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A Comparison of the Coefficients in the Richardson and Zaki's and Steinour's Equations Relating to the Behavior of Concentrated Suspensions

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Abstract

Steinour and Richardson and Zaki proposed relationships to explain the hindered settling phenomena from their independent experiments about 10 years apart. An attempt has been made to compare the coefficients and derive a relationship between Steinour's parameter A and Richardson and Zaki's parameter n. It is possible to express this relationship in the form of an equation involving parameters for which values can be assigned. Theoretically, this derived relationship should be applicable to any sedimenting suspension which obeys both Steinour's and Richardson and Zaki's equations. This derived expression has been evaluated for various experimentally determined values of A and n. The experimental systems which have been tested include calcium carbonate suspensions in water, sucrose–water, and glycerin–water solutions, and ethyl alcohol and magnesium hydroxide suspensions in glycerin–water, sucrose–water and sorbitol–water solutions. The calculated values have been shown to agree well with experimentally predicted values.

INTRODUCTION

The sedimentation behavior of concentrated suspensions has been described by various workers. In the present study, Steinour's empirical equation (*1*) and Richardson and Zaki's equation (*2*) are examined. The relationship between Steinour's parameter A and Richardson and Zaki's parameter n has been mathematically derived. The data obtained from the sedimentation behavior of calcium carbonate and magnesium hydroxide suspensions in various media are presented with a view to test this relationship.

The behavior of a single particle falling in an infinite volume of fluid follows from a consideration of Stokes' law. However, above a certain

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concentration, the fall of any particular particle is "hindered" by the presence of other particles, and the suspension settles as a contracting plug with a well-marked upper boundary. On one side, above this boundary, is a relatively clear supernatent liquid and below the boundary is the settling suspension. Theoretical and empirical relationships lead to a variety of methods for the calculation of the average particle (or floc) radius in the suspension based on simple experiments. The derived relationships are all based on observation of the rate of fall of the interface. Two distinct classes of theories emerge to explain the behavior of the concentrated suspension. The first set of theories regard this problem as essentially a modification which must be applied to the classical equations for dilute suspensions based on Stokes' law. The second set of theories regard the suspension as a packed bed through which a fluid is allowed to flow and is based on the phenomenon of permeability (*3*). In the present study the discussion is primarily centered on Steinour's and Richardson and Zaki's equations which fall under the first set of theories.

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EXPERIMENTAL

The calcium carbonate used in the present study is ACS certified calcium carbonate (C-64) supplied by Fisher Scientific Co., New Jersey. The sucrose used is D(+) sucrose obtained from Sargent-Welch, Skokie, Illinois. The magnesium hydroxide used is Magnesium Hydroxide, N.F., Po., the sorbitol is 70% Sorbitol Solution, USP, and the glycerin is Glycerin, USP, all from Sherman Research Laboratories, Toledo, Ohio. The ethyl alcohol used is Ethyl Alcohol, USP, Dehydrated 200 proof obtained from Pharmco Products, Inc., Dayton, New Jersey.

The hindered settling experiments involve the use of Pyrex measuring cylinders of approximately 250 mL capacity with an internal diameter of 3.6 cm. The total volume of the suspension used throughout the experiments was 150 mL. A scale was attached to the side of the cylinder to ascertain the position of the "sludge line" at any time. It was calibrated in 0.1 cm increments, each 0.1 cm corresponding to 1 mL in the cylinder. The suspension was prepared by adding known amounts of solid calcium carbonate or magnesium hydroxide to the cylinders. The external phase (water, ethanol, or aqueous solutions of glycerin, sorbitol, or sucrose) was then added up to the 100-mL mark. The suspension was allowed to stand overnight to saturate the solid. The next day the volume was made up to 150 mL and the suspension was dispersed. The system was redispersed prior to the hindered settling experiment by inverting the cylinder 20 times (approximately 50–60 s). The actual experiment involved measuring the height of the interface at different time intervals.

