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Enhancement of solid dissolution process

A. Kannan*, Sadhi Khan Pathan

Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

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Abstract

The enhancement of the dissolution rate of the sparingly soluble benzoic acid in aqueous solution by solid rotation, ultrasound and chemical reaction was investigated. The analysis indicated the strong influence of the ultrasound energy dissipation rate on the enhancement. The overall enhancements due to the three means were compared. The enhancement due to ultrasound was found to be much greater than mechanical rotation and comparable to that of chemical reaction.

Keywords: Rate of solid dissolution; Mass transfer coefficient; Ultrasound energy dissipation rate; Mechanical agitation; Ultrasound and chemical reaction

1. Introduction

Acoustic cavitation is a versatile option for enhancing several physical and chemical processes. The physical effects of ultrasound include cleaning, degassing, extraction of perfumes, emulsification and homogenization [1]. The chemical effects include enhanced reaction yields, alternate pathways for reactions, synthesis of chemicals and treatment of toxic wastes. An extensive review on acoustic cavitation has been provided by Thompson and Doraiswamy [2]. The focus of the present study was on the enhancement of solid dissolution process through mechanical rotation, ultrasound, and rapid chemical reaction.

Typical situations involving solid dissolution includes treatment of acid lakes by dissolving limestone [3], dissolution of metals in contact with hot liquids [4] and rotating electrodes [5,6]. The dissolution of a sparingly soluble cylindrical solid rotating in an aqueous solution is considered here. This geometry provides uniformity in accessibility of surface, concentration field and boundary layer conditions [7]. Early work on the rotating cylinder dissolving in the aqueous solution include studies by Bennett and Lewis [4], Sherwood and Ryan [8] and Holman and Ashar [9]. Models were developed by Gabe and Robinson [5,6] for both laminar and turbulent flows. While the physical and chemical dissolution mechanisms have been studied in detail earlier, the ultrasound effect in combination with cylinder rotation is demonstrated in this work.

2. Details of experiments

Molten benzoic acid was cast in a 60 mm long and 30 mm diameter aperture to obtain a smooth cylindrical solid which was supported by a central steel shaft. The Schmidt number was estimated at 933 based on the transport properties predictions from the standard Aspen Plus property package [10]. Density was given by Rackett's model, diffusivity by Wilke–Chang equation and viscosity by Andrade's model, respectively.

The solubility limit for benzoic acid in water was determined to be 0.034 mol/l. The solid was rotated at a constant and pre determined rpm in an airtight container filled with distilled water or aqueous sodium hydroxide solution (Fig. 1). The container was immersed in a constant temperature water bath that maintained $31 \pm 1\,^{\circ}\mathrm{C}$ (not shown in Fig. 1). Sampling were carried through a 6 mm opening in the top plate covered with a septum. The microprocessor controlled ultrasound probe (Sonics and Materials Inc., USA) was introduced vertically primarily prevent damage to the probe and to avoid leaks. The instrument was rated at 500 W and 20 kHz frequency. The probe tip mean diameter was 12 mm. The power input into the solution was fixed at 0, 45 and 70% of the maximum value. The actual power input to the solution at different intensities of ultrasound was verified separately by the calorimetry procedure as outlined by Thompson and Doraiswamy [2].

A series of mass transfer runs were conducted for differing durations, the shorter times applying when ultrasound or chemical effects prevailed. Five to six samples were taken, each corresponding to around 1% of the total initial volume of the solution. Samples were immediately replaced with

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* Corresponding author. Tel.: +91-44-2257-8224; fax: +91-44-2257-0509.

E-mail address: kannan@iitm.ac.in (A. Kannan).

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Nomenclature

a	first model parameter in Eq. (3)
A	surface area of cylinder (m^2)
b	second model parameter in Eq. (3)
C_A	concentration of benzoic acid ($kmol/m^3$)
C_B	concentration of sodium hydroxide ($kmol/m^3$)
I^0	enhancement factor due to ultrasound
I^*	enhancement factor due to chemical reaction
j_D	Chilton–Colburn factor for mass transfer
k_c	mass transfer coefficient (m/s)
k^*	mass transfer coefficient due to chemical reaction (m/s)
k_c^0	mass transfer coefficient due to only cylinder rotation (m/s)
rpm	revolutions per minute
Re	Reynolds number
Sc	Schmidt number
t	time (s)
U	velocity of rotating cylinder (m/s)
V	volume of solution (m^3)
Greek letter	
ε	specific energy dissipation rate (m^2/s^3)

equal volumes of water. The average diameter and length of the benzoic acid cylinder was used for surface area calculations. Trial experiments using ultrasound without temperature control bath resulted in a fast temperature rise and rapid solid dissolution. The actual runs were carried out at a constant temperature resulting in much lower and more uniform solid dissolution. The runs involving ultrasound were of relatively short duration while runs involving without ultrasound showed very low dissolution rates. Both these factors contributed to small variation in cylinder surface area without compromising on the number of data points required to estimate the mass transfer coefficients. Typically the cylinder area changed from 1.9 to 4% while at maximum ultrasound intensity the change in area was 5.6%. For the chemical reaction case, the duration of the runs were much smaller and the maximum change in area was 6.9%. Hence an average value of the cylinder area was used. Further measuring the area as a function of time would have involved either measurement through the water bath as well as the container filled with solution or taking out the wet cylinder after every sampling and replacing it causing more errors.

