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Mass Transfer of Water from Single Thoria Sol Droplets Fluidized in 2-Ethyl-1-hexanol

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The rate at which water is extracted from thoria sols was investigated by fluidizing single thoria sol droplets in 2-ethyl-1-hexanol (2EH) and measuring the diameter of a droplet over a period of time until shrinkage no longer occurred. Diameter data from both water and sol drops were obtained at 25°C. The experimental variables were initial drop diameter (0.1 to 0.2 cm), sol molarity (0 to 2.5 $\underline{M}$ ThO_2), and water concentration in the 2EH (2-12 mg./cc.). The water and sol droplet data were correlated by Equation (5). The single relationship for the fluidized water and sol drops verified that an organic-phase film surrounding the drop is the rate-controlling resistance. The sphere Reynolds number was based on the approach velocity and varied from 0.4 to 14. The Schmidt number for the system was fixed at 35,700. During the extraction of water, the mass transfer coefficients for fluidized sol drops were found to depend only on the molarity of the sol. By expressing the mass transfer coefficients as a function of the density difference between the aqueous sol and the organic phase, an equation was derived to predict the gelation time required for any initial sol molarity and drop diameter fluidized in 2 EH at 25°C.

The sol-gel process which was developed at the Oak Ridge National Laboratory is a method for preparing a wide variety of ceramic fuel materials for use in nuclear reactors. As compared with conventional preparation procedures, the sol-gel process has at least three distinct advantages: simplicity, flexibility, and a low calcination temperature for obtaining particles of near theoretical density (*4*).

The original objective of the sol-gel process was to produce thoria-urania fragments suitable for vibratory compaction in metal tubes; however, during the past five years emphasis has been shifted toward the preparation of spherical particles, or microspheres. Microspheres are prepared by dispersing uniformly sized drops of the appropriate sol into a partially miscible alcohol such as 2-ethyl-1-hexanol (2EH). The sol droplets must be fluidized in the organic phase until enough water is extracted from the aqueous sol to cause gelation. After drying, the gelled spheres are calcined at 1,150°C. to yield an oxide product having a density within 1% of theoretical (*10*).

In this study, various sizes of thoria sol droplets of different initial molarities were fluidized, and the diameter of a particular droplet was measured as a function of time until shrinkage no longer occurred (3). Mass transfer coefficients were determined from the decrease in drop diameter over a period of time for different water concentrations in the 2EH. Diameter data from droplets of both water and sol were obtained in order to test the validity of a mass transfer model based on an organic-phase film as the controlling resistance. In most of the runs, either 0.01 or 0.1 vol. % Ethomeen S/15 was added to the 2EH to produce a rigid sol droplet having no induced circulation. The mass transfer results obtained when this surfactant was present in the organic phase are representative of the conditions that are proposed for a production microsphere column.

LITERATURE REVIEW

The processes by which mass may be transferred through a fluid film surrounding a sphere are radial diffusion and natural and forced convection. For any given problem, these three transport processes may act independently or in different combinations, depending on the flow and diffusional characteristics of the system.

For an infinitely small sphere in a stagnant fluid, mass transfer will occur by radial diffusion alone (*13*). As the size of the sphere increases, natural convection currents are induced in the surrounding fluid as a result of the density difference between the surface fluid and bulk solvent (*6*). Forced convection closely resembles natural convection except that the flow pattern is imposed upon the fluid by an external force. Many experimental data on forced convection mass transfer for rigid spheres have been correlated by a relationship of the following form (*5, 7* to *9, 11, 13, 15*):

$$N_{Sh} = A + B\,(N_{Re}{}^{1/2}\,N_{Sc}{}^{1/3}) \tag{1}$$

where A and B are constants to be determined from experimental data. The value of the coefficient B is generally between 0.5 and 1.0; however, the reported value of A varies widely depending on the physical properties of the system.

