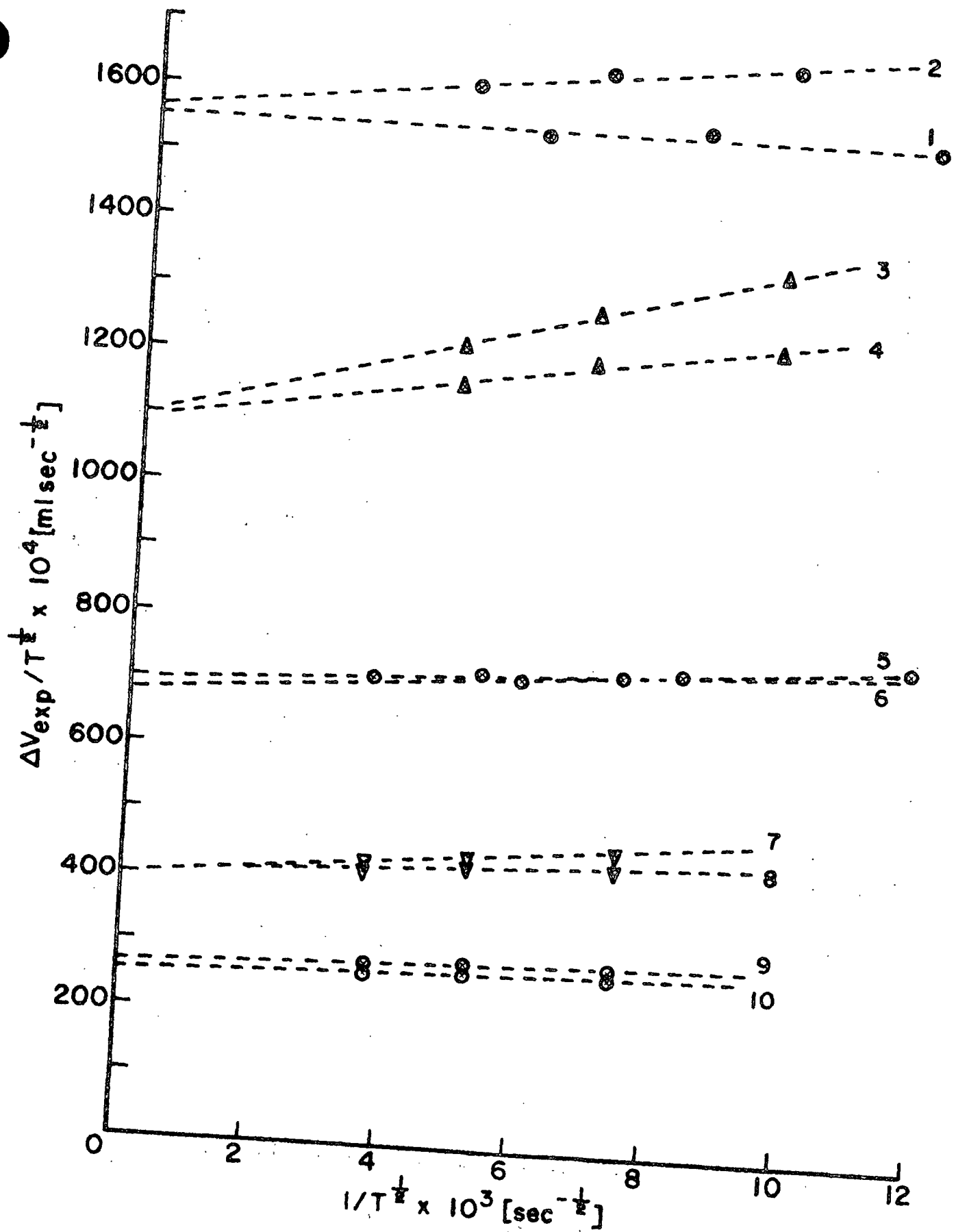


Figure 4. BSA, 0.10M sodium acetate, 4.7 pH

--- Integral Method Solution, $C_g = 58.5 \text{ g}/100 \text{ cc}$, $D = 6.91 \times 10^{-7} \text{ cm}^2/\text{sec}$
 — Film Theory Model,
 Δ Experimental Data, $[\Delta V/T^2]_{lim}$

