DRUG DEVELOPMENT AND INDUSTRIAL PHARMACY, 17(13), 1731-1751 (1991)

HYDRODYNAMICS OF DISSOLUTION IN A NEWTONIAN AND A NON-NEWTONIAN SOLUTION

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ABSTRACT

The dissolution rate of benzoic acid was measured in various concentrations of aqueous solutions of propylene glycol and colloidal solutions of guar gum. In polymeric solutions of guar gum the dissolution rate was influenced primarily by the effect of viscosity on the hydrodynamic shear in the dissolution medium. In the aqueous solutions of propylene glycol the dissolution rate was a complex function of kinematic viscosity, solubility, diffusivity and rotational speed. By means of dimensionless analysis it appears that the difference in the hydrodynamics of the true and colloidal solutions causes a difference in dissolution rate because of dissimilar fluid flow patterns.

INTRODUCTION

It has been demonstrated that the dissolution rate of a nondisintegrating compact in a stirred vessel is decreased in polymeric solutions as the viscosity is increased (1, 2). This may be interpreted in terms of the influence of viscosity on diffusivity. Viscosity calculated by the Stokes-Einstein equation appeared to fit the experimental data better than bulk viscosity measured by a viscometer (1). Florence et al. (3) concluded that dissolution rate into viscous solutions was not a simple function of the diffusivity because the resistance encountered by the solute molecules in polymeric solutions is not directly related to measured bulk viscosity and the thickness of the diffusion layer is dependent on the diffusion coefficient.

Nelson and Shah (4) reported that the decrease in dissolution rate of ethyl p-aminobenzoate in aqueous solutions of sucrose was related to the diffusivity of the solute; however, the dissolution rate in solutions of hydroxypropyl cellulose remained constant under a fixed fluid flow because of the negligible effect of the polymer on the diffusivity of the solute. A change in fluid flow rate altered the dissolution rate and was correlated with the rate of shear.

The slowing of dissolution rate with increased viscosity may be caused by two mechanisms. In solutions of small molecules the microviscosity is inversely proportional to the diffusivity and as the viscosity is increased and the diffusion coefficient becomes smaller, the dissolution rate is slowed. In dilute solutions of a polymer the solute molecules infrequently encounter a polymeric chain during diffusion, and consequently, the bulk viscosity has little effect on diffusivity. In the second mechanism the bulk viscosity affects the flow characteristics of the dissolution medium with a reduction of shear rate in the vicinity of the solid solute as the viscosity is increased resulting in a slower dissolution rate.

The purpose of this study was to consider the extent to which each of the two mechanisms influenced dissolution in aqueous solutions of propylene glycol and colloidal solutions of guar gum. Following the suggestion of Carstensen (5) dimensionless parameters were used to characterize the hydrodynamics of dissolution into a stirred medium.

EXPERIMENTAL

The methodology and procedures have been reported (1, 6). Under sink conditions the dissolution rates of benzoic acid (Fisher Scientific Co., Lot 783313) from spherical 0.956 ± 0.001 cm compacts compressed at 2270 kg of force were determined in various concentrations of aqueous propylene glycol (Barton Solvent, Lot CB16171087) and guar gum (Colony Import & Export Corp., Lot 0-59-241) solutions at 25°C.

RESULTS AND DISCUSSION

Dissolution Rate and Mass Transfer Parameters. For guar gum colloidal solutions that exhibit pseudoplastic behavior it was shown in a previous report (6) that for dilute solutions at rotational speeds of the Brookfield viscometer exceeding 10 rpm, the upper Newtonian viscosity was attained (7). The shear rates

TABLE 1

Parameters of Aqueous Guar Gum and Propylene Glycol Solutions and Benzoic Acid in These Solutions at 25°C

Concentration, % w/v	Density, g/cm^3	Viscosity, cps	10^6 Diffusion Coefficient, cm^2/s	Solubility, mg/mL
Guar Gum Solution				
0.1	0.998	5.46	5.875	3.27
0.2	0.998	13.06	5.802	3.29
0.3	0.998	34.92	5.729	3.24
Propylene Glycol Solution				
10.0	1.005	2.88	8.797	4.26
20.0	1.010	3.33	6.137	5.44
40.0	1.030	5.88	2.387	14.33

encountered in the dissolution apparatus also produced the upper Newtonian viscosity, which may be considered as the bulk viscosity of the polymeric solution.