As compared with the literature concerning solid spheres, the literature on forced convection mass transfer from liquid drops is complicated because conditions at the interface can induce internal circulation of the drop. For a fully circulating drop and a large Peclet number, the classical mass transfer equation based on potential flow in the continuous phase is (*1*):

$$N_{Sh} = 1.13\,(N_{Re}\,N_{Sc})^{1/2} \tag{2}$$

Although a number of experimental studies support the validity of Equation (2), the actual mass transport process for a liquid drop can be a very complex phenomenon and may involve interfacial turbulence effects varying from mild circulation near the interface to spontaneous emulsification (*1*). In the past, some investigators have tried to attribute unexpected mass transfer results to a significant interfacial resistance caused by the accumulation of high molecular weight materials at the interface (*16*). However, it has become increasingly evident from later studies with liquid-liquid systems that, instead of acting as interfacial barriers, surface-active agents merely modify the hydrodynamics of the drop (*2*).

In contrast with the situation for gases, the theory of liquid state diffusion is only partly developed, and existing theories do not provide as good a basis for the prediction of diffusion coefficients as the available empirical equations. Sherwood and Reid (*14*) have recommended that the diffusivity of water in organic solvents be estimated by calculating a value from the Wilke-Chang relationship (*17*) and then dividing the result by 2.3. Previously, the comparison of calculated and experimental values for the diffusivity of water in different organic solvents had led Orlander (*12*) to suggest this factor of 2.3. Orlander concluded that the molar volume of water as a diffusing species in an organic solvent is four times the expected value due to polymerization of the water molecules.

THEORY

A proposed model for describing the removal of water from a sol drop assumes that the controlling mass transfer resistance is in a thin organic-phase film located at the interface of the droplet. With this model, mass transfer coefficients for water or sol drops fluidized in 2EH can be defined by the following equation:

$$N = K(C_s - C_0) \tag{3}$$

The water concentration C_s is assumed to be that of saturation; therefore, C_s is a function only of temperature. With a known concentration driving force $C_s - C_0$ the mass flux N must be measured in order to determine K from Equation (3). If the proposed mass-transfer model is valid, the mass-transfer coefficients will be the same for both water and sol drops under identical hydrodynamic conditions. Certainly, no resistance to mass transfer should exist within the droplets of pure water; and similar reasoning will apply to thoria sol drops during gelation if water can be supplied to the interface rapidly enough to maintain C_s at saturation.

At 25°C., the solubility of water in 2EH is 0.020 g./cc. and the solubility of 2EH in water is 0.001 g./cc. The amount of 2EH that can be transferred into the aqueous drop is negligible; thus the change in drop diameter is a direct measure of the amount of water transferred into the organic phase. The mass flux can be related to the change in drop diameter with time as follows

$$N = \frac{-\rho_w}{\pi D_p{}^2}\left(\frac{\pi}{6}\right)\frac{d(D_p{}^3)}{d\theta} = \frac{-\rho_w}{2}\,\frac{dD_p}{d\theta} = K\,(C_s - C_0) \tag{4}$$

The mass transfer coefficient can be determined from Equation (4) by measuring the change of drop diameter with time and knowing the value of the concentration driving force $C_s - C_0$.

EQUIPMENT

The equipment used in this study consisted of an 8-in. high tapered column, a light source, a photomacro lens positioned to magnify the droplet by a factor of 20 on a ground-glass viewing screen, a Polaroid camera, a timer, flowmeters, and a centrifugal pump to circulate the 2EH.

The tapered column was machined from a block of Plexiglas with a convergent-divergent flow channel. A vertical, laminar velocity profile was developed in the convergent section so that an aqueous drop could be fluidized along the central axis of the divergent channel with no detectable horizontal motion. The vertical position of a fluidized sphere in the column was controlled by the 2EH flow rate.

The general experimental procedure was to form and fluidize a single aqueous droplet in 2EH at 25°C. and then to measure the drop diameter (to within ± 10 microns) and 2EH flow rate as a function of time. The predetermined variables in each run were the initial sol molarity (0 to 2.5 $\underline{M}$ ThO_2), the initial drop diameter (0.1 to 0.2 cm.), and the water concentration in the bulk solvent (2-12 mg./cc.). Nine runs were made without adding surface-active agents to the organic phase. In the remaining 41 runs, Ethomeen S/15 (a tertiary amine marketed by Armour Industrial Chemical Company) was added to the 2EH in concentrations of 0.01 or 0.1 vol. %.

