ESTIMATION OF BUBBLE-TO LIQUID MASS TRANSFER RATE COEFFICIENT BY TRANSIENT RESPONSE TECHNIQUE AND BY STEADY STATE REACTION STUDIES

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Bubble-to-liquid mass transfer rate coefficient of hydrogen in n-heptane was determined by three methods: (1) measurement of reaction rate, hydrogenation of a-methylstyrene, under the limitation of mass transfer, (2) moment analysis from break-through curve and (3) moment analysis from pulse response. The values obtained by the three methods agreed within allowable experimental error, indicating that the latter two methods, which are easy in experimental practice, can be used for the evaluation with good accuracy. Of the latter two, the estimation from breakthrough curve showed better agreement and smaller scattering of experimental points.

Introduction

One of the present authors has recently presented a method of calculating mass transfer rate coefficient in a gas-liquid-solid three-phase slurry reactor4. The method is to calculate “moments” of input-response data and to compare them with theoretically derived expressions which are functions of mass transfer rate coefficients.

Dynamic methods for the evaluation of the rate coefficients were already reported by Misic and Smith3, where the analytical solution of the response function including unknown parameters of the rate coefficients is compared with an experimentally obtained curve. The method is, however, of limited use because it is difficult to separate the contribution of dispersion effect, which unavoidably occurs in any experimental apparatus, from total response. Successful analysis was done for the system where absorption-adsorption capacity is so large that the contribution of the dispersion effect is insignificant. In “moment” expression, such contribution is additive to the total moment and correction can readily be made.

Such method, however, cannot always be applied because surface catalysis itself is a very complicated phenomenon. Also, experimental reaction studies are rather difficult in comparison with dynamic experiments. It is therefore of considerable interest to compare mass transfer rate coefficients evaluated by the two methods.

Evaluation of the moments can be made either from delta (or pulse) response or from breakthrough curve. The latter evaluation was recommended in the previous report4, without any experimental support. One purpose of this paper is to give some experimental evidence to justify the above recommendation.

Hydrogenation of a-methylstyrene (AMS) was chosen as a test reaction. It is known6 that the reaction is first order with respect to hydrogen and zero order to AMS.

1. Theory

1.1 Steady-state reaction under the limitation of mass transfer rates

Under steady state of reaction, all the mass transfer rate should be equal. If all the rate processes are linear, global rate of reaction is proportional to $C^*$ with a proportionality constant $K$. Here, $C^*$ is concentration of limiting reactant (for the present case, $H_2$) at gas-liquid interface and $K$ is global rate coefficient, which is a function of $k_{LaB}$, $k_{as}$ and $k_{E_f}$. That is,

$$r = KC^*$$  

(1)
Plots of \( C^*/r \) vs. \( 1/M_s \) should give a straight line and
\( 1/k_l a_b V_b \) and \( 1/k_a + 1/k_e E_f \) can be calculated from the intercept and the slope, respectively.

1. 2 Moment analysis

When a pulse of sorbable gas was introduced into an inert gas stream at the absorber entrance, the shape of response curve at the exit is affected by mass transfer rate processes. In such a situation, with the restriction that all the rate processes be linear, that liquid phase be completely mixed and that gas bubbles be in plug flow*, moments of the response curve are related to the rate and equilibrium coefficients.

\[
\mu'_{1,\text{absorber}} = \frac{1}{H} \left( \frac{V_L}{Q} \right)
\]

\[
\mu'_{2,\text{absorber}} = \frac{1}{H^2} \frac{1+e^{-a_L}}{1-e^{-a_L}} \left( \frac{V_L}{Q} \right)^2
\]

\[
a = k_l a_b / \nu_b V_L H
\]

The derivation of the theory was given elsewhere in detail.

Before Eqs. (3)-(5) are compared with the moments calculated from experimentally obtained response curves, corrections must be applied for timelag and dispersion effect due to dead volumes. These corrections can be made by the use of insoluble gas as a tracer. Helium as a tracer gas and NaCl-saturated water were used for such purpose. Evaluation of the first absolute and second central moment from experimentally obtained response curves can be made by the use of Eqs. (6) and (7).

\[
\mu_1 = \int_0^\infty t C_{g,s} \, dt = \int_0^\infty C_{g,s} \int_0^\infty (C_{g,e,b} - C_{g,b}) \, dt
\]

\[
\mu_2 = \int_0^\infty (t-\mu_1)^2 C_{g,s} \, dt = 2 \int_0^\infty (C_{g,e,b} - C_{g,b}) \, t \, dt - \mu_1^2
\]

Here, subscripts \( \delta \) and \( b \) refer to delta response and breakthrough curve, respectively.