Aqueous solutions of propylene glycol are true solutions consisting of small molecules of solvent and solute, and the viscosities of the solutions are independent of the applied shear rates (Newtonian behavior). The viscosites and densities of various concentrations of guar gum and aqueous propylene glycol solutions are given in Table 1. The high viscosity of guar gum solutions at low concentrations of guar gum is due to the entanglement of the long chains of the macromolecules.

The dissolution rates of benzoic acid in guar gum solutions and in aqueous propylene glycol solutions at various rotational speeds are given in Tables 2 and 3. For the guar gum solutions at each speed the dissolution rate is decreased as the viscosity is increased. For the dissolution of benzoic acid in propylene .pat glycol solutions at each speed as the viscosity of the aqueous propylene glycol solutions is increased, the dissolution rate does not necessarily decrease. Thus, for the true solutions in aqueous propylene glycol the dissolution rate is not solely a function of viscosity.

As the speed of rotation is increased, the dissolution rate is faster for all viscosites studied as shown in Tables 2 and 3. As illustrated in Table 1 the solubility and diffusion coefficient of benzoic acid in guar gum solutions did not change measurably as a result of the low volume fraction of polymer in dilute solutions. The influence of polymeric molecules on the diffusivity of the benzoic acid only occurs when the diffusant encounters an obstruction due to a polymeric chain. As the volume fraction of polymer is very low in dilute solutions, the change in diffusivity of the diffusant is insignificant compared to the marked change of the viscosity and flow characteristics.

In contrast as shown in Table 3 the dissolution rate of benzoic acid is not always faster in lower concentrations of

TABLE 2

Mass Transfer Data* of Benzoic Acid in Various Concentrations of Aqueous Guar Gum Solutions at 25°C

Concentration, % w/v	n, rpm	ωr, cm/s	R, $mg/cm^2/hr$	10^4 K, cm/s	Re, ωrdρ/η	Sh, Kd/D	Sc, η/ρD
0.1	50	7.85	6.14	5.22	1808.83	1119.99	9312.24
	100	15.71	14.07	11.97	3617.66	2566.48	
	150	23.56	20.77	17.67	5426.49	3789.22	
	324	50.89	38.76	32.97	11721.22	7070.14	
	500	78.54	44.37	37.73	18088.31		
0.2	50	7.85	4.01	3.39	756.22	735.64	22554.59
	100	15.71	7.23	6.10	1512.44	1324.65	
	150	23.56	11.39	9.61	2268.66	2087.18	
	324	50.89	28.01	23.64	4900.30	5133.62	
	500	78.54	28.29	23.88	7562.19	5185.56	
0.3	50	7.85	2.00	1.71	282.82	376.88	61075.20
	100	15.71	3.07	2.63	565.65	577.89	
	150	23.56	5.38	4.61	848.47	1013.81	
	324	50.89	12.24	10.49	1832.70	2306.52	
	500	78.54	20.37	17.46	2828.24	3839.18	

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[*] see Appendix for description of symbols

TABLE 3

Mass Transfer Data* of Benzoic Acid in Various Concentrations of Aqueous Propylene Glycol Solutions at 25°C

