Dimensional Analysis in Photochemical Reactor Design

WILLIAM J. DOLAN
Columbia University, New York, New York

CARL A. DIMON and JOSHUA S. DRANOFF
Northwestern University, Evanston, Illinois

The equations which describe the performance of a continuous tubular photochemical reactor have been formulated and analyzed by dimensional analysis. Experimental data obtained in a study of the decomposition of hexachloroplatinic acid in water were correlated as suggested by the dimensional analysis, thus partially confirming the validity of the approach.

The analysis and design of photochemical reactors until recently have been largely neglected in the chemical engineering literature. As a result, relatively little background is available as a guide in the engineering development of such devices. The present work is part of a research program on photochemical reactor design and scale-up aimed at providing such background. The approach taken in this study was to formulate the partial differential equations which describe a continuous tubular photochemical reactor and to extract from the dimensionless form of these equations the dimensionless groups upon which reactor-performance should depend. Scale-up from small scale laboratory equipment as well as correlation of experimental data should be possible in terms of these groups. An experimental program to check the validity of this approach was then initiated, and some results are presented below.

PREVIOUS WORK

The essential literature in this area has recently been reviewed by Harris and Dranoff (*1*); therefore only those papers which pertain directly to this work will be mentioned here. Experimental studies of tubular photochemical reactors have been carried out previously by Baginski (*2*), Gaertner and Kent (*3*), and Huff and Walker (*4*). Baginski's work concerned the liquid phase reaction of hydrogen sulfide and *n*-1-octene. It is of interest primarily because the basic reactor design has been used in subsequent studies, including the present one. Gaertner and Kent studied the photolysis of aqueous uranyl oxalate under laminar flow conditions. They were able to correlate low conversion ($< 12\%$) data in terms of average reactor contact time. Such behavior was also predicted theoretically, but cannot be safely generalized from this work alone, because of the small changes in reactor conditions associated with the low conversions which were involved. Huff and Walker studied the gas phase photochlorination of chloroform over a range of flow rates, compositions, reactor diameters, and illuminated length. They were able also to correlate low conversion data obtained under turbulent flow in terms of average contact time, but this approach was not satisfactory for laminar flow data.

There have also been two theoretical publications of interest. Schechter and Wissler (*5*) considered a laminar flow, isothermal reactor with molecular diffusion. For a reaction first-order with respect to light intensity and concentration and by assuming a constant absorption coefficient, they solved the differential equation for composition in the reactor and presented the results graphically. Foraboschi (*6*) analyzed a similar system by dimensional analysis with the Buckingham theorem. However, generalizations based on both these analyses are unsafe because of the restricted assumptions made in the developments.

THEORETICAL DEVELOPMENT

The analysis of a photochemical reactor is based on the application of the equations of change to the device in question, with due attention to its special characteristics. In particular, the equations for conservation of mass, energy, and momentum are required, along with expressions for the rate processes involved. The appropriate forms of these relations for a continuous photochemical reactor are developed below.

The reactor of interest is a round quartz tube of radius R through which reactant fluid flows in well-developed flow. The tube is irradiated uniformly from without by radially incident, monochromatic, ultraviolet radiation. Light passing into the reactor is absorbed by the solvent fluid and the reactant species and initiates a chemical reaction which consumes the reactant. By assuming that the fluid is dilute with respect to reactant and incompressible, and that isothermal conditions are maintained, one can solve the steady state momentum and overall continuity equation with the usual no-slip boundary conditions to determine the velocity profile within the tube, $v_z = v_z(r)$. (Note that in turbulent flow, v_z represents the time-averaged velocity profile.) The steady state continuity equation for reacting species may then be shown to be (*7*)

$$v_z(r)\frac{\partial c}{\partial z} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right] + P \qquad (1)$$

This form assumes angular symmetry and neglects axial diffusion, both of which normally are acceptable assumptions. For cases in which the primary photochemical reaction is the rate controlling process (that is, in the absence of light induced chain reactions or postirradiation

W. J. Dolan is with the U.S. Army, Edgewood Arsenal, Maryland. C. A. Dimon is with Mobil Oil Company, Dallas, Texas.

effects), P may be set equal to the rate of light absorption in the reactor multiplied by an appropriate quantum efficiency factor. Thus

$$P = -(E\phi/Nhf \tag{2}$$

The group E/Nhf represents the number of moles of quanta absorbed per unit time and volume. A suitable expression for E, the rate of light absorption per unit volume, may be obtained from a balance on electromagnetic energy within the reactor. Thus, if I represents the point light intensity, or energy flux, and if one assumes that a fraction μ of the incident light is absorbed per unit path length through the reactor, the intensity profile can be described by the following equation:

$$\frac{1}{r}\frac{\partial}{\partial r}(rI) = -\mu I \tag{3}$$

and it may be seen that

$$E = -\mu I \tag{4}$$

Thus, Equation (1) becomes

$$v_z(r)\frac{\partial c}{\partial z} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right] + \frac{\mu\phi I}{Nhf} \tag{5}$$

Equations (3) and (5) must now be solved with the boundary conditions on concentration and light intensity which follow:

$$I(R, z) = I_o \tag{6}$$

$$c(r, o) = c_o \tag{7}$$

$$\frac{\partial c}{\partial r}(R, z) = 0 \tag{8}$$

$$\frac{\partial c}{\partial r}(o, z) = \lim_{r\to 0}\left[\frac{\mu\phi Ir}{NhfD}\right] \tag{9}$$

The boundary conditions are all self explanatory with the exception of Equation (9), which arises because the light intensity approaches infinity at the reactor center line, although the volume at that point approaches zero. In order to arrive at this equation, one necessarily must make a material balance over a small cylinder around the center, and then take the limit of this balance as the radius shrinks to zero. A similar technique was reported previously by Schechter and Wissler (5). Their boundary condition differs slightly due to the different form of reaction expression used in that work.