2. Experimental

2. 1 Reaction studies

The reactor was a cylindrical Pyrex bottle, about 20 cm high and 4.6 cm ID, containing 300 ml of liquid consisting of 10 mol% of AMS in \( n \)-heptane. The height of liquid level from gas disperser was 14.6 cm. The gas stream was introduced through a gas disperser made of a fritted glass disk, 2 cm in diameter. A magnetic stirrer was placed at the bottom of the reactor to prevent settling of catalyst particles. The stirrer, under mild rotating motion, has no effect on the moving behavior of bubbles, as revealed by visual observation. Under similar conditions, Misic and Smith stated that the complete mixing of liquid phase was established by the agitation induced by rising bubbles and that the stirrer has no effect on bubble-to-liquid and liquid-to-particle mass transfer rate.

In the course of reaction, liquid sample was taken from a sampling valve occasionally and analysed by gas chromatography, from which the rate of reaction was calculated. The catalyst used was 5% palladium-carbon supplied from Nippon-Engelhard Ltd., bulk density of which was 0.5 g/cm³. The reaction was carried out at room temperature (20±3°C) without any special temperature control. AMS and \( n \)-heptane were of reagent grade. Commercially available gases, H₂, He and N₂, were used for the reactant, tracer and carrier gases, respectively, without further purification.

2. 2 Dynamic experiments

Since we are particularly interested in the comparison of the two methods for evaluation, reaction studies vs. dynamic method, the simplest system was chosen, i.e., absorption of H₂ into \( n \)-heptane. Dynamic experiments were done with the same apparatus as that for reaction studies. Nitrogen was first introduced until steady state was established. Step function of sample gas, 10% of H₂ in N₂, was introduced by turning a four-way valve. Attention was paid to minimizing pressure fluctuation. Concentration of tracer gas was detected by TC cell.

Pulse, rather than step function, of hydrogen was introduced by a six-way valve. 100% of the H₂ was used as a pulse gas.

3. Results and Discussion

3. 1 Reaction studies

Pressure dependence of global rate, in moles of AMS reacted per unit time, is examined in Fig. 1. It is apparent that the rate is first order with respect to H₂ and zero to AMS. This is also supported by the finding that the plots of conversion versus time showed good straight lines through origin up to 70% conversion. The rate equation obtained here is the same as that reported by Sherwood and Farkas.

Global rates were determined as a function of catalyst loadings for various particles of different diameter. The results are plotted in Fig. 2, 1/r vs. 1/Mₚ. Reasonably good straight lines are obtained with the same intercept regardless of particle size. \( k_l a_b V_b \) was calculated from the intercept, with a* As will be described in experimental section, no back mixing of bubbles occurred. It is worth noting, however, that the plug flow approximation is not essential for the present case, where absorption capacity is rather low. Discussion is given elsewhere.
Table 1 Values of bubble-to-liquid mass transfer rate coefficients by the three methods

<table>
<thead>
<tr>
<th>Reaction studies</th>
<th>Moment analysis from breakthrough curve</th>
<th>Pulse response</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{Ld}a_dV_p$ [cm$^3$/sec]</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>$k_L$ [cm/sec]$^*$</td>
<td>0.14</td>
<td>0.17</td>
</tr>
<tr>
<td>Henry's constant (reference 2)</td>
<td>8.8</td>
<td>9.7</td>
</tr>
<tr>
<td>Standard deviation** for $\mu'_1$</td>
<td>—</td>
<td>0.00016</td>
</tr>
<tr>
<td>Standard deviation** for $\mu'_2$</td>
<td>—</td>
<td>0.0068</td>
</tr>
</tbody>
</table>

$^*$ With the help of Calderbank and Moo Young's correlation, the value of $k_L$, which is a function of bubble diameter, is expected to be 0.04-0.10 cm/sec.

** Let $\mu_i$ be individual values, $\mu$ be the mean value and $n$ be number of samples, standard deviation is defined as $\sqrt{(1/n)\sum(\mu_i - \mu)^2/\mu^2}$.

knowledge of Henry's constant from the literature$^2$. The values are listed in Table 1.