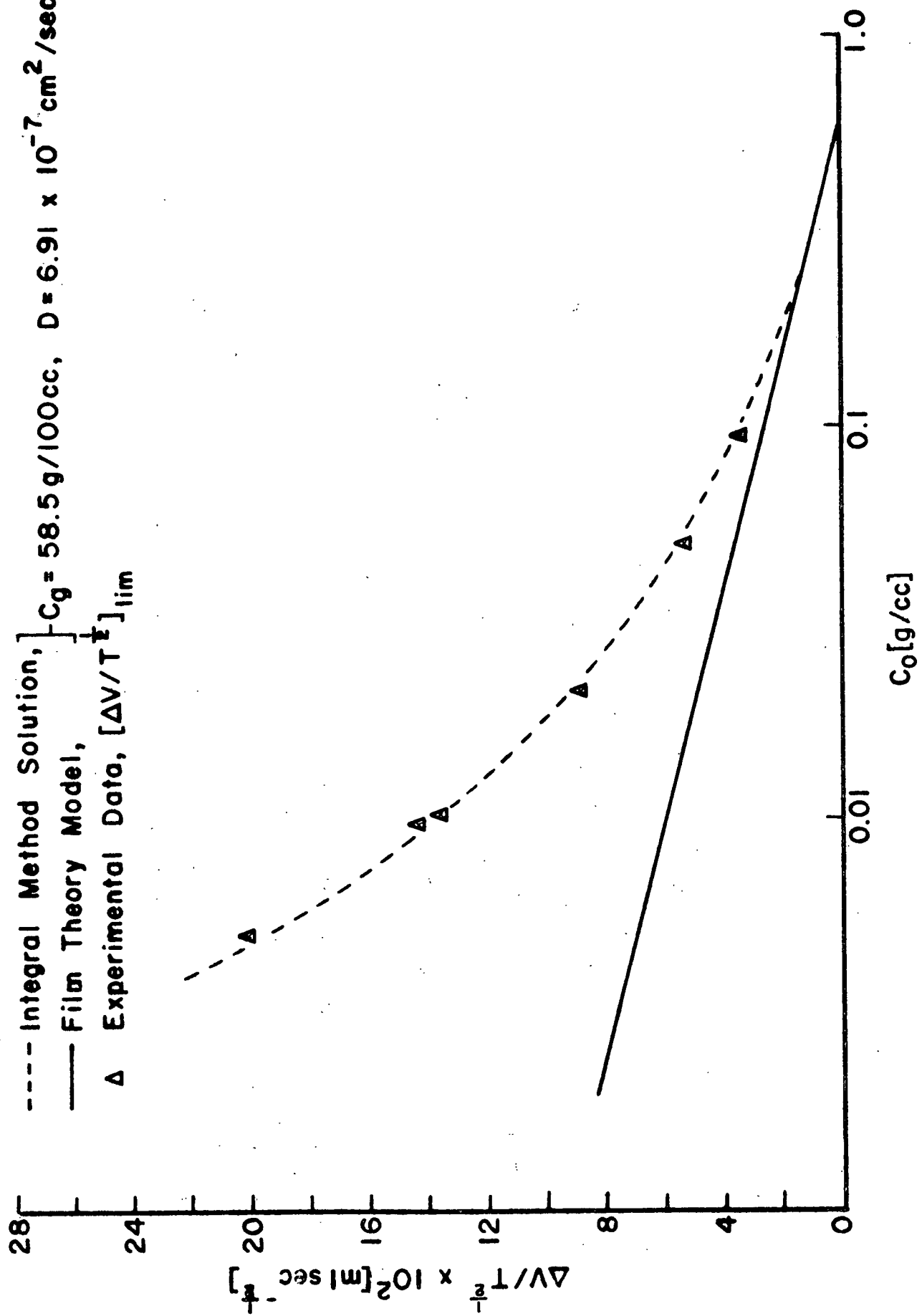


Figure 5. BSA, 0.15M NaCl, 7.4 pH