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RESULTS AND DISCUSSION

The experimental plots of height of the interface against time for the various systems examined were of the type shown in Fig. 1. This allows the constant rate of fall of the interface (Q) to be determined. An inspection of the plot shows three regions—an initial region (A), a subsequent "linear" region (B), and finally a compressive region (C) in which only a small change takes place when considered against time. Region B is the region from which calculations for either the Stokes' law modification or permeability relationships can be made. It is described as the hindered settling region or as a region where falling particles interact by collision. Lower concentrations of particles would not show this effect and will fall unimpeded. Inspection of Fig. 1 shows that the major portion of the plot is the linear region (B) identified here as hindered settling.

The Modified Stokes' Law Approach

A spherical particle falling by itself and obeying Stokes' law achieves a terminal velocity V_s under gravity given by

$$V_s = \frac{2gr^2(\rho_s - \rho_l)}{9\eta} \tag{1}$$

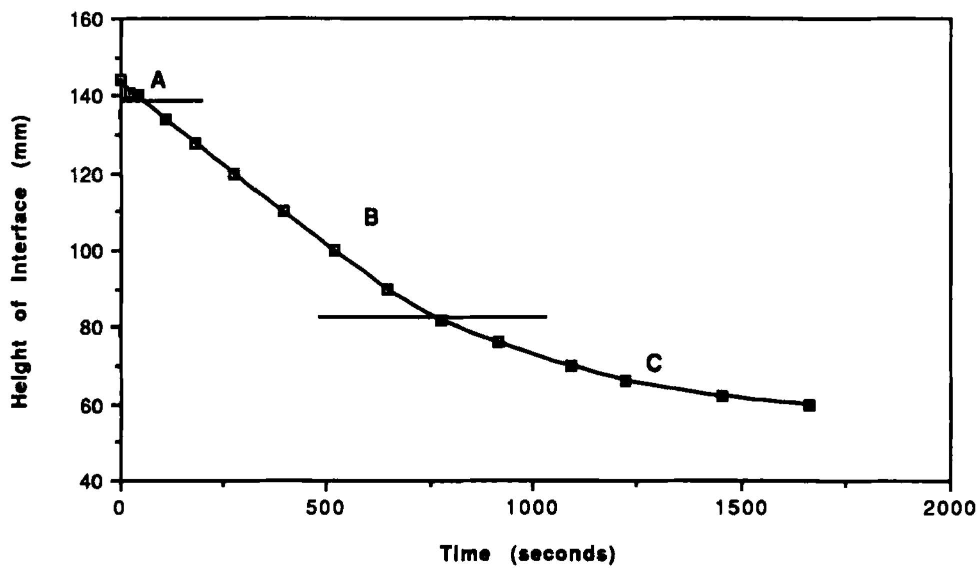

FIG. 1. A typical plot of the height of the interface versus time (quoted here for 35 g $CaCO_3$ in 150 mL of a suspension made up in a 15% w/v sucrose solution).

where r is the radius of the particle; g is the acceleration due to gravity; ρ_s and ρ_l are the densities of the solid and liquid, respectively; and η is the coefficient of viscosity of the liquid.

Steinour (*1*) modified this equation by the introduction of a single function $\theta(\epsilon)$ to account for hindered fall and a term for the porosity ϵ which gives

$$Q = V_s \frac{\epsilon^3}{(1 - \epsilon)} \theta(\epsilon) \tag{2}$$

where Q is the rate of fall of the interface, V_s is the Stokes' terminal velocity given by Eq. (1), and $\theta(\epsilon)$ represents those effects of shape not evaluated by using the hydraulic radius and is given by the equation

$$\theta(\epsilon) = \left(\frac{1 - \epsilon}{\epsilon}\right) \times 10^{-A(1-\epsilon)} \tag{3}$$

where A is a constant for a given system.

Steinour (*1*) thus introduced the empirical equation

$$Q = V_s\epsilon^2 \times 10^{-A(1-\epsilon)} \tag{4}$$

Plots of log Q/ϵ^2 against ϵ allow the calculation of A. Plots for the calcium carbonate data are shown in Figs. 2 and 3, and the A values so obtained are shown in Table 1.