Slope of the plots in Fig. 2 shows combined resistances of liquid-to-particle mass transfer and surface reaction. It should be noted that approximate calculation of $k_L$ from Brian and Hale's$^5$ correlation showed that the main resistance is due to the $k_{Ld}$ term in the region of low catalyst loading.

3.2 Dynamic methods

To reduce random experimental error, several runs were repeated at each set of operating conditions. The extent to which the experimental points scatter is described later (Table 1).

The plots of first moment vs. $V_L/Q$, Fig. 3, show good straight lines through origin, both for He-NaCl-water and H$_2$-n-heptane systems. First moment is the sum of dead volume contribution and absorption terms. The former term for both systems is the same. Hence, the difference of first moment plots, the broken line in Fig. 3, is

$$\Delta \mu'_i = \frac{H_1 - H_2}{H_1 H_2} \frac{V_L}{Q} = \frac{1 - H_2 H_1}{H_2} \frac{V_L}{Q}$$

where $H_1$ and $H_2$ are Henry's constant for He-NaCl-water and hydrogen-n-heptane, respectively. If, as a first approximation, we neglect the term, $H_2/H_1$, the slope of the broken line directly gives $H_1$. Calculated values of $H$ are given in Table 1. Reasonable agreement with the literature value was obtained. The error arising from the complete neglect of $H_2/H_1$ can be calculated. With a knowledge of salting-out coefficient$^2$, through which $H_1$ was calculated to be 245, the error amounted to only 3-5%.

The second-moment data for different flow rates are plotted against $(V_L/Q)^2$ in Fig. 4. Again, good straight lines were obtained. Experimentally obtained second moment, $\mu_{2_\text{total}}$, is the sum of dispersion effect in the dead volume and mass transfer effect in the absorber. Since these two contributions to the "moment" are additive, we can separate the contribution of mass transfer effect by taking the difference of $\mu_{2_\text{H}_2\text{-heptane}}$ and $\mu_{2_\text{He-NaCl-water}}$.

From the slope of the difference, the broken line, $k_{Ld}a_dV_p$, was calculated and values are listed in Table 1.

Moments from pulse response data instead of breakthrough curve were also calculated from Eqs. (6) and (7). Correction for the contribution of the dead

Fig. 1 Reaction rates vs. partial pressures of H$_2$

Fig. 2 Plots of 1/r vs. 1/M$_S$ for the verification of Eq. (1)

Fig. 3 First moments calculated from breakthrough curves vs. $V_L/Q$
volume effect was made by a similar method: pulse of $H_2$ was introduced into NaCl-water. First- and second-moment plots against $V_l/Q$ and $(V_l/Q)^2$, respectively, again showed good straight lines through origin. Their slopes give rate and equilibrium coefficients, and these values are shown in Table 1.

Plots from pulse response data scattered from the line to a greater extent than for the breakthrough curve. This was shown by the calculation of standard deviation from the curve for both methods.

### 3.3 Measurements of bubble properties

To separate $k_L$ from the product $k_La_BV_B$, bubble diameter and bubble volume are measured. Bubble diameter was estimated from photographs of rising bubbles. Large bubbles are elliptical in shape whereas smaller bubbles are spherical. From the examination of about one hundred bubbles, average bubble diameter is calculated to be 1.4 mm. Bubble volumes are measured from the rise of liquid level when gas was bubbled, from which bubble velocity was estimated to be 24 cm/sec. The value lies within reasonable deviation from literature value ($\approx 20$ cm/sec$^3$). It was found, however, that the determination of $V_B$ and $d_B$ contained errors to a considerable extent. It follows that trials to separate $k_L$ from the product, $k_La_BV_B$, are carried out only for a restricted purpose, i.e., to show that the value of $k_L$, which is given in Table 1, lies in a reasonable order of magnitude.

From Calderbank and Moo-Young's correlation$^{1}$, $k_L$ can be calculated to be 0.04 cm/sec (for small bubbles; $d_B < 0.25$ cm) or 0.01 cm/sec (for large bubbles; $d_B > 0.25$ cm). Our values obtained are 2 to 5 times larger than calculated values. However, such difference is often found for this kind of experiment (for example, references$^{3,4}$).

### 3.4 Comparison of the three methods for evaluation

The rate parameter for absorption, $k_La_BV_B$, evaluated from the three methods agreed with one another within an allowable experimental error.