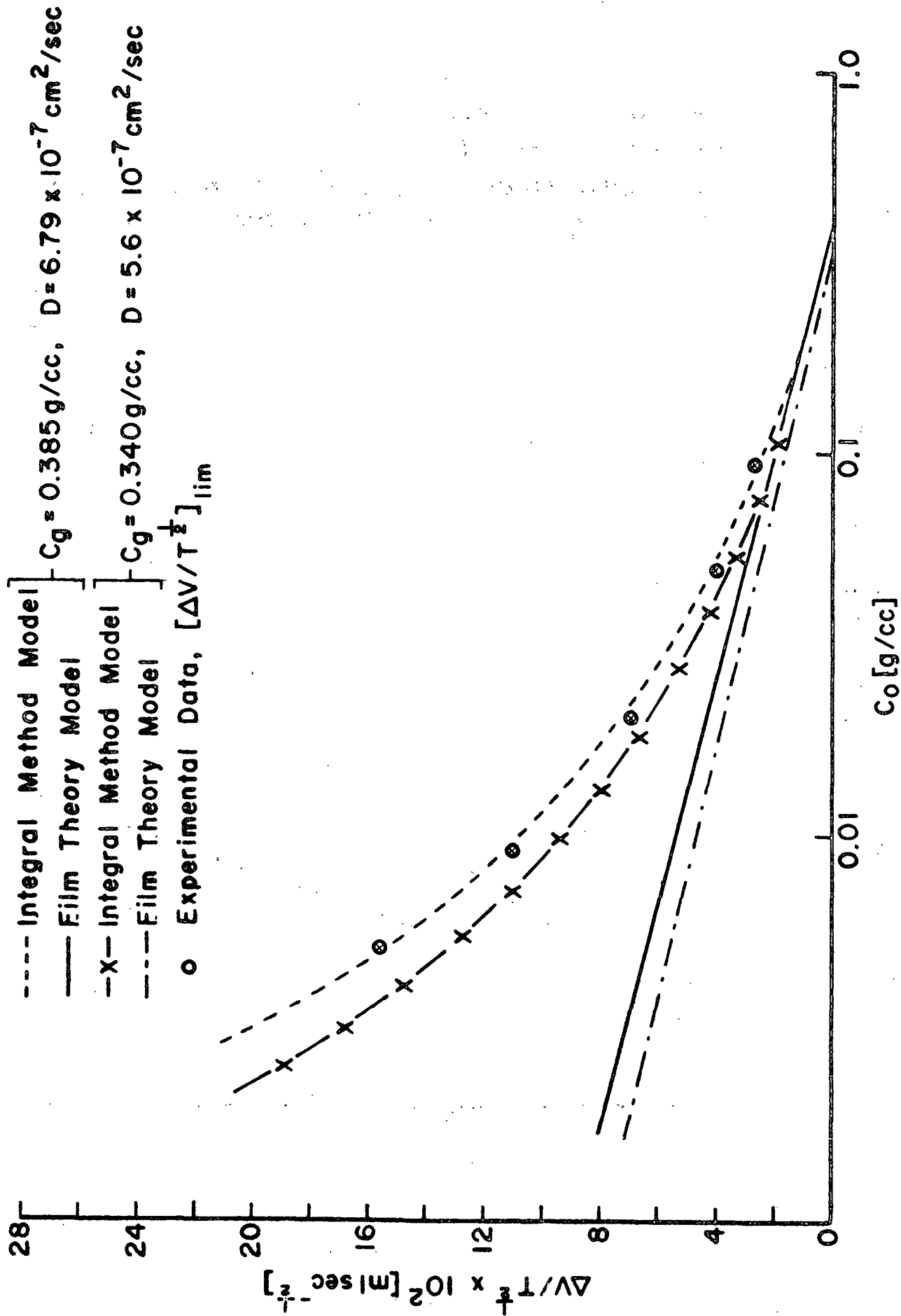


Figure 6. BSA, 0.10M sodium acetate, 4.7 pH

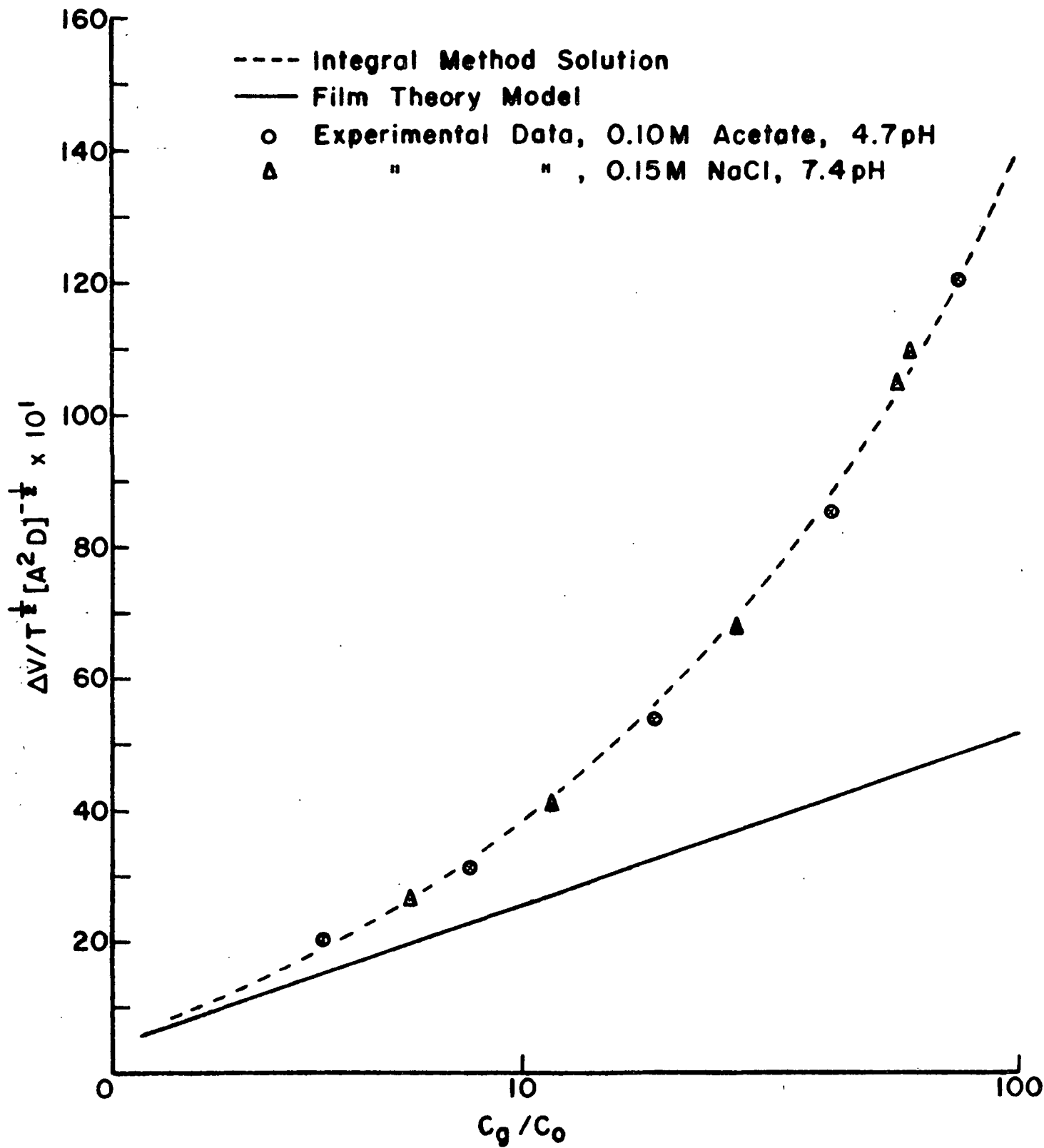