Concentration, % w/v	n, rpm	ωr, cm/s	R, $mg/cm^2/hr$	10^4 K, cm/s	Re, $\omega r d \rho/\eta$	Sh, Kd/D	Sc, $\eta/\rho D$
10.0	50	7.85	12.76	8.32	3453.29	1191.13	3257.56
	100	15.71	22.88	14.91	6906.59	2137.07	
	150	23.56	34.90	22.75	10359.88	3259.03	
	324	50.89	43.03	28.05	22377.35	4017.53	
	500	78.54	48.33	31.51	34532.95	4513.03	
20.0	50	7.85	12.38	6.32	3001.49	1298.23	5372.38
	100	15.71	20.89	10.67	6002.98	2189.69	
	150	23.56	32.27	16.48	9004.48	3383.43	
	324	50.89	41.59	21.24	19449.67	4360.16	
	500	78.54	47.68	24.35	30014.92	4998.96	
40.0	50	7.895	12.14	2.35	1733.48	1242.97	23915.95
	100	15.71	23.04	4.47	3466.97	2357.98	
	150	23.56	31.44	6.10	5200.45	3217.79	
	324	50.89	47.85	9.28	11232.98	4898.16	
	500	78.54	59.73	11.58	17334.84	6113.49	

*see Appendix for description of symbols aqueous propylene glycol solutions with a low viscosity than in higher concentrations possessing a higher viscosity. The parameters listed in Table 1 change with the concentration of propylene glycol. For example, the solubility of benzoic acid is increased as the concentration of propylene glycol is increased.

In solutions of small molecules the diffusivity is inversely proportional to viscosity (Stokes-Einstein relation), and hence, the diffusion coefficient of benzoic acid in aqueous propylene glycol solutions is decreased with an increase in concentration of propylene glycol as shown in Table 1. The dissolution rate of benzoic acid in various concentrations of aqueous propylene glycol is a combined function of kinematic viscosity, solubility, diffusion coefficient and rotational speed.

Hydrodynamics. The general equation for forced-convection mass transfer in an agitated fluid is (see Appendix)

$$\frac{Kd}{D} = C\left(\frac{\eta}{\rho D}\right)^{\alpha} \left(\frac{\omega r d \rho}{\eta}\right)^{\beta} \qquad \text{(Eq. 1)}$$

or

$$Sh = C\,(Sc)^{\alpha}\,(Re)^{\beta} \qquad \text{(Eq. 2)}$$

in which Sh is the Sherwood number, Sc is the Schmidt number, Re is the Reynolds number, and C, α and β are coefficients.

The dissolution rates of benzoic acid in various concentrations of aqueous guar gum and propylene glycol solutions at various rotational speeds are given in Tables 2 and 3 from which the values of the three dimensionless parameters were computed. Assuming the diffusion coefficient of benzoic acid in a particular medium is independent of the shear rate, the Schmidt number is constant for each concentration as under isothermal conditions η, ρ and D are constant. Therefore, Eq. 2 reduces to

$$Sh = C \quad (Re)^{\beta} \qquad \text{(Eq. 3)}$$

In its logarithmic form

$$\log (Sh) = \log C_1 + \beta \log (Re) \qquad \text{(Eq. 4)}$$

Theoretically a plot of the logarithm of Sherwood number against the logarithm of the Reynolds number is linear with a slope of β. As shown in Figure 1 for solutions of guar gum the slopes of the lines are unity so that

$$Sh = C_1 \ (Re)^{1.0} \qquad \text{(Eq. 5)}$$

The deviation of the curve from linearity at high Reynolds numbers probably arises due to the difference in hydrodynamic flow. At a low Reynolds number the flow in the dissolution apparatus is laminar; however, at high Reynolds numbers the flow

