STUDIES ON THE DISSOLUTION RATE OF SPARINGLY SOLUBLE CALCIUM CITRATE IN WATER

Yung-Ho Chou[a]; L. K. Doraiswamy[a]; Maurice A. Larson[a]

[a] Department of Chemical Engineering, Iowa State University, Ames, IA

PLEASE SCROLL DOWN FOR ARTICLE

STUDIES ON THE DISSOLUTION RATE OF SPARINGLY SOLUBLE CALCIUM CITRATE IN WATER

YUNG-HO CHOU*, L. K. DORAISWAMY and MAURICE A. LARSON

Department of Chemical Engineering, Iowa State University, Ames, IA 50011

The mass transfer coefficient of calcium citrate-water system was determined by the conductivity measurement. The range of the measured coefficient is 2.65×10^{-6} m/s $\pm 35\%$ at 25.5°C, independent of particle size and rpm under a full solid suspension condition. The prediction of the effects of particle size and agitation on the coefficient based on the classic mass trafer theories is also discussed.

Keywords: Dissolution; Mass transfer; Mass transfer coefficient; Calcium citrate; Conductivity

INTRODUCTION

Many chemical processes require the dissolution of a suspended solid with a reaction which produces solid crystalline product. The rates of such reactions depend on particle size, rate of diffusion to the reaction surface, and the reaction rate. In processes in which the liquid phase reactant is a strong acid, the reaction rate is extremely rapid and thus the diffusion step becomes the rate controlling step. When one of the reaction products is insoluble and forms small crystals, these crystals can act as a microphase enhancing the rate of mass transfer to the reaction boundary (Mehra and Sharma, 1988; Saraph and Mehra, 1994). The autocatalytic effect of such a microphase on the mass transfer rate and thus the reaction rate has been

---

* Address for correspondence: Department of Chemical Engineering, Ohio State University, Columbus, OH 43210. e-mail: chou@er6.eng.ohio-state.edu

observed qualitatively. However, quantitative evaluations have not been achieved. In order to quantitatively measure the autocatalytic effect of a reaction-produced microphase, it is necessary to measure the mass transfer coefficient and thus the dissolution rate of the solid reactant in the absence of the liquid phase reactant.

The model reaction system chosen to study this phenomenon is also one of industrial importance : the reaction of sulfuric acid with calcium citrate crystals in an aqueous solution of citric acid. It is assumed that the reaction of sulfuric acid and calcium citrate occurs in the liquid phase; thus for the reaction to proceed, calcium citrate must diffuse from the surface of the suspended crystals into the bulk liquid. The purpose of this investigation is to determine the effect of particle size and that of agitation on the mass transfer of calcium citrate from the solid state into water to define the conditions for a further study of dissolution rates of calcium citrate into citric acid solution and ultimately into a solution when sulfuric acid is present.

The mass transfer coefficient is a function of particle size, agitation, vessel geometry, and the physical properties of the solid and liquid (Barker and Treybal, 1960; Harriot, 1962; Levins and Glastonbury, 1972). In this work, because only calcium citrate and water are involved, the physical properties are constants. The agitated vessel will be an unbaffled tank, and the other geometric shapes will be fixed throughout the study, so these will not be variables. The effect of particle size will be investigated and that of agitation will be evaluated on the base of power consumption.

BACKGROUND

The literature provides contradicting results in regard to the effect of particle size. Levins and Glastonbury (1972) summarized the results of the previous investigations and pointed out that if a power law correlation, $k_L \propto d_p^x$, where k_L is the mass transfer coefficient and d_p is the particle size, was used to correlate the data, then the exponent x would range from -0.7 to 0.33. In Harriott's study (1962), x was -0.7 for small particles, and was nearly zero for large particles.

Agitation invariably has a marked effect on the mass transfer coefficient. Its principal effect is the reduction of the thickness of the boundary layer if the film model is adopted, in other models, its effect is to change some other parameters, and will be discussed later.

Correlations of this effect usually relates the mass transfer coefficient to power consumption. If a power law correlation, $k_L \propto P_m^x$, where P_m is the

power consumption per unit mass, is used to correlate the data, then in the previous works, the minimum range of x is from 0 to 1.4 (Levins and Glastonbury, 1972).