Runs were made with stirrer speeds up to 250 rpm. The concentration values were estimated by titration. The effect of chemical reaction with 0.1N NaOH was also studied and the results analyzed as outlined by Sherwood and Ryan [8].

The mass transfer coefficients under physical dissolution conditions both in the presence and absence of ultrasound were estimated by solving the following equation:

$$V\frac{dC_A}{dt} = k_c^0 A(C_{Ai} - C_A) \qquad (1)$$

The variables are defined in the Nomenclature. The mass transfer coefficient was estimated by integrating Eq. (1) and plotting the resulting expression as $-\ln(1 - C_{A0}/C_A)$ versus time. The slope of the fitted linear line, using POLYMATH program, gave $k_c^0\ A/V$. For physical dissolution experiments, with and without sonication, good linear fits were obtained. A small correction factor for the mass transfer coefficient to take into account the sampling was incorporated as recommended by Johnson and Huang [11]. Typically the runs involving no ultrasound took 5 h at low cylinder speed (50 rpm). Upon introducing ultrasound at settings of 45 and 70%, the run time were 70 and 40 min, respectively, in order to attain approximately the same concentration of benzoic acid in the solution. Typically a run with only chemical reaction took 40 min (at lowest stirrer speed of 50 rpm).

For the mass transfer with chemical reaction runs, the Schmidt numbers of benzoic acid (A) and sodium hydroxide (B) were estimated by the Nernst Hartley model for

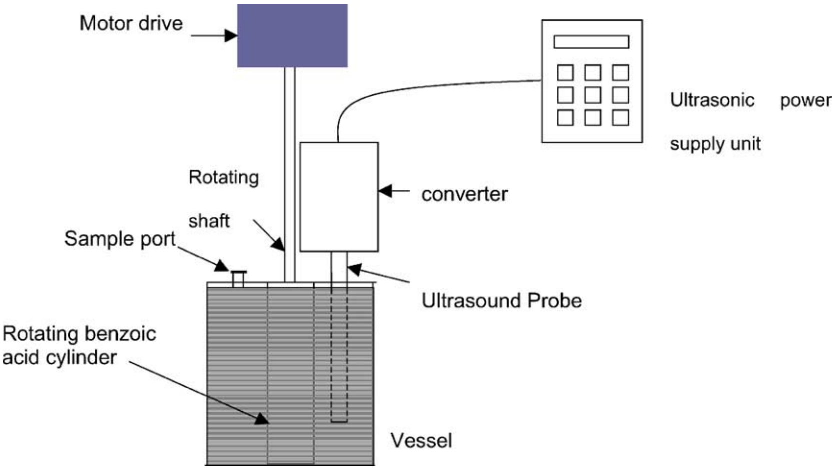

Fig. 1. Experimental arrangement with sonication.

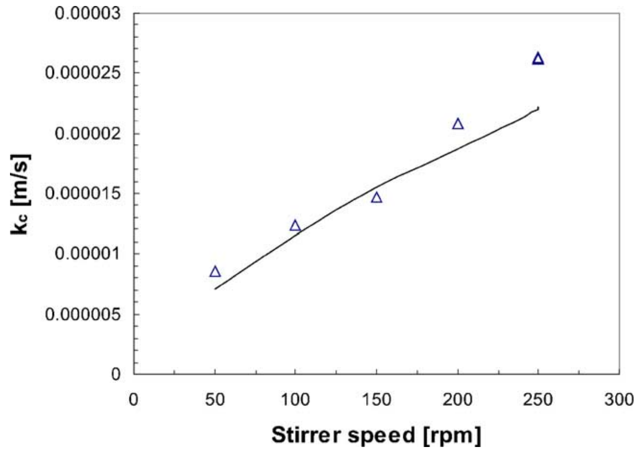

Fig. 2. Effect of mass transfer coefficient enhancement due to mechanical agitation alone. The solid line represents Eq. (2).

diffusivities and the Jones Dole model for liquid viscosities using Aspen Plus [10]. Sc_A was estimated to be 637 and Sc_B was estimated to be 285.