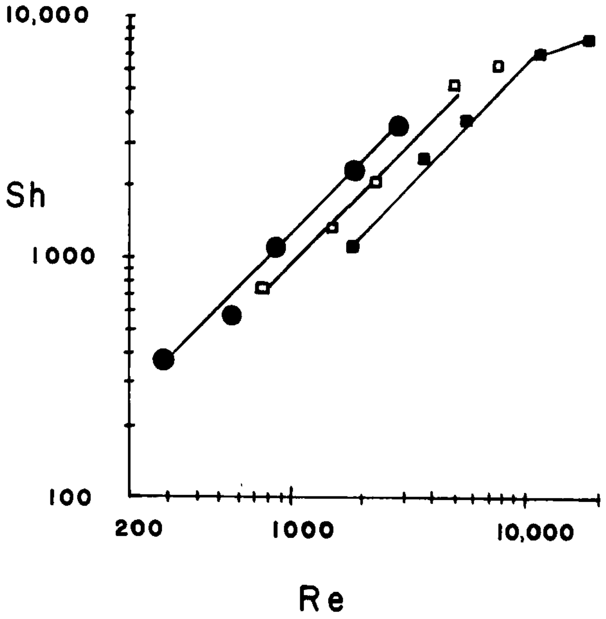

Figure 1. Log-log relationship of Sherwood number and Reynolds number for solutions of guar gum. Key: ■ , 0.1%; □ , 0.2%; and ● , 0.3% w/v.

is turbulent. The dissolution kinetics in laminar and turbulent flow are not identical.

A similar plot is shown in Figure 2 for the dissolution of benzoic acid in aqueous propylene glycol solutions. The value of the Reynolds number at which the curve deviates from linearity (critical Reynolds number) is decreased as the concentration of propylene glycol is increased. Using the average slope

$$Sh = C_2 \, (Re)^{0.88} \qquad \text{(Eq. 6)}$$

The value of the Schmidt number increases as the concentration (and viscosity) of the aqueous propylene glycol

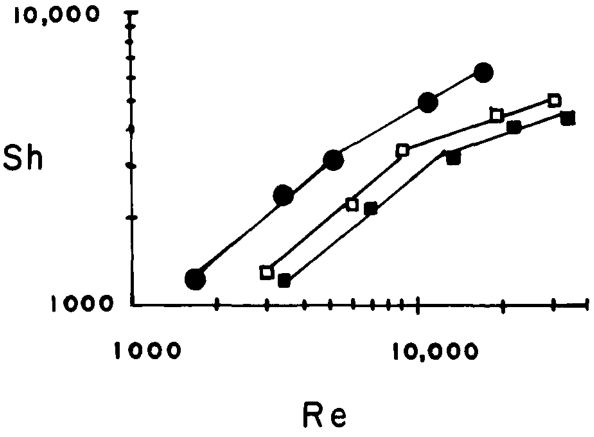

Figure 2. Log-log relationship of Sherwood number and Reynolds number for aqueous solutions of propylene glycol. Key: ■ , 10% ☐ , 20%; and ● , 40% w/v.

solution increases, and consequently, values of the slope of the linear portion of the curve becomes greater. Thus, there is a tendency as the solution becomes more viscous for the slopes of the two linear curves to approach a single value (form a single straight line).

As seen in Figures 1 and 2 for a given Schmidt number the value of the Sherwood number increases proportionally on a logarithmic scale with an increase of Reynolds number, and then the increase of the Sherwood number with respect to the Reynolds number slows at a critical Reynolds number to another linear relationship. This phenomenon may be attributed to the hydrodynamics in the dissolution apparatus as a velocity profile is a function of position and time. Above the critical Reynolds number the spherical benzoic acid compact was restricted in movement and did not move freely throughout the dissolution medium. In less viscous fluids (aqueous propylene glycol solutions) the spherical compact moved freely in the dissolution medium.

In a diffusion layer model, the thickness of the diffusion layer is decreased as the agitation is increased. However, when the speed is increased to a certain value, further increases in speed become progressively less effective in reducing the thickness of the diffusion layer. Thus, in Figures 1 and 2 after the critical Reynolds number is reached, the curve has a concave, downward profile.