Figure 1 is a composite photograph of two thoria sol drops fluidized in 2EH as a function of time. The initial thoria sol concentration is 2.5 $\underline{M}$, and the diameter of each drop at 0.5 min. after formation is about 1,500 microns. The top row of photographs shows a single sol drop formed with no addition of surfactant; the bottom row shows a similar sol drop formed in 2EH containing 0.01 vol. % Ethomeen S/15. With no surfactant in the 2EH, circulation is induced within the aqueous drop, and the thoria concentration appears to be uniform around the entire surface of the drop. In the presence of surfactant, the sol droplet is rigid, and the concentration of thoria tends to increase at the forward stagnation point where the local mass transfer rate should be the greatest. The time required to reach a given degree of gelation is shorter for the droplet that is suspended in 2EH containing no surfactant.

EXPERIMENTAL DATA

The diameters of fluidized drops of water and thoria sol were measured as a function of time in a series of 50 runs. Typical data obtained for single water drops fluidized in 2EH

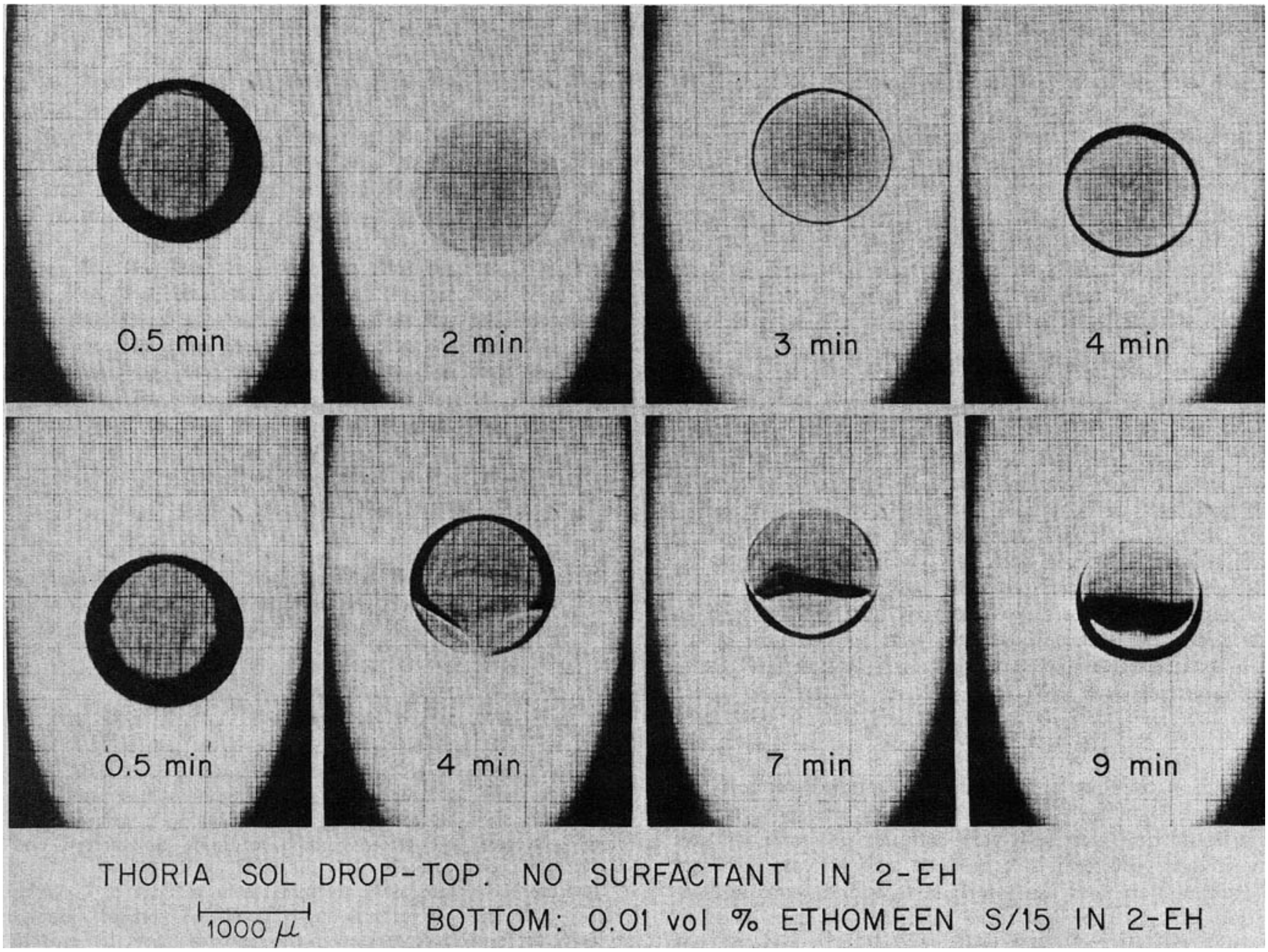

Fig. 1. Initial stages of gelation of two thoria sol drops fluidized at 25°C. in 2EH.

are shown in Figure 2. In Runs 1, 2, 4, 9, and 20, the water concentration in the bulk 2EH was 2 mg./cc.; the water content of the 2EH used in Run 3 was 4 mg./cc. No surfactant was added to the organic phase in Runs 1, 2, 3, and 4, but the 2EH contained 0.1 vol. % Ethomeen S/15 in Runs 9 and 20. In the absence of surfactant, the initial mass transfer rate was high; however, after 5 to 10 min., the rate of shrinkage decreased to a constant rate equivalent to that of droplets in the presence of Ethomeen. The constant slope of the water-drop-diameter data with time when surfactant was present indicates a constant mass flux of water from the drop.