In 1954, Richardson and Zaki (*2*) proposed the equation

$$Q = V_s\epsilon^n \tag{5}$$

where n is a constant. Plots of log Q against log ϵ allow the calculation of n. These plots for calcium carbonate are shown in Figs. 4 and 5, and the n values are shown in Table 2.

It should be noted that some of these relationships have a limiting value such that $Q \rightarrow V_s$ as $\epsilon \rightarrow 1$.

As the initial porosity increases, the solid flux $[Q(1 - \epsilon)\rho_s]$ increases up to a maximum at $\epsilon = \epsilon_1$ and then decreases to zero. The solid flux indicates mass transfer of solid per unit cross-section per unit time down the sedimentation column. Davis et al. (*4*) identified ϵ_1 as the initial liquid volume fraction (initial porosity) of a suspension at which hindered settling commences. An examination of the solid flux relationship and the Rich-

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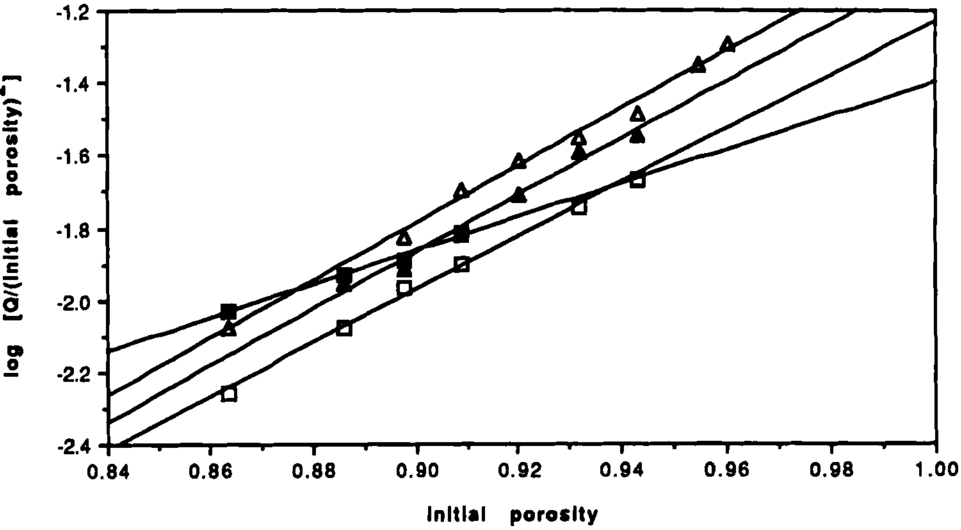

FIG. 2. Plots of log (Q/ϵ^2) versus initial porosity (ϵ) for $CaCO_3$ suspensions in different sucrose systems: (△) 100% water, (▲) 10% w/v sucrose, (□) 15% v/v glycerin, (■) ethyl alcohol.

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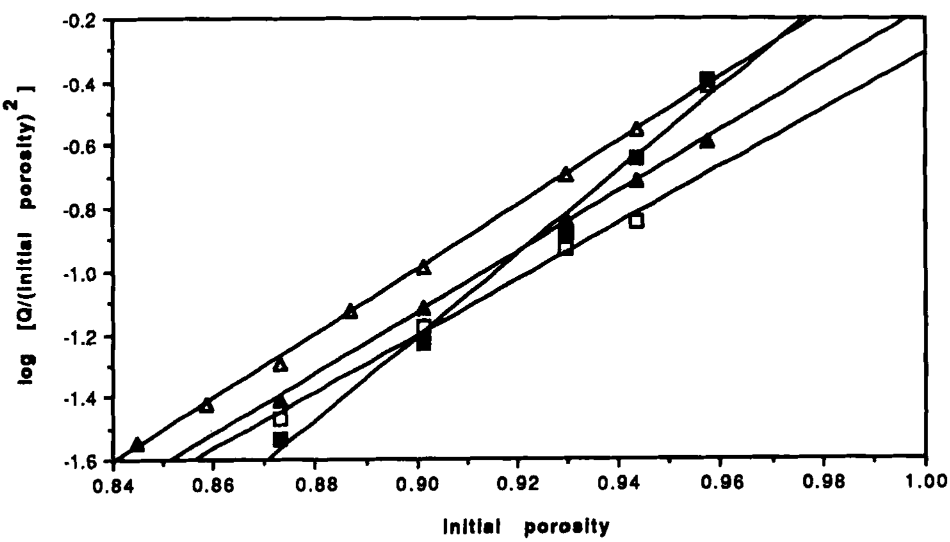