From the comparison of the two methods of obtaining moments, pulse response vs. breakthrough curve, the latter was found to be better in the sense that the experimental points scattered to a lesser extent. It is considered that such scattering is induced not only from the measurements of response curve but also from the numerical calculation of moments from the obtained curve. For the calculation from pulse response data, integration of concentration multiplied by a factor of $t^2$ must be carried out. Reading error of the uncertain tail of the response curve is significant because it is emphasized by the factor of $t^2$. On the other hand, the multiplication factor is $t$ in the case of breakthrough curve and we can avoid, at least partially, the emphasis of the uncertain tail.

### Conclusion

The moment analysis of dynamic response data was successfully applied for the estimation of bubble-to-liquid absorption rate parameter.

Since bubble-to-liquid mass transfer often becomes the rate-controlling step of a reaction in a three-phase slurry reactor, and since the evaluation of such rate parameter from theoretical or semiempirical equations is often impossible, a method of experimental evaluation of such rate parameter with easy practice will be useful.

### Nomenclature

- $a_B = \text{surface area of bubbles per unit volume of bubbles}$ [cm$^{-1}$]
- $a_s = \text{outer surface area of particles per unit volume of particles}$ [cm$^{-1}$]
- $C_g = \text{concentration in gas}$ [mol/cm$^3$]
- $C_{L*} = \text{concentration in liquid which is in equilibrium with gaseous concentration}$ [mol/cm$^3$]
- $d_B = \text{bubble diameter}$ [cm]
- $E_f = \text{effectiveness factor of catalyst}$
- $H = \text{Henry's constant}$
- $k_L = \text{bubble-to-liquid mass transfer coefficient}$ [cm/sec]
- $k_r = \text{intrinsic rate constant}$ [sec$^{-1}$]
- $k_s = \text{liquid-to-particle mass transfer coefficient}$ [cm/sec]
- $L = \text{height of liquid level measured from the entrance of gas bubbles}$ [cm]
- $M_s = \text{mass of catalyst particles in the reactor}$ [g]
- $Q = \text{gas flow rate at room temp. and 1 atm}$ [cm$^3$/sec]
- $r = \text{global rate of reaction}$ [mol/sec]
- $v_B = \text{vertical bubble velocity}$ [cm/sec]
- $V_B, V_L = \text{total volume of bubbles and liquid in the reactor}$ [cm$^3$]
- $\alpha = \text{absorption rate parameter defined by Eq. (5)}$ [-]
- $\mu_1, \mu_2 = \text{first absolute and second central moments}$ [sec and sec$^2$]
- $\rho_p = \text{particle density}$ [g/cm$^3$]
APPLICATION OF PARTICLE ENLARGEMENT BY CONDENSATION TO INDUSTRIAL DUST COLLECTION

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Application of the phenomena of particle growth by condensation to industrial dust collection was studied. The analysis to evaluate the extent of size enlargement was first introduced to the two essential and industrially useful methods, one of which is the mixing of hot saturated air with cold air, the other being injection of steam into air. Four typical processes are proposed for effective application to industrial exhaust gas and the procedure of using these processes is illustrated according to the various conditions of exhaust gas. The technique for size enlargement of aerosol particles by condensation was found to be essentially applicable to any industrial exhaust gas which contains submicron dust particles in low number concentration when the appropriate process shown herein is selected.

Introduction

Fundamental analysis and experimental studies of the growth of aerosol particles by condensation were discussed in our previous paper, where it was suggested that particle growth by condensation is one of the most promising preconditioning techniques for the collection of submicron dust particles. Industrial application of the fundamental results is developed in this paper.

Condensation of water vapor on aerosol particles not consisting of soluble substances will essentially occur wherever a certain degree of supersaturation is produced around the particles. The fundamental analysis of the method of producing supersaturation by mixing hot saturated air with cold air, which was reported already, is first briefly cited, and then that of the additional method of injecting steam into air is proposed. The establishment of economical processes to produce supersaturation using these methods will be important from the industrial point of view. Processes for this purpose are discussed and developed under consideration of various conditions, such as temperature and humidity, of industrial exhaust gas. Some processes are proposed according to various conditions of exhaust gas and are arranged into charts for facility of design of a preconditioner of industrial dust collection. The applicability of particle growth by condensation to dust collection was studied experimentally by observing the actual increase in particle size by condensation and the improvement of dust collection efficiency of the wet scrubber.

1. Basic Considerations

In this section the fundamental aspects of particle growth by condensation will be briefly introduced. The point “i” on the humidity chart of Fig. 1 indi-