Typical diameter data for single thoria sol drops fluidized in 2EH are shown in Figure 3. The initial molarity of the thoria sol was 2.5, and the water concentration in the bulk 2EH was 2 mg./cc. In Runs 17, 18, and 19, the organic phase contained 0.1 vol. % Ethomeen; the 2EH in Run 49 contained 0.01 vol. % Ethomeen. In Run 50, no surfactant was added to the organic phase, and the initial rate of mass transfer was comparably higher until the surface of the drop became immobile. In Runs 17, 18, 19, and 49, the slope of the diameter data curves, which is proportional to the mass flux or the mass transfer coefficient, increases with increasing sol density or molarity. The discontinuity in each of the curves provides information concerning the gelation time and the diameter of the gelled product. The average thoria concentration of the gelled spheres produced in all of the runs was 16 $\underline{M}$.

For each measured diameter, a fluidizing velocity was determined from a rotameter reading. The fluidizing or approach velocity is two times the average solvent velocity that would exist in the column with no drop present. The approach velocity and drop diameter are used to calculate a sphere Reynolds number.

At 25°C. the viscosity and the density of the 2EH are 7.4 centipoises and 0.83 g./cc. respectively. By using the recommendation of Sherwood and Reid (*14*), the predicted diffusivity of water in 2EH is 0.25 × 10^{-5} sq.cm./sec. For the constant temperature of 25°C., the Schmidt number is fixed at 35,700.

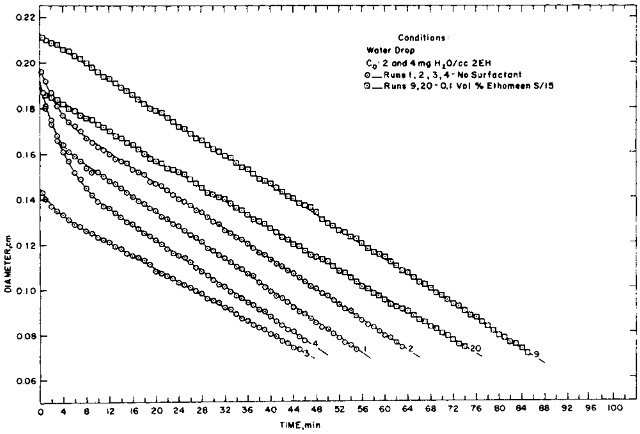

Fig. 2. Diameter of water drops fluidized in 2EH at 25°C. as a function of time.