There is a good discussion relating power consumption and reaction vessel shape factors in McCabe et al.'s book (1985). The power consumption is a function of stirrer speed, stirrer diameter and several shape factors, and can be written as:

$$P = f\left(n, d_a, S_1, S_2\right) \tag{1}$$

where n is the impeller speed, d_a is the impeller diameter, and S is the shape factor. By dimensional analysis, these variables are grouped into several dimensionless groups. In a dilute suspension, the weight ratio will not be a factor. The dimensionless correlation usually takes the form:

$$\text{Po} = f\left(\text{Re}_i, \text{Fr}, S_1, S_2 \ldots \ldots\right) \tag{2}$$

where Po is the power number, Re_i is the impeller Reynolds number, and Fr is the Froude number. The effects on the Power number of the shape factors, S_1, S_2, can be small or very large (McCabe et al., 1985). The interior design of the agitated tank may also significantly influence the process (Thring and Edwards, 1990).

Empirical Mass Transfer Correlation

Many studies have been directed towards using a generalized equation to express the relationship between these variables, and most of the equations use dimensionless groups, such as the Reynolds number Re and the Sherwood number Sh. However, because of the large number of variables, there is also a wide divergence of the correlations and theories.

For example:

Barker and Treybal (1960) used the following empirical equation for relating baffle tank volume and impeller to the mass transfer coefficient:

$$\ln(k_L) = a + 0.85 V^{0.02875} \ln\left(\frac{\text{Re}_i}{10000}\right) \tag{3}$$

where V is the liquid volume. The corresponding equation for an unbaffled tank was:

$$\ln(k_L) = 0.747 \ln\left(\frac{\text{Re}_i}{10000}\right) - 2.974 \tag{4}$$

They also used dimensional analysis to obtain the correlation:

$$Sh = 0.02 \, Re_i^{0.833} Sc^{0.5} \tag{5}$$

where Sc is the Schmidt number.

And the common form of correlation is the following:

$$Sh = a \, Re^b Sc^c \tag{6}$$

which is frequently referred to as the Gilliland – Sherwood correlation (Miller, 1964), and has been used by the numerous investigators (Wakao and Kaguei, 1982). The difference between the correlations is the value of the a, b and c, used to fit the data.

Harriott (1962) utilized the semitheoretical equation of Frössling (1938) to get

$$Sh = 2 + 0.6 \, Re^{0.5} Sc^{0.33} \tag{7}$$

This type of equation has also been used by some other investigators, with different values of the index on Re, *e.g.*, by Miller (1971).

Levins and Glastonbury (1972) used two empirical equations to correlate the data:

$$\frac{k_L d_p}{D_v} = 2 + 0.47 \left(\frac{d_p^{4/3} P_m^{1/3}}{\nu} \right)^{0.62} \left(\frac{d_a}{d_T} \right)^{0.17} \left(\frac{\nu}{D_v} \right)^{0.36} \tag{8}$$

and
$$\frac{k_L d_p}{D_v} = 2 + 0.44 \left(\frac{d_p v}{\nu} \right)^{0.5} \left(\frac{\nu}{D_v} \right)^{0.38} \tag{9}$$

where D_v is the diffusivity, ν is the kinematic viscosity, and d_T is the tank diameter where v is the slip velocity. Equation (8) is applicable to cases where there is little density difference between the particle and the solvent, and Eq. (9) where the density difference is significant.