In the region of laminar flow for colloidal solutions of guar gum

$$Sh = C\ (Re)^{1}\ (Sc)^{\alpha} \qquad \text{(Eq. 7)}$$

and for aqueous propylene glycol solutions

$$Sh = C\ (Re)^{0.88}\ (Sc)^{\alpha} \qquad \text{(Eq. 8)}$$

To evaluate α the Sherwood numbers calculated at some fixed Reynolds numbers are plotted on log-log grids against the corresponding Schmidt numbers as shown in Figures 3 and 4 utilizing the data in Table 4. The slopes for the aqueous guar gum solutions range from 0.336 to 0.344 with correlation coefficients exceeding 0.993. The slopes for the aqueous

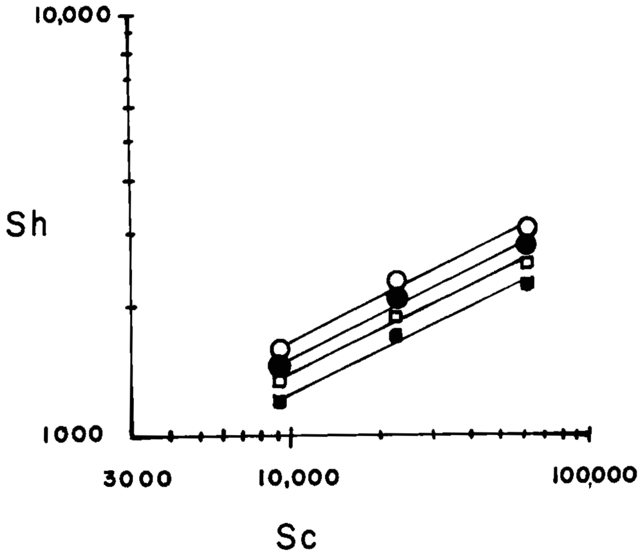

Figure 3. Log-log relationship of Sherwood number to Schmidt number for solutions of guar gum. Key: Reynolds number: ■ , 1800; □ , 2000; ● , 2200; and ○ , 2400.

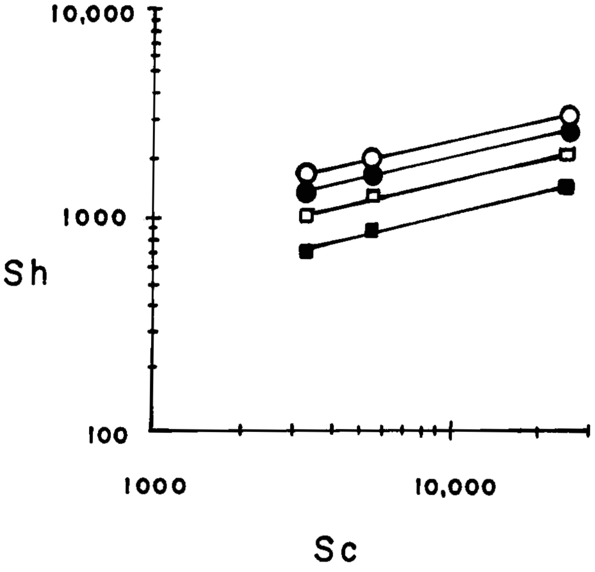

Figure 4. Log-log relationship of Sherwood number to Schmidt number for aqueous solutions of propylene glycol. Key: Reynolds number ■ , 2000; □ , 3000; ● , 4000; and ○ , 5000.

TABLE 4

Schmidt and Sherwood Numbers for Various Reynolds Numbers

Concentration, % w/v	Re	Sh	Sc
Aqueous Guar Gum Solutions			
0.1	1800	1200.33	9312.24
	2000	1331.16	
	2200	1461.76	
	2400	1592.14	
0.2	1800	1709.73	22554.59
	2000	1908.88	
	2200	2108.95	
	2400	2309.85	
0.3	1800	2262.77	61075.20
	2000	2524.02	
	2200	2786.24	
	2400	3049.35	
Aqueous Propylene Glycol Solutions			
10.0	2000	716.46	3257.56
	3000	1035.45	
	4000	1344.64	
	5000	1646.74	
20.0	2000	898.13	5372.38
	3000	1272.45	
	4000	1629.27	
	5000	1973.61	
40.0	2000	1421.74	23915.95
	3000	2024.80	
	4000	2602.16	
	5000	3161.14	