RESULTS

The mass transfer data for all of the thoria sol and water drop runs in which a surfactant was added to the 2EH were correlated by plotting the Sherwood number against the product of the square root of the Reynolds number and the cube root of the Schmidt number (see Figure 4) according to Equation (1). The Reynolds number varied from 0.4 to 14, and even though the Schmidt number for the system is constant, the dimensionless number was retained in the correlation so that mass transfer coefficients could be calculated for temperatures other than 25°C. The water drop data (about 1000 determinations) can be represented by the following relationship, which is shown as the solid line in Figure 4:

$$N_{Sh} = 5 + 0.82\ (N_{Re}{}^{1/2}\, N_{Sc}{}^{1/3}) \tag{5}$$

All of the water drop data in Figure 4 are enclosed by the dashed lines. The points represent the data for sol droplets at thoria molarities from 0.85 to 16. Although the thoria data tend to scatter around the lower limit of the water data, the mass transfer coefficients for both sol and water drops are essentially the same for a given value of the sphere Reynolds number. The overlap of the thoria sol and water data confirms that the controlling mass transfer resistance is in the continuous phase.

From a practical point of view, a satisfactory system without surfactant is difficult to achieve. In Runs 1, 2, 3, and 4 (see Figure 2), in which no surfactant was added to the organic phase, the initial rate of shrinkage of the water drops was very rapid, but decreased after 5 to 10 min. to a constant value equivalent to that for water drops in the presence of Ethomeen S/15. Apparently, the 2EH acquired a surface-active contaminant from the system. The ratio of Equations (2) and (5) predicts that the mass transfer coefficient for a fully circulating drop should be greater than the coefficient for a rigid drop. For the water-2EH system at 25°C., the ratio of $N_{Sc}{}^{1/2}$ to $N_{Sc}{}^{1/3}$ is 5.7, which would account for the high initial shrinkage rates in the runs with no surfactant addition.

With surfactant in the organic phase and a fixed-concentration driving force, the slope of the water-drop-diameter data (see Figure 2) is constant and hence independent of the magnitude of the diameter. Because of the proportionality in Equation (4), the mass transfer coefficient appears to be independent of the diameter of the drop over the diameter range covered in this study. The nondependence of mass transfer coefficient on drop diameter is further supported by the thoria sol data. When the diameter of the initial sol drop is the only variable (for example, see Runs 17, 18, 19, and 49 in Figure 3), the curves through the data show a geometric similarity.

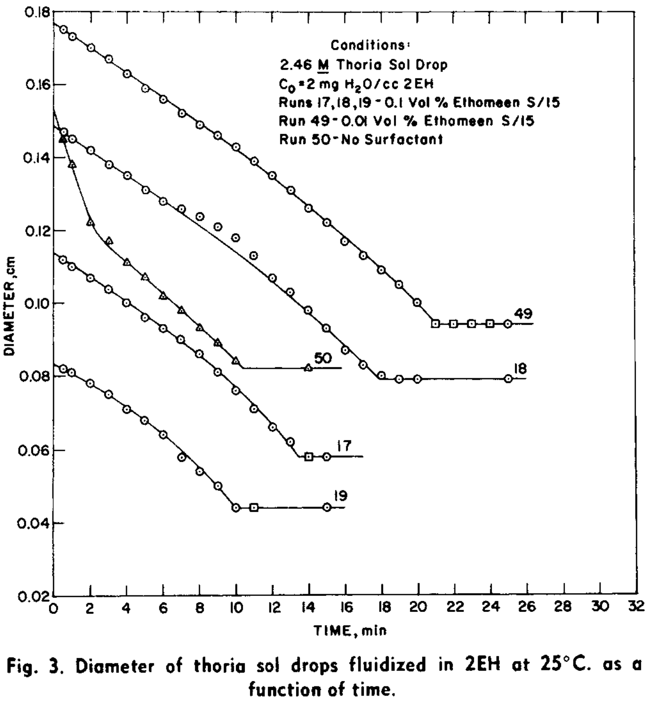

Fig. 3. Diameter of thoria sol drops fluidized in 2EH at 25°C. as a function of time.