3. Discussion of results

3.1. Mass transfer without chemical reaction

The Chilton–Colburn (j_D) for mass transfer coefficient for a rotating cylinder in the absence of ultrasound effects has been correlated by Eisenberg et al. [8] and given as Eq. (2). The cylinder diameter was chosen as the characteristic dimension in the Reynolds number term.

$$k_c^0 = 0.0791\, Re^{-0.3}\, U\, Sc^{-0.644} \tag{2}$$

k_c^0 is the physical mass transfer coefficient without ultrasound effects. Eisenberg et al. [8] correlation is valid for Reynolds number over the range of 112–241,000 and Schmidt number ranging from 835 to 11,490. The present data (Reynolds number: 2000–12,000, $Sc = 933$) falls within this range.

Eq. (2) indicates that the mass transfer coefficient would increase with the velocity of the cylinder as $U^{0.7}$. The enhancement effect of the speed of rotation of the benzoic acid cylinder is indicated in Fig. 2. It is clear that a five-fold increase in speed of rotation brings about only approximately three-fold increase in the mass transfer coefficient indicating the need for further improvement in the solid dissolution rate.

The enhancement due to ultrasound is modeled in terms of energy dissipation rate per unit mass (ε) as an additional term and given in Eq. (3).

$$k_c = 0.0791\, Re^{-0.3}\, U\, Sc^{-0.644}[1 + a\varepsilon^b] = k_c^0[1 + a\varepsilon^b] \tag{3}$$

The parameters obtained using the non-linear regression option in POLYMATH are $a = 0.4295$ and $b = 0.50771$. The fit of the experimental data with Eq. (3) is given in Fig. 3. The average absolute relative deviation was estimated at 10.86%. The enhancement effect due to ultrasound obtained from Eqs. (2) and (3) is given by Eq. (4) and illustrated in Fig. 4.

$$I^0 = \frac{k_c}{k_c^0} = 1 + 0.4295\varepsilon^{0.50771} \tag{4}$$

Strictly, while calculating the enhancement from experimental data, both the silent and sonicated runs should have identical values of the Reynolds number for these to cancel out while obtaining Eq. (4). In actual practice, however the two runs under identical rpm of the stirrer can have slightly different values of the Reynolds number due to minor differences between the dissolving cylinder dimensions in both cases. For purpose of illustration, this effect is ignored in Fig. 4. It can be seen that an enhancement of mass transfer

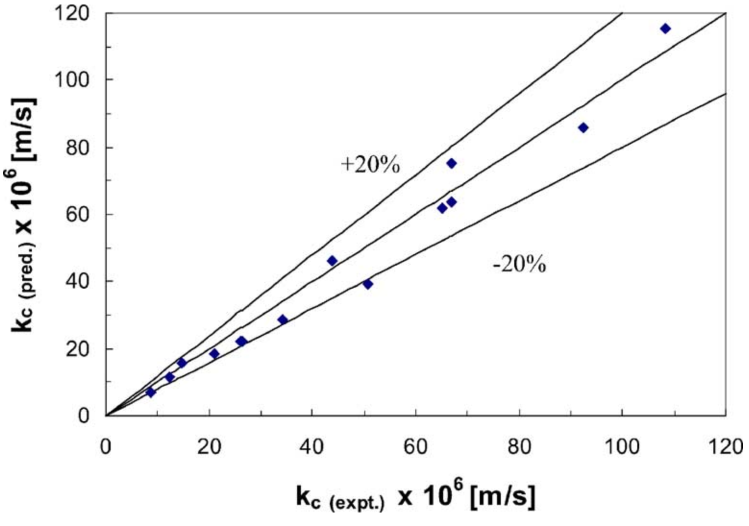

Fig. 3. Comparison of model prediction (Eq. (3)) with experimental data.

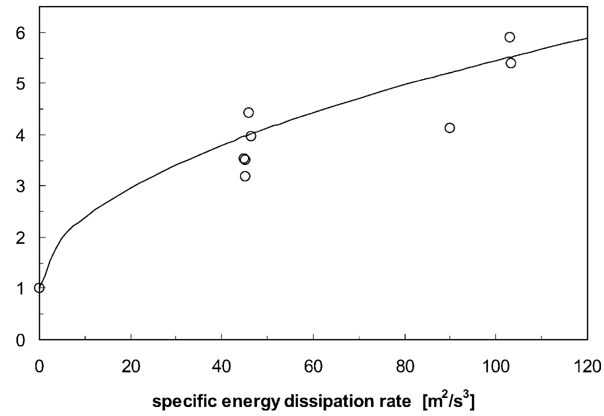

Fig. 4. Enhancement of mass transfer coefficient by ultrasound. The solid line represents Eq. (4).

coefficient up to 5.5 times can be obtained using ultrasound depending upon the specific power input. This enhancement is non inclusive of the contribution from the cylinder rotation. The mechanism for the enhancement would likely be due to enhanced turbulence and consequent reduction of the mass transfer resistance by the solvent impinging on the solid. The combined effects of mechanical rotation and ultrasound are illustrated in the three-dimensional plot in Fig. 5.