FIG. 3. Plots of log (Q/ϵ^2) versus initial porosity (ϵ) for $Mg(OH)_2$ suspensions in different systems: (△) 100% water, (▲) 10% w/w glycerin, (□) 10% w/w sorbitol, (■) 10% w/w sucrose.

TABLE 1
Steinour's Parameter A for Calcium Carbonate and Magnesium Hydroxide Suspensions in the Presence of Various Liquid Media

System	A
$CaCO_3$–100% water	8.411
$CaCO_3$–10% w/w sucrose	7.818
$CaCO_3$–10% w/w glycerin	7.410
$CaCO_3$–ethyl alcohol, USP	4.704
$Mg(OH)_2$–100% water	10.210
$Mg(OH)_2$–10% w/w glycerin	9.677
$Mg(OH)_2$–10% w/w sorbitol	8.979
$Mg(OH)_2$–10% w/w sucrose	13.250

ardson and Zaki equation (Eq. 5) led them to the conclusion that

$$n = \frac{\epsilon_1}{1 - \epsilon_1} \quad \text{or} \quad \epsilon_1 = \frac{n}{n + 1} \tag{6}$$

where ϵ_1 is the value for ϵ at the maximum of the plot of $Q(1 - \epsilon)$ against ϵ and can be considered to be the lowest concentration at which hindered settling is observed.

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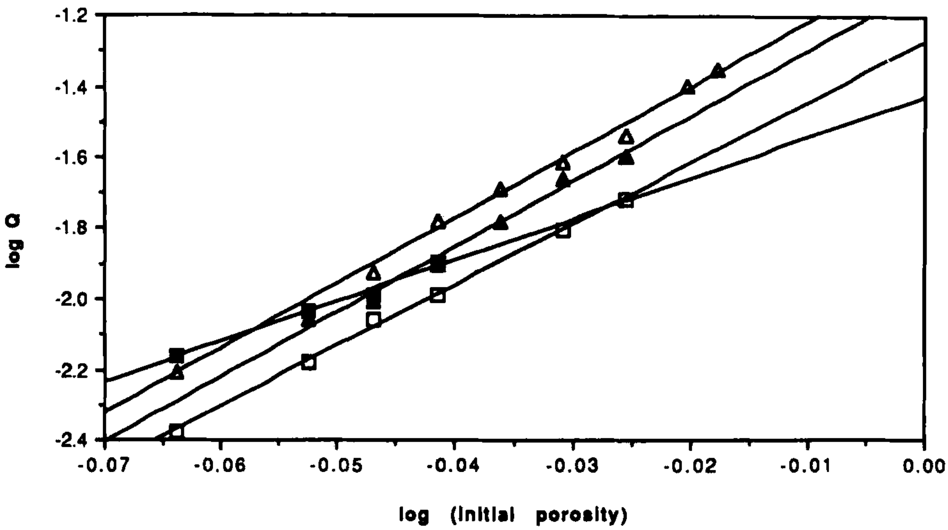

FIG. 4. Plots of log (Q) versus log (initial porosity) for $CaCO_3$ suspensions in different systems: (△) 100% water, (▲) 10% w/v sucrose, (□) 10% v/v glycerin, (■) ethyl alcohol.