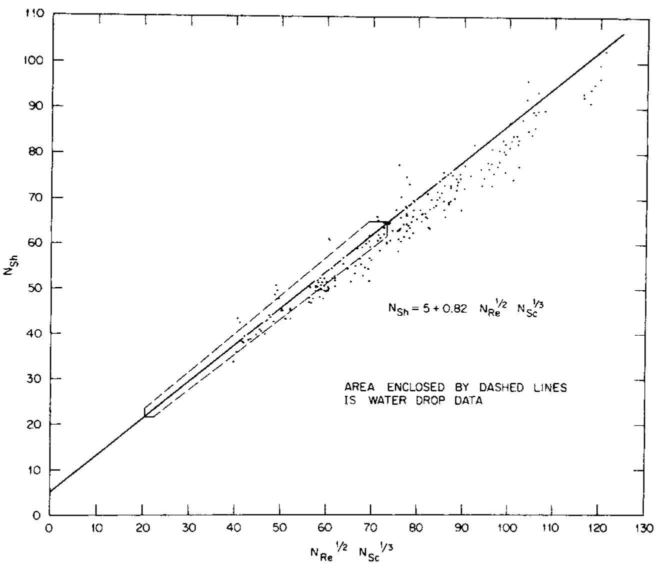

Fig. 4. Mass-transfer correlation for water and thoria sol droplets fluidized in 2EH at 25°C.

Since the mass transfer coefficient for a thoria sol drop definitely increases with fluidization time, the most obvious independent variable relating to this change is the sol density or molarity. If the temperature is constant and the mass-transfer coefficient is independent of the drop diameter, then, from Equation (5) K should be a function of the difference in the density of the sol drop ρ_p and the density of the solvent ρ_s. For 2EH at 25°C., $(\rho_p - \rho_s)$ can be related to the molarity of the thoria sol by the following equation:

$$(\rho_p - \rho_s) = 0.238\ \underline{M}_p + 0.17 \tag{6}$$

To test the proposed correlation, all the mass transfer coefficients used in establishing Figure 4 were plotted against $(0.238\ \underline{M}_p + 0.17)$ on log-log graph paper, as shown in Figure 5. The equation for the solid line is

$$K = (150 \times 10^{-5})\ (0.238\ \underline{M}_p + 0.17)^{0.38} \tag{7}$$

The water data are at a value of 0.17 g./cc. on the abscissa; the thoria sol data lie between 0.4 and 4 g./cc. In Figure 5, essentially all the data fall within the dashed lines that are obtained by replacing the coefficient of 150 in Equation (7) by either 135 or 165.

The diameter of the sol drop can be related to the sol molarity by the following equation

$$D_p = \left(\frac{\underline{M}_c}{\underline{M}_p}\right)^{1/3} D_c \tag{8}$$

where the calculated value of $\underline{M}_c$ is 37.9. By using Equations (7) and (8), Equation (4) can be integrated to give the following expression for the time required for gelation of the sol drop:

$$\theta_G = \frac{6.2\ D_c}{(C_s - C_0)} \int_{\underline{M}_I}^{16} \frac{d\ \underline{M}_p}{(\underline{M}_p)^{4/3}\ (0.238\ \underline{M}_p + 0.17)^{0.38}} \tag{9}$$

The limits of integration in Equation (9) are from the initial sol molarity to the molarity of the gelled product. For a desired theoretically dense product size D_c, Equation (9) can be used to determine the gelation time or the required fluidization time for a sol drop when the initial sol molarity and water concentration in the bulk organic phase C_0 are known. However, Equation (9) applies only when 2EH is used as the fluidizing medium and the solvent temperature is 25°C.

At the initial sol molarities of 0.85, 1.77, and 2.46 used in this study, the respective values of the integral in Equation (9) are 2.11, 1.19, and 0.89. Gelation times calculated by using Equation (9) were compared with the experimentally determined gelation times of the thoria sol drop runs in which a surfactant was added to the organic phase (see Figure 6). The calculated gelation times are plotted on the abscissa; the experimental values are shown on the ordinate with a solid line drawn at 45°. The maximum error between the calculated and experimental gelation times is 7%.