3.2. Mass transfer with chemical reaction

For comparison a limited number of experiments were performed only with chemical reaction. The rapid reaction regime has been assumed by Sherwood and Ryan [8] and Marangozis and Johnson [12] for this chemical system. The turbulent boundary layer analysis estimates were in reasonable agreement with observed enhancements. The enhancement was given by Eq. (5):

Table 1
Effect of chemical reaction on mass transfer

No.	Enhancement factor due to reaction (I^*)		
	rpm	Experimental	Predicted (Eq. (5))
1	50	6.27	6.48
2	100	6.19	
3	250	5.12	

$$I^* = \frac{k_c^*}{k_c^0} \approx \left(\frac{Sc_B}{Sc_A}\right)^{1/3} + \left(\frac{Sc_A}{Sc_B}\right)^{2/3}\left(\frac{C_B}{C_{Ai}}\right) \tag{5}$$

The enhancement in this case is also independent of the cylinder rotational speed. The results given in Table 1 are close to those predicted by Eq. (5). The results indicate that the enhancement factor is nearly independent of cylinder speed. This result is also corroborated by the correlation given by Holman and Ashar [9] for the ratio of Sherwood numbers with and without chemical reaction in which a small exponent (0.076) to the Reynolds number was obtained.

It can be observed that the enhancement of the mass transfer coefficient (k_c^0) due to ultrasound (up to a specific energy dissipation rate of 100 m^2/s^3) is comparable to that of chemical reaction. The two enhancement factors may be compared using Eqs. (4) and (5).

$$\frac{I^*}{I^0} = \frac{1 + a\varepsilon^b}{(Sc_B/Sc_A)^{1/3} + (Sc_A/Sc_B)^{2/3}(C_B/C_{Ai})} \tag{6}$$

In the present study Eq. (6) becomes

$$\frac{I^*}{I^0} = \frac{1 + 0.4295\varepsilon^{0.50771}}{6.48} \tag{7}$$

The two enhancements would be equal when specific energy dissipation rate is around 150 m^2/s^3.

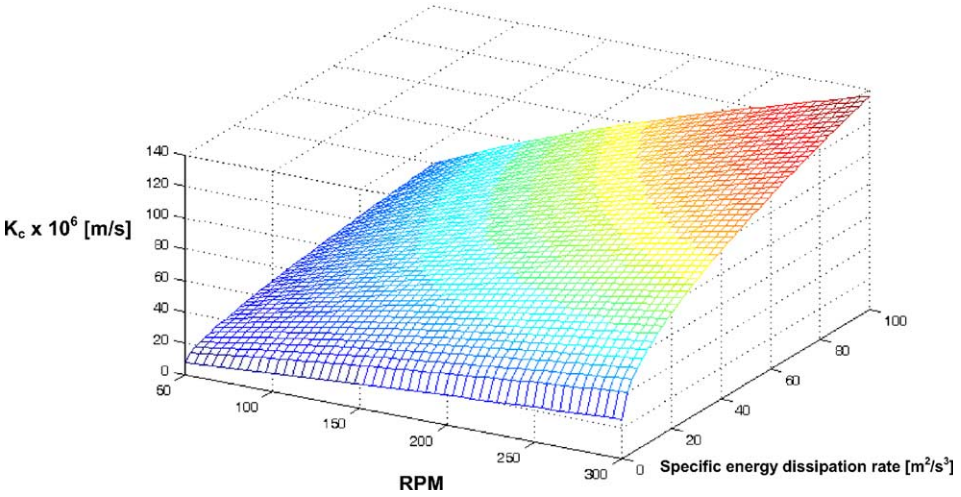

Fig. 5. Enhancement of mass transfer coefficient due to cylinder rotation and ultrasound.

4. Conclusions

The study of ultrasound effects on the solid of nearly constant geometry enables the focus to be on the mass transfer coefficient. Ultrasound results in significant enhancement of the solid dissolution rate. The mass transfer coefficients obtained in the presence of ultrasound indicated a strong dependency on the energy dissipation rate per unit mass. Enhancements of ultrasound to the mass transfer coefficient were higher than the contribution from mechanical rotation and comparable with those due to chemical reaction. Further studies of both theoretical and experimental nature are required to optimize the combined effects of ultrasound and mechanical rotation as well as understand the mechanism of enhancement.

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