Comments

A general expression for the mass transfer coefficient is:

$$k_L = f \, \{\text{particle size, [rpm, (draft tube, baffle), impeller, vessel geometry],} \\ \text{weight ratio, [solid, liquid properties]}\} \tag{10}$$

The power factor is somehow related to some variables in the equations. In a vessel, more power consumption may cause more velocity fluctuation, and thus to increase the mass transfer rate. The use of power factor has some advantages and disadvantages. In Barker's approach (1960), at least two different empirical equations are necessary, one for the baffled tank, and the other for the unbaffled one. In their study, they found that the mass transfer coefficients in the unbaffled tank were smaller than those in the baffled vessel. Usually, the power consumption in the unbaffled vessels are smaller than in the baffled ones under the same agitation speed and the same vessel geometry. Therefore, the power factor may become a link between the two equations. But the same power consumption does not have to mean the same fluid dynamics pattern. It can be expected that if the power becomes a factor in a generalized equation, then the actual transfer rate is probably also dependent on the "efficiency" of the vessel. Some power may be wasted in heat, and different vessels have different dead zones. An empirical equation may be suitable for several vessels, but not for all kinds of vessels or impellers. Miller (1964) reported that the mass transfer coefficient maybe varied by an order of magnitude under the same power consumption.

The power consumption is very easily measured. This provides a simple guide for the estimation of the mass transfer coefficient and for vessel scale-up. It also provides a simple guide for On-Line operation. For example, if it is desired to increase the mass transfer rate, alternatives other than increasing agitation need to be sought if power consumption has little effect on the mass transfer coefficient.

Mass Transfer Theory

The mechanism of mass transfer has been widely studied and many theories have been developed. This section will examine the predicted effects of particle size and agitation on mass transfer coefficient based on the theories. All of the theories assume that the controlling step for the mass transfer is on the liquid side. Another important assumption is that the coefficient is independent on the concentration.

Film Theory

The film theory predicts the mass transfer coefficient to be:

$$k_L = D_v/\delta \tag{11}$$

where δ is the thickness of the film. If the mass transfer rate is affected by the power consumption, the baffles, and the related vessel geometry, it can be deduced that the film thickness is determined by the power consumption and these factors. However, another factor, particle size, is not included in the equation.

Penetration Theory

The penetration theory predicts the mass transfer coefficient to be:

$$k_L = 2\sqrt{\frac{D_v}{\pi t_c}} \tag{12}$$

where t_c is the contact time. Power consumption and vessel geometry exert considerable influence on the contact time. It can be expected that if more power produces a more rigorous flow pattern, the frequency of the replacement will be higher, and thus the mass transfer rate will be higher. This point of view may explain why the mass transfer rate increases with increasing impeller speed or power consumption. If the new element is not fresh, then it can be deduced that the mass transfer rate will be lower than the equation predicts. This point can explain why different impellers affect the rate differently. Each impeller has its own efficiency and mixing time (Rewatkar and Joshi, 1991). The more efficient impeller will have a larger transfer rate. However, the particle size is also not included in the equation.

Danckwerts' Penetration Model

The Danckwerts' model predicts the mass transfer coefficient to be:

$$k_L = \sqrt{D_v w} \tag{13}$$

where w is the fractional rate of displacement of fluid element. In a more rigorous mixing, w is larger, thus the mass transfer rate will be higher. However, the particle size is also not included in the equation.

Boundary Layer Model

With the assumption that during the period of mass transfer, solute does not penetrate into the boundary layer beyond the point where $u/u_\infty = 0.5$, this

model predicts the mass transfer coefficient to be (Schlichting, 1960; Miller, 1964):

$$k_L = 0.852 \frac{D_v^{0.67}}{v^{0.17}} \left(\frac{u_\infty}{\ell}\right)^{0.5} \tag{14}$$

where ℓ is the contact length and u_∞ is the bulk fluid velocity.

It can be expected that if the impeller speed is larger, the power consumption is also larger, then, the u_∞ is probably larger as well. Thus, the mass transfer rate is faster. This equation also indicates that k_L is inversely proportional to the square of the distance. It implies that smaller particles are inclined to have larger mass transfer coefficients.

Gilliland – Sherwood Correlation

This correlation is (Miller, 1964):

$$Sh = a\,Re^b Sc^C \tag{15}$$

The effects of particle size and power consumption will depend on the value of b and the definitions of Re.