CONCLUSIONS

Results obtained from this study permit the following conclusions to be drawn for the mass transfer of water from thoria sol drops fluidized in 2EH at 25°C. 1. The addition of a surface-active agent to the organic phase produces a rigid sol drop with no induced circulation. 2. The controlling mass-transfer resistance for a thoria sol drop is in the organic phase surrounding the drop. 3. If the water concentration in the organic phase is known, the time required for the gelation of a fluidized sol drop can be predicted for any initial sol molarity and drop size.

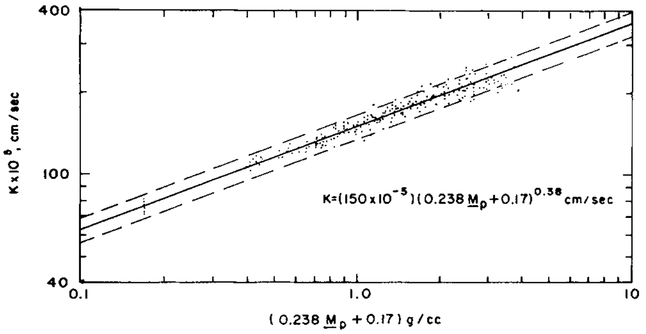

Fig. 5. Correlation of mass-transfer coefficient and thoria sol molarity of sol drop.

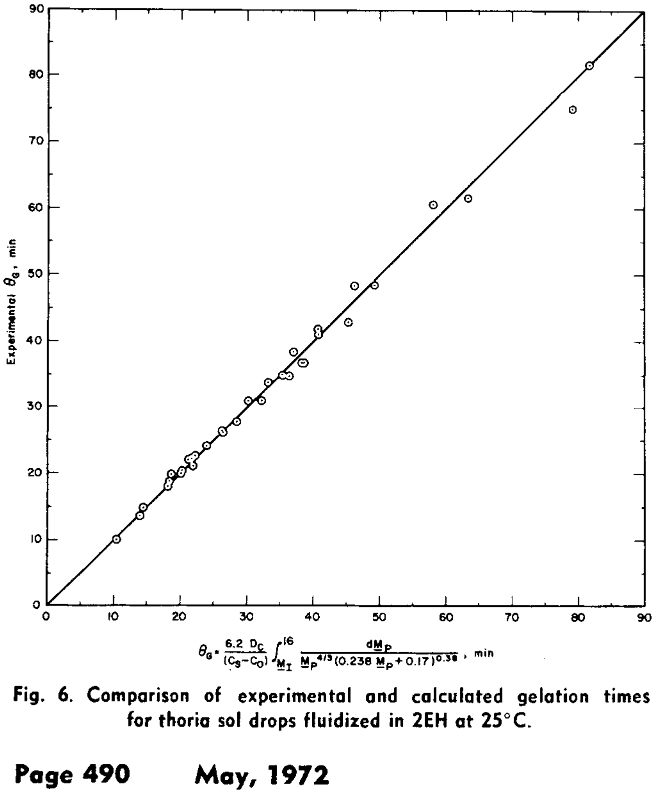

Fig. 6. Comparison of experimental and calculated gelation times for thoria sol drops fluidized in 2EH at 25°C.

NOTATION

C_0 = concentration of water in the bulk 2EH stream, g./cc.
C_s = concentration of water in 2EH at the drop interface, g./cc.
D_c = diameter of theoretically dense thoria sphere, cm.
D_p = diameter of water or sol drop, cm.
D_v = diffusion coefficient, sq.cm./sec.
K = mass transfer film coefficient, cm./sec.
$\underline{M}_c$ = molarity of theoretically dense thoria, moles/liter
$\underline{M}_I$ = initial thoria molarity of sol drop, moles/liter
$\underline{M}_p$ = thoria molarity of sol drop, moles/liter
N = mass flux of water from drop, g./(sq.cm.)(sec.)
N_{Re} = sphere Reynolds number, $D_p\rho_s U/\mu$
N_{Sc} = Schmidt number, $\mu/\rho_s D_v$
N_{Sh} = Sherwood number, KD_p/D_v
U = solvent fluidizing velocity, cm./sec.
θ = time, sec.
θ_G = gelation time, min.
μ = viscosity of solvent, g./(cm.)(sec.)
ρ_p = density of sol drop, g./cc.
ρ_s = density of bulk solvent, g./cc.
ρ_w = density of water, g./cc.

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