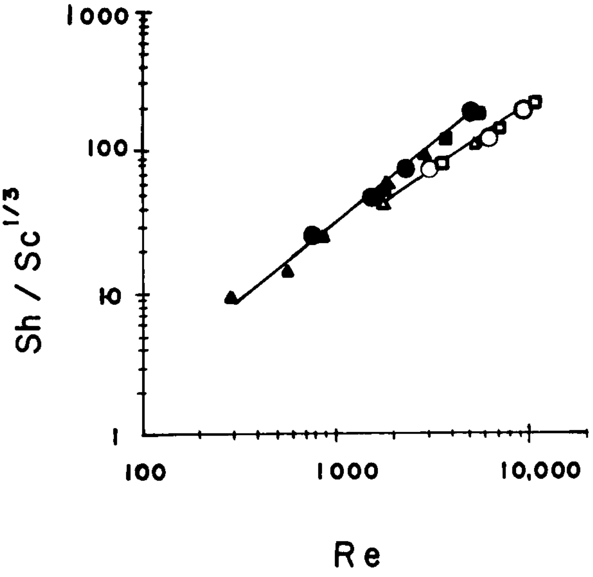

Figure 5. Log $[(Sh)/(Sc)^{0.333}]$ as a function of log (Re) for aqueous propylene glycol and guar gum solutions. Key: Guar gum: ■ , 0.1%; ● , 0.2%; and ▲ , 0.3% w/v. Propylene glycol: □ , 10%; ○ , 20%; and △ , 40% w/v.

propylene glycol solutions range from 0.324 to 0.335 with correlation coefficients exceeding 0.996. It appears that for both the colloidal and the true solutions $\alpha = 0.33$, if the Reynolds number is small (laminar flow).

The experimental and theoretical reports on mass transfer in Newtonian fluids (8) and in non-Newtonian fluids (9, 10) support the experimental result that the Sherwood number is proportional to the cube root of the Schmidt number. Thus, for Newtonian and non-Newtonian fluids

$$Sh = C\ (Sc)^{0.33}\ (Re)^{\beta} \qquad \text{(Eq. 9)}$$

for dissolution of a solid into laminar flow agitation.

Equation 9 may be rearranged and expressed in logarithmic form

$$\log\ [Sh/(Sc)^{0.33}] = \log C + \beta \log (Re) \qquad \text{(Eq. 10)}$$

In Figure 5 a plot of $\log\ [Sh/(Sc)^{0.33}]$ against $\log (Re)$ is linear with a slope of β. The values of β are 1.0 and 0.89 for guar gum solutions and aqueous propylene glycol solutions, respectively, and agree well with those evaluated from Figures 1 and 2.

From the above analysis the equation for forced-convection mass transfer of benzoic acid in the dissolution apparatus described is for non-Newtonian, colloidal solutions of guar gum

$$Sh = 0.029\ (Re)\ (Sc)^{0.33} \qquad \text{(Eq. 11)}$$

and for Newtonian solutions of aqueous propylene glycol

$$Sh = 0.058\ (Re)^{0.89}\ (Sc)^{0.33} \qquad \text{(Eq. 12)}$$

Although attempts have been made to develop a single mass transfer equation for Newtonian and non-Newtonian fluids (11, 12), deviations occur at low or high Reynolds numbers, and it seems that each system is best represented by its own equation because the flow pattern with diluted polymeric solutions is different from that with Newtonian fluids (13-14).

In this study the effect of the Schmidt number on the Sherwood number is the same for colloidal, polymeric solutions and true solutions. The effect of the Reynolds number on the Sherwood number is different in dilute polymeric solutions than in Newtonian solutions as seen in Eq. 11 and 12. It appears that macromolecules in solution not only increase the viscosity (while having minimal effect on diffusivity) but alter the fluid flow pattern.

ACKNOWLEDGMENTS

This study was abstracted in part from a dissertation submitted by Shu-Hwa Chang to the Graduate College, the University of Iowa, in partial fulfillment of the Doctor of Philosophy degree requirement.