The values of the Gilliland – Sherwood parameters are judiciously selected to get the best possible fit (Miller, 1964; Lakota and Levec, 1990; Dudukovic et al., 1996). In some studies, the length parameter in Sh and Re was the impeller diameter, instead of the distance along the interface (Miller, 1964). The velocity term in Re also from the speed of the rotating element, such as the peripheral speed (Miller, 1964). In the author's opinion, the peripheral speed is somehow related to the bulk flow velocity, but the impeller diameter seems irrelevant to the contact distance, and the particle size should be theoretically more suitable as the length parameter in the model.

Calderbank and Moo-Young Correlation (1960)

The coefficient in their correlation is:

$$k_L = a\left[\frac{P_m \nu}{\rho}\right]^{0.25} Sc^{-0.67} \tag{16}$$

where a is a constant and ρ is the density of the bulk fluid. Their equations indicate that more power can increase the mass transfer rate, and the particle size will not affect the coefficient.

Comments About These Equations

Due to the large number of variables in the agitated vessel, to obtain an equation to fit all situations proves difficult. This difficulty can also be seen in other types of equipment, such as fluidized beds (Nikov and Karamanev, 1991).

Frössling equation is originally developed for evaporation from liquid drops falling in air, this equation has since been successfully applied to characterize mass transfer from single, fixed spheres of solute suspended in moving fluids (Miller, 1964). After some rearrangement, Eq. (7) becomes:

$$k_\mathrm{L} = \frac{1}{d_\mathrm{p}^{0.5}} \left(\frac{2D_v}{d_\mathrm{p}^{0.5}} + 0.6 \frac{v^{0.5} D_v^{0.67}}{\nu^{0.17}} \right) \tag{17}$$

If the first term in the brackets dominates, then the coefficient should be inversely proportional to the particle size. If the second term dominates, the coefficient should be inversely proportional to the square root of particle size. In other words, larger particle sizes always have smaller transfer coefficients. Therefore, Eq. (7) can not explain why in some studies the coefficient is independent of the particle size. Furthermore, the equation does not include any variable related to the density difference between the particle and the fluid.

Some workers used the analogy between mass transfer and heat transfer without reservation (Briends et al., 1993; Kendoush, 1994), and that is where the mass transfer equations, such as Eq. (7), come from (Thring and Edwards, 1990). Numerous workers used Eq. (7) or other similar equations to fit their data, and it showed success not only for some conventional processes, but also for some other processes, such as supercritical extraction (Wakao and Kaguei, 1982; Madras et al., 1994). However, some investigators showed that this kind of analogy equations can not be applied to agitated systems, and adopted other empirical equations (Ahn and Lee, 1990). Some investigators criticized this and proved that the analogy did not apply in some cases (Briends et al., 1993). An examination can justify the validity of analogy or other "analogy equations". If an equation can be applied, it should include all variables, and should not include the variables which do not affect the particular system. For instance, if the density difference between solid and the fluid will affect the rate significantly, then Eq. (7) is not applicable because it does not include density difference as a variable.

EXPERIMENT METHOD AND MATERIAL

The mass transfer coefficient can be written as

$$k_L = \frac{N}{A(C_s - C)} \tag{18}$$

where N is the mass transfer rate, A is the contact area, C_s is the solubility, C is the concentration, and k_L is not a function of the concentration or the driving force. The unsaturated calcium citrate solution (1300 ml) was put into the agitated vessel (see Fig. 1, the mixer and the controller: Cole-Parmer Company model H-5000-00, H-50000-30, H-04553-52, H-04553-64), and the concentration of the solution was close to the saturation point to provide a small driving force. Then, a certain amount of calcium citrate (Spectrum Chemical Corporation) in a predetermined size range was introduced into the vessel (sieves: Newark Wire Cloth Company). The run time was kept short (about 20 second), so that the change of concentration was small, and the contact area could be considered to remain constant through the run. The vessel was put in a temperature bath with a temperature 25.5°C. The concentration of calcium citrate and the solubility were analyzed by conductivity measurements (Cole-Parmer model H-01481-90) and the calibration table.
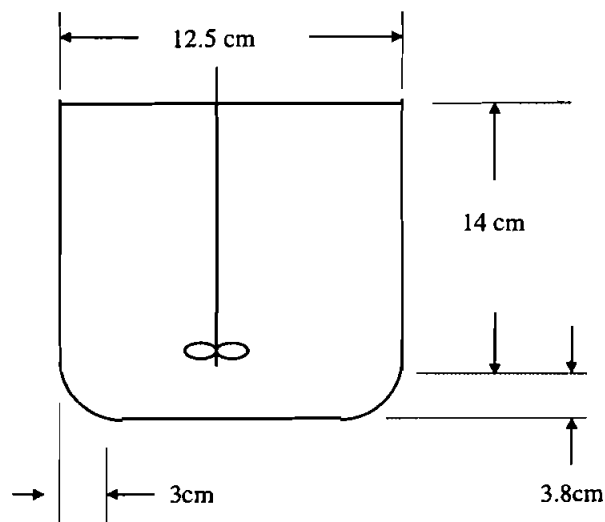