Figure 7. V_w versus c_g/c_o

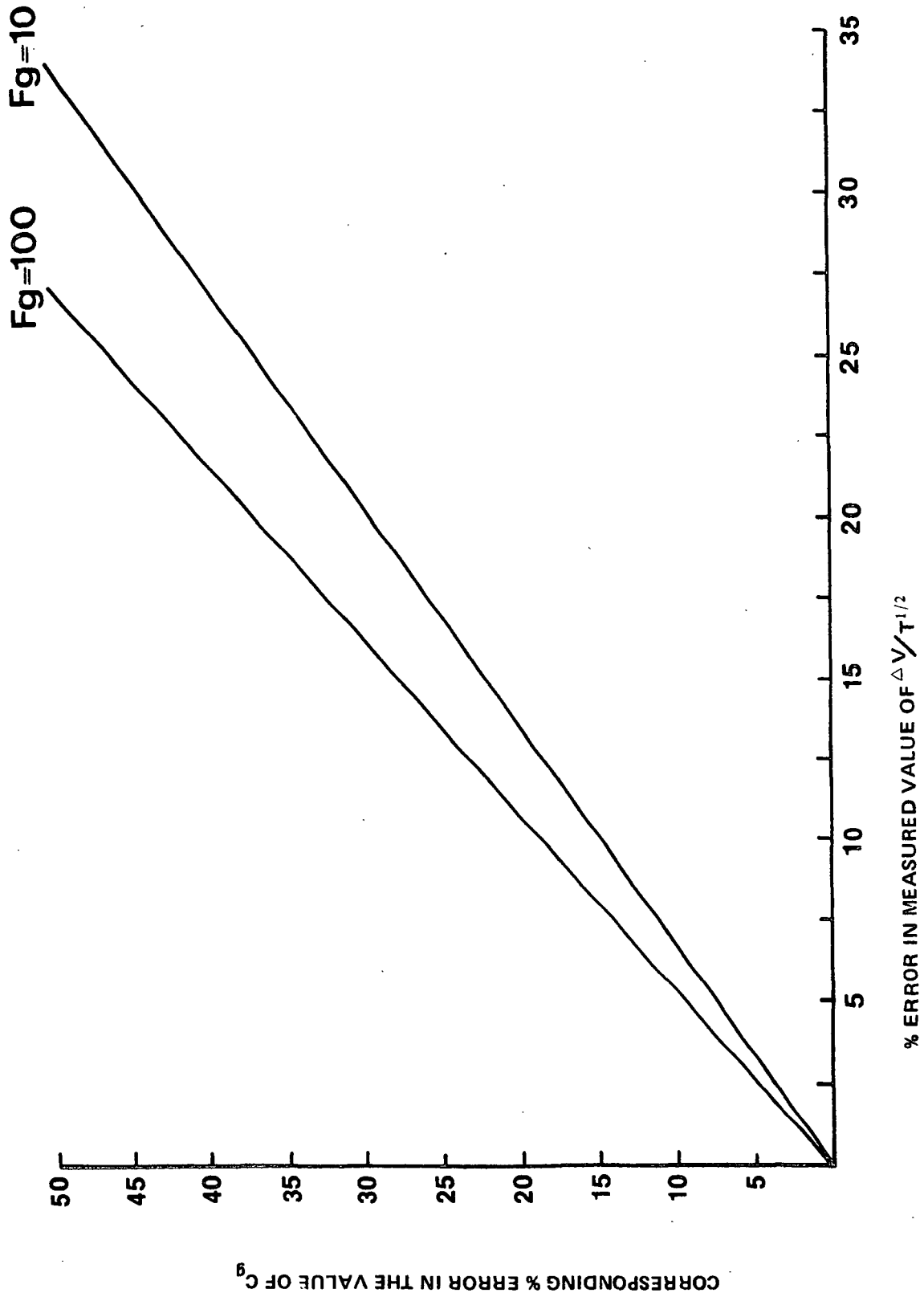


Figure 8. Error analysis - approximate sensitivity of the C_g to change in $\Delta V/T^{1/2}$