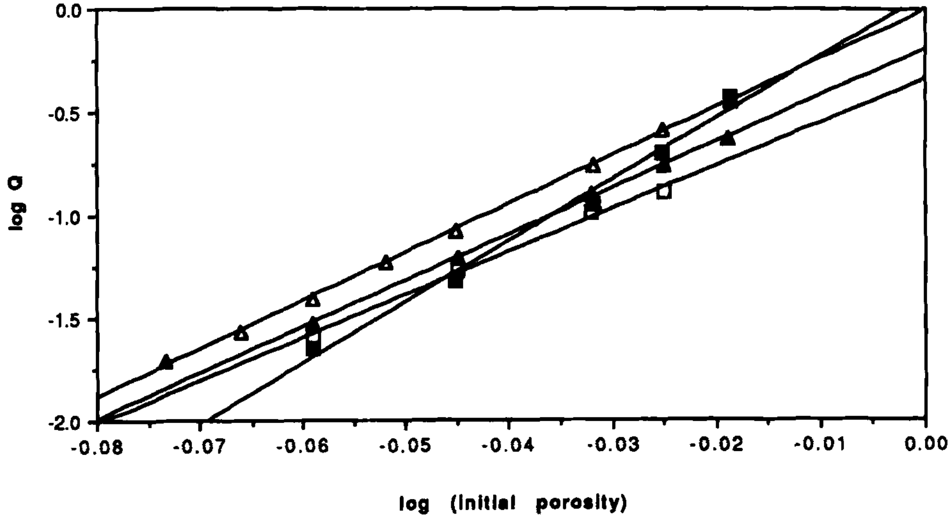

FIG. 5. Plots of log (Q) versus log (initial porosity) for $Mg(OH)_2$ suspensions in different systems: (△) 100% water, (▲) 10% w/w glycerin, (□) 10% w/w sorbitol, (■) 10% w/w sucrose.

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The Relationship between the Coefficients of Steinour's and Richardson and Zaki's Equations

By rearranging Eqs. (4) and (5), we get

$$Q/V_s = \epsilon^2 \times 10^{-A(1-\epsilon)} \tag{7}$$

$$= \epsilon^n \tag{8}$$

TABLE 2
Richardson-Zaki Parameter n and Porosity at Maximum Sedimentation Transfer ϵ_1 for Calcium Carbonate and Magnesium Hydroxide Suspensions in the Presence of Various Liquid Media

System	n	$\epsilon_1 = [n/(n+1)]$
$CaCO_3$–100% water	19.73	0.9518
$CaCO_3$–10% w/v sucrose	18.46	0.9486
$CaCO_3$–10% v/v glycerin	17.42	0.9457
$CaCO_3$–ethyl alcohol, USP	11.58	0.9205
$Mg(OH)_2$–100% water	23.41	0.9590
$Mg(OH)_2$–10% w/w glycerin	22.48	0.9570
$Mg(OH)_2$–10% w/w sorbitol	23.41	0.9544
$Mg(OH)_2$–10% w/w sucrose	29.81	0.9676

If ϵ^n is plotted vs $\epsilon^2 \times 10^{-A(1-\epsilon)}$ (Fig. 6), a straight line should be observed, making an angle of 45° with the x-axis. This will show that both equations apply equally to the system. If the angle is significantly different from 45°, the system favors one or the other equation.

From Eqs. (7) and (8), we get

$$\epsilon^n = \epsilon^2 \times 10^{-A(1-\epsilon)} \tag{9}$$

$$\epsilon^{n-2} = 10^{-A(1-\epsilon)}$$

$$(n - 2) \log \epsilon = A(1 - \epsilon) \tag{10}$$

Steinour's constant (A) can be determined from Richardson and Zaki's constant (n) by rewriting Eq. (10) as

$$A = \frac{(2 - n) \log \epsilon}{1 - \epsilon} \tag{11}$$

where ϵ can be any value between 0 and 1. However, for hindered settling experiments, the practical range for ϵ is approximately between 0.8 and 0.99. Equation (11) has been determined to best fit our data when ϵ is between 0.8 and 0.85.