FIGURE 1   Sketch of the agitated vessel.

At a temperature, the conductivity of calcium citrate solution is related to the concentration. To find the relationship, several calcium citrate solutions with known concentration were carefully prepared, and their conductivities were measured for the calibration table.

In the mass transfer experiment, the conductivities of the solution were measured before and after the run. The concentrations and the driving force were determined by the calibration table. By the change of the concentration of the solution and the known volume of the solution, the mass transfer rate can also be calculated. The contact area was determined by the usual BET method (Micrometetics 2100E Accusorb).

RESULT AND DISCUSSION

Table I shows the calibration table, and Table II shows the results of the runs. The solubility is 0.911 g calcium citrate in one liter water at 25.5°C. The conductivity meter is very sensitive to detect the small change of the concentration, as shown in Table I. On the other hand, under the same operation conditions, a two-fold variation in the mass transfer coefficient could be achieved in this study. In the previous study, Miller (1964) reported that the mass transfer coefficient may be varied by an order of magnitude under the same power consumption. The mass transfer in the agitated vessel is a chaotic phenomena, and nearly all of the experiment uncertainty is due to this phenomena.

To study the effect of power consumption, the data with the same particle size range are used, and a power law equation of the form, $k_L = a(rpm)^b$, used for correlation. The values of b are between 0.05 and -0.01, therefore the power does not affect the mass transfer coefficient. To explain this result, the transfer regime is probably not in the liquid film controlling regime. The controlling step for the mass transfer is that the molecule at the outermost layer of the particle releases into the liquid film.

TABLE I   Concentration *versus* conductivity

Concentration g Ca citrate/lit.	Conductivity μv	Concentration g Ca citrate/lit.	Conductivity μv
0.322	127	0.756	238
0.421	150	0.803	250
0.534	164	0.867	268
0.655	211	0.911g, saturation	275
0.720	226		

TABLE II   The calculated data of mass transfer coefficient in each run

Run	Size (μm)	rpm	Coefficient ($10^6 m/s$)
1	355–297	300	3.19
2		300	1.73
3		350	1.82
4		350	1.92
5		450	2.09
6		450	1.86
7		550	2.48
8		550	2.03
9	250–212	300	3.04
10		300	2.68
11		350	3.26
12		350	2.90
13		450	3.25
14		450	2.22
15		550	3.63
16		550	2.47
17	180–125	300	2.20
18		300	2.32
19		350	2.46
20		350	2.10
21		450	1.81
22		450	2.14
23		550	2.11
24		550	2.85
25	106–53	300	1.67
26		300	2.41
27		350	2.06
28		350	2.53
29		450	1.75
30		450	2.31
31		550	2.52
32		550	1.91

300 rpm appears the minimum speed to keep the particles in full suspension. If the agitation speed could be lowered and if the full suspension could be maintained, then the results may show that the mass transfer coefficient increases with agitation speed.

Because the agitation does not influence the mass transfer coefficient, the mass transfer coefficient is a constant for each particle size range. The mean of the mass transfer coefficients are 2.14×10^{-6}, 2.93×10^{-6}, 2.24×10^{-6}, 2.15×10^{-6} m/s for the size range 355–297, 250–212, 180–125, 106–53 μm respectively. All the means are very close except that the second is a little higher. It suggests that the mass transfer coefficient is independent of particle size. The average of the measurement of all 32 runs is 2.37×10^{-6} m/s at 25.5°C. The range of the measured coefficient is 2.65×10^{-6} m/s $\pm$ 0.93×10^{-6} m/s or $\pm 35\%$ at 25.5°C.