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APPENDIX

Dimensionless Analysis. Dimensionless analysis is a method by which the experimental data may be correlated with a set of dimensionless parameters. If the variables are expressed in the same dimensions, they may be manipulated mathematically so that the separate variables can be reduced to a smaller number of independent dimensionless groups of variables. Thus, the variables may be arranged into a dimensionless equation that predicts how the variables are related.

In the hydrodynamics of forced-convection mass transfer at sink conditions the pertinent variables are dissolution rate (R) or mass transfer coefficient (K), solubility (C_s), diffusion coefficient (D), kinematic viscosity (ν) or coefficient of viscosity (η), density (ρ), velocity (V) or rotational speed (ω) of fluid flow, and characteristic length (d). The dissolution rate is directly proportional to the solubility of a solid in the dissolution medium (16). The proportionality constant is known as the mass transfer coefficient (K). The significant variables can be included in a functional equation

$$K = \frac{R}{C_s} = f(d,\ \rho,\ D,\ \eta,\ V) \qquad \text{(Eq. 13)}$$

The dimensions of the variables are

$$\begin{aligned}
[K] &= L/T \\
[d] &= L \\
[\rho] &= M/L^3 \\
[D] &= L^2/T \\
[\eta] &= M/LT \\
[V] &= L/T
\end{aligned}$$

The mass term can be eliminated from Eq. 13 by combining ρ with all variables that have the mass dimension, $[\eta/\rho] = L^2/T$, such that M is cancelled

$$K = f_1\left(d,\ D,\ \frac{\eta}{\rho},\ V\right) \qquad \text{(Eq. 14)}$$

The time dimension may be eliminated by combining D with the variables that have a time dimension so

$$K = f_2\left(d,\ \frac{\eta}{\rho D},\ \frac{V}{D}\right) \qquad \text{(Eq. 15)}$$

where

$$[K/D] = 1/L$$
$$[d] = L$$
$$[\eta/\rho D] = 1$$
$$[V/D] = 1/L$$

The remaining groups of variables have only the dimension of length. These are made dimensionless by combining with the length variable d

$$\frac{Kd}{D} = f_3\left(\frac{\eta}{\rho D}, \frac{Vd}{D}\right) \qquad \text{(Eq. 16)}$$

The Reynolds number (Re) is a recognized parameter in hydrodynamic flow to express the relationship of viscous forces to velocity, density and length (d). By dividing Vd/D by $\eta/\rho D$ Eq. 16 has the form

$$\frac{Kd}{D} = f_4\left(\frac{\eta}{\rho D}, \frac{Vd\rho}{\eta}\right) \qquad \text{(Eq. 17)}$$

in which

$$\frac{Kd}{D} = \text{Sherwood number (Sh)}$$

$$\frac{\eta}{\rho D} = \text{Schmidt number (Sc)}$$

$$\frac{Vd\rho}{\rho} = \text{Reynolds number (Re)}$$

The variables of Eq. 13 have been reduced to three dimensionless parameters, which are related

$$\frac{Kd}{D} = C\left(\frac{\eta}{\rho D}\right)^{\alpha}\left(\frac{Vd\rho}{\eta}\right)^{\beta} \qquad \text{(Eq. 18)}$$

in which C, α and β are coefficients of a system.

The dissolution apparatus used in this study was a beaker containing a fixed volume of liquid that was rotated about a vertical axis. Thus the velocity term V of Eq. 18 may be expressed as the product of the angular velocity (ω) in radians per second and the radius, which is one half the length of the agitator blade so that

$$\frac{Kd}{D} = C\left(\frac{\eta}{\rho D}\right)^{\alpha}\left(\frac{\omega rd\rho}{\eta}\right)^{\beta} \qquad \text{(Eq. 19)}$$

in which $\omega rd\rho/\eta$ is a modified Reynolds number. All variables except C, α and β may be determined by independent methods. The coefficients may be evaluated by determining the mass transfer coefficients in solutions of various viscosities and at various rotational speeds.