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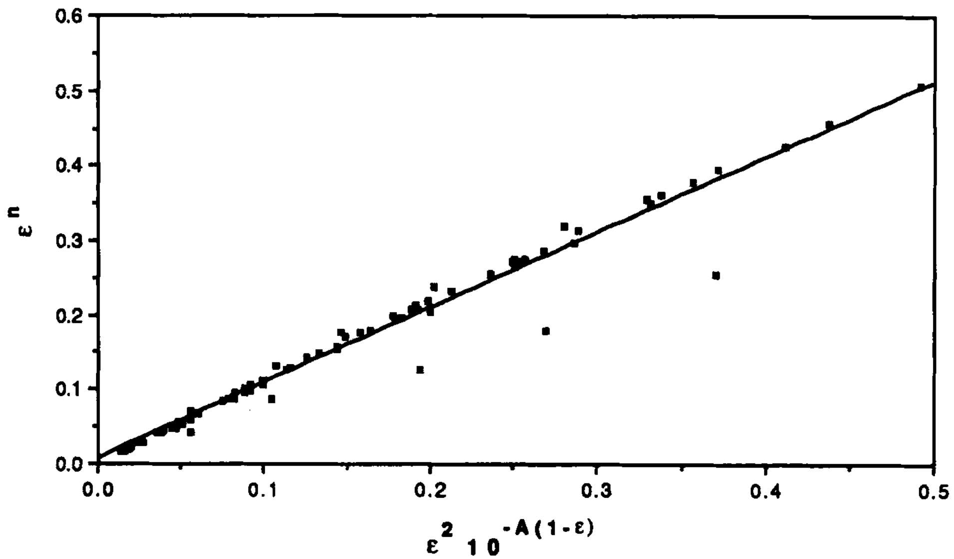

FIG. 6. Plot of ϵ^n versus $\epsilon^2 \times 10^{-A(1-\epsilon)}$ for $Mg(OH)_2$ suspensions in different media.

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At the porosity for maximum solid flux ϵ_1, A can be expressed entirely in terms of ϵ_1. If we substitute the value of n as given in Eq. (6) and put $\epsilon = \epsilon_1$, we get

$$A = \frac{(2 - 3\epsilon_1) \log \epsilon_1}{(1 - \epsilon_1)^2} \tag{12}$$

Since the coefficients of the two equations have been related, the shape factor $\theta(\epsilon)$ can also be determined from Richardson and Zaki's parameter (n) by the equation

$$\theta(\epsilon) = \left(\frac{1 - \epsilon}{\epsilon}\right) \times 10^{(n-2)\log\epsilon} \tag{13}$$

It has been shown that the ϵ_1 value in the simplest of systems, i.e., monodisperse spheres in laminar flow as used by Bhatty et al. (*5*) and Richardson and Zaki (*2*), will be 0.80 or higher. Changing the value of ϵ_1 from 0.80 to 0.99 causes various values of n and A to be generated. This plot is shown in Fig. 7. The equation for the regression analysis line was determined as $n = 2.29A + 1.699$, which gives the final relationship

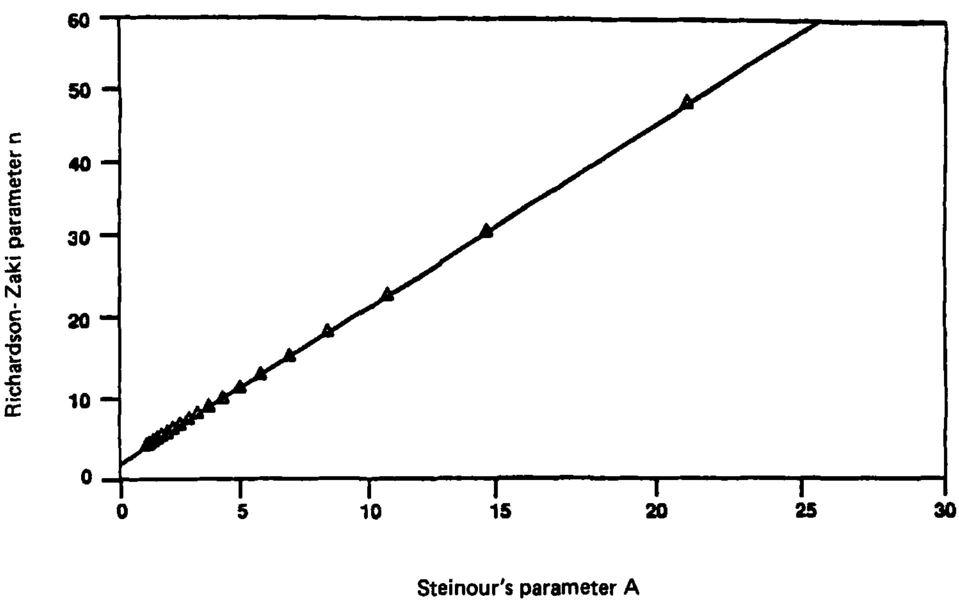

FIG. 7. Plot of Steinour's parameter A vs Richardson-Zaki's parameter n.