CONCLUSION

Different mass transfer theories are applicable for some systems, and all of them assume the controlling step of mass transfer is on the liquid side. The mass transfer coefficient is usually assumed to be independent of the concentration.

Under ordinary agitation, power consumption and particle size does not affect the mass transfer coefficient or the mass transfer rate of calcium citrate in water. It suggests that the controlling step of the dissolution of calcium citrate is the release of the molecules at the outermost layer of the particles.

FUTURE WORK

Future work will focus on the measurement of the dissolution rate with the presence of the liquid reactant.

NOMENCLATURE

C solute concentration, g solute/lit.
C_s saturation concentration of solute, g solute/lit.
D_v diffusivity, m^2/s
d_a diameter of impeller, m
d_p particle size, m
d_T tank diameter, m
N mass transfer rate, g solute/s
k_L mass transfer coefficient, m/s
n impeller speed, 1/s
p power, kg m^2/s^3
P_m power consumption per unit liquid, kg/s^3m
t_c contact time, s
ℓ contact length, m
u_∞ velocity of bulk fluid, m/s

v slip velocity, m/s

V vessel volume, m^3

w fractional rate of displacement of fluid element

Greek Letters

δ film thickness, m

ρ liquid density, g/cm^3

ρ_p particle density, g/cm^3

μ liquid viscosity, kg/s m

ν kinematic viscosity, m^2/s

η turbulence microscale, m

Dimensionless Groups

Po   power number

Re   Reynold number

Re_i impeller Reynolds number

Fr   Froude number

S_1 shape factor

Sh   Sherwood number

Sc   Schmidt number

References

Ahn, B. S. and Lee, W. K. (1990) *Ind. Eng. Chem. Res.*, **29**.

Barker, J. J. and Treybal, R. E. (1960) *AIChE*, **6**(2).

Briens, C. L., Del Pozo, M. and Chiu, K. (1993) *Chemical Engineering Science*, **48**(5).

Calderbank, P. H. and Moo-Young, M. B., *International Symposium on Distillation*, Brighton, England, May (1960).

Dudukovic, A., Milosevic, V. and Pjanovic, R. (1996) *AIChE*, **42**(1).

Frössling, N. (1938) *Gerlands Beitr. Geophys.*, **52**.

Harriott, P. (1962) *AIChE*, **8**(1).

Kendoush, A. A. (1994) *AIChE*, **40**(9).

Lakota, A. and Levec, J. (1990) *AIChE*, **36**(9).

Levins, D. M. and Glastonbury, J. R. (1972) *Trans. Instn Chem. Engrs.*, **50**.

Madras, G., Thibaud, C., Erkey, C. and Akgerman, A. (1994) *AIChE*, **40**(5).

McCabe, W. L., Smith, J. C. and Harriott, P. (1985) *Unit Operation*, 4th ed., McGraw-Hill, New York.

Mehra, A. and Sharma, M. M. (1988) *Chemical Engineering Science*, **43**(5).

Miller, D. N. (1964) *Industrial and Engineering Chemistry*, **56**(10).

Miller, D. N. (1971) *Ind. Eng. Chem. Process Des. Develop.*, **10**(3).

Nikov, I. and Karamanev, D. (1991) *AIChE*, **37**(5).

Rewatkar, V. B. and Joshi, J. B. (1991) *Chemical Engineering Communication*, 1991, **102**.

Saraph, V. S. and Mehra, A. (1994) *Chemical Engineering Science*, **49**(7).
Schlichting, H. (1960) *Boundary Layer Theory*, 4th ed., McGraw-Hill, New York.
Thring, R. W. and Edwards, M. F. (1990) *Ind. Eng. Chem. Res.*, **29**.
Wakao, N. and Kaguei, S. (1982) *Heat and Mass Transfer in Packed Beds*, Gorden and Breach, New York.