TABLE 3
Evaluation of the Relationship between Steinour's Parameter A and Richardson-Zaki's Parameter n

System	Experimental value of A	Experimental value of n	Theoretical Prediction,[a] n
$CaCO_3$–100% water	8.411	19.73	20.96
$CaCO_3$–10% w/v sucrose	7.818	18.46	19.60
$CaCO_3$–10% v/v glycerin	7.410	18.67	18.67
$CaCO_3$–ethyl alcohol, USP	4.704	11.58	12.47
$Mg(OH)_2$–100% water	10.210	23.41	25.08
$Mg(OH)_2$–10% w/w glycerin	9.677	22.48	23.86
$Mg(OH)_2$–10% w/w sorbitol	8.979	23.41	22.26
$Mg(OH)_2$–10% w/w sucrose	13.25	29.85	32.04

[a]The theoretical prediction utilizes the experimental A value and the regression analysis equation ($n = 2.29A + 1.699$) to determine n.

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between n and A. The validity of this relationship was tested by using the actual sedimentation data obtained from calcium carbonate and magnesium hydroxide suspensions in the presence of various liquid media, as shown in Table 3. Table 3 provides direct comparison of the data, which show that the predicted values closely match the experimental values. Theoret-

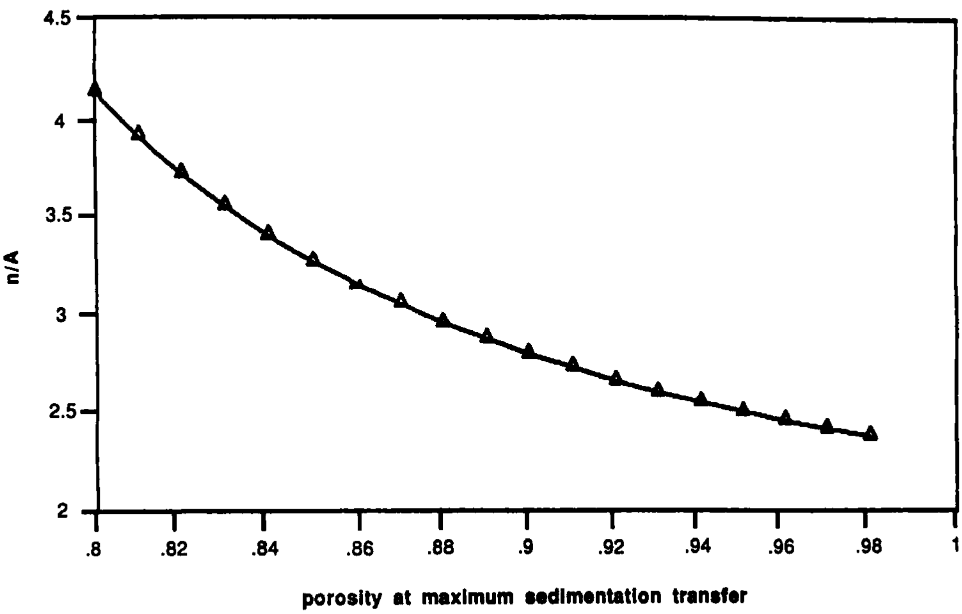

FIG. 8. Plot of n/A vs porosity at maximum sedimentation transfer ϵ_1.

ically, this equation should also be applicable to any sedimenting suspension which obeys both Steinour's empirical equation and Richardson and Zaki's equation. It is interesting to note that n/A varies as ϵ_1 changes, as shown in Fig. 8.

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