The mathematical description of the reactor is now complete, and these equations could, in principle, be solved to yield the concentration and light intensity profiles throughout the reactor. However, this is essentially an impossible task, because the absorption coefficient μ is normally a strong function of reactant concentration. The quantum efficiency ϕ likewise is a function of concentration as well as light intensity. In addition, these two factors are usually functions of wavelength of the incident radiation, thus further complicating practical problems. Because of this interdependence, the equation system involved is a coupled nonlinear system, and analytical solution techniques are not available for such mathematical problems.

The equations are useful, however, for dimensional analysis of the problem at hand. For this purpose, the equations may be rewritten in dimensionless form with the following definitions:

$$v^* = v_z/v_{avg} \tag{10}$$

$$c^* = c/c_o \tag{11}$$

$$I^* = I/I_o \tag{12}$$

$$\mu^* = \mu/\mu_o \tag{13}$$

$$\phi^* = \phi/\phi_o \tag{14}$$

$$r^* = r/2R \tag{15}$$

$$z^* = z/L \tag{16}$$

In Equations (13) and (14), μ_o and ϕ_o are the values of μ and ϕ, respectively, when c is c_o and I is I_o.

In these terms the system equations become

$$\frac{1}{r^*}\frac{\partial}{\partial r^*}(r^* I^*) = -A\mu^* I^* \tag{17}$$

$$v^*\frac{\partial c^*}{\partial z^*} = \frac{1}{(N_{Re})(N_{Sc})(N_{Le})}\left[\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial c^*}{\partial r^*}\right)\right] + P_o\mu^*\phi^* I^* \tag{18}$$

$$I^*\left(\frac{1}{2}, z\right) = 1 \tag{19}$$

$$c^*(r^*, o) = 1 \tag{20}$$

$$\frac{\partial c^*}{\partial r^*}\left(\frac{1}{2}, z^*\right) = 0 \tag{21}$$

$$\frac{\partial c^*}{\partial r^*}(o, z^*) = (N_{Re})(N_{Sc})(N_{Le})(P_o)\lim_{r^*\to 0}[\mu^*\phi^* I^* r^*] \tag{22}$$

Of the dimensionless groups thus introduced, only the absorption factor

$$A = 2R\mu_o \tag{23}$$

and the reaction group

$$P_o = \left(\frac{\mu_o\phi_o I_o}{Nhf}\right)\left(\frac{\pi R^2 L}{c_o v_{avg}\pi R^2}\right) = \left(\frac{\mu_o\phi_o I_o L}{Nhf\, c_o v_{avg}}\right) \tag{24}$$

are unusual. The latter can be seen to represent the ratio of the overall molar reaction rate at inlet concentration and incident intensity to the input molar flow rate of reactant.

From Equations (17) to (22), one can see that the flow averaged concentration at the end of a reactor of length L will have the functional form

$$\overline{c^*} = \overline{c^*}[(N_{Re})(N_{Sc})(N_{Le}), P_o, A] \tag{25}$$

Therefore, it should be possible to correlate experimental data as well as to predict reactor scale-up in terms of the dimensionless parameters A, P_o, and the group $(N_{Re})(N_{Sc})(N_{Le})$. Application of this approach to real systems will, however, be affected by the validity of two principal assumptions mentioned earlier: the nature of the rate controlling process and the use of a monochromatic light source. Whereas the former may be satisfied by proper choice of the reacting system, the latter assumption is violated by most commercially available light sources. The significance of deviations from monochromatic radiation will depend on the specific system under consideration, but as an initial approximation it is assumed that the basic functional form of Equation (25) will be valid even for polychromatic sources.

An experimental test of this approach has been carried out in part with the results described below.

EXPERIMENTAL

Two important decisions made at the outset of the experimental study were the choice of the reacting system and the reactor configuration to be used. The reaction selected was the liquid phase hydrolysis of chloroplatinic acid. This reaction has

been rather extensively studied by Boll (*8*), who deduced the stoichiometry to be given by

$$2H_2PtCl_6 + 11H_2O \rightarrow 11HCl + H_2PtCl(OH)_5 \cdot H_2Pt(OH)_6 \quad (26)$$

followed by a slower reaction

$$H_2PtCl(OH)_5 \cdot H_2Pt(OH)_6 + H_2O \rightarrow HCl + 2H_2Pt(OH)_6\downarrow \quad (27)$$

As noted previously (*1*), the reaction is very suitable for this type of program in that it can be carried out in the liquid phase in very dilute solutions. Furthermore, the extent of the reaction can be followed easily by measurement of electrical conductivity. The reaction takes place at room temperature under the influence of ultraviolet light and is apparently only very slightly affected by temperature. Finally, in the ultraviolet region the reactant solution has an extinction coefficient and quantum efficiency which are strong functions of composition as well as wavelength. Thus, this is a complex nonchain reaction and any generalities which may appear from work with such a system should be applicable to simpler systems as well.

There are two minor disadvantages in the use of this reaction system. One is that the solution prepared from hexachloroplatinic acid undergoes a dark reaction, with the apparent liberation of two chlorine atoms to form a solution of tetrachloroplatinic acid. This can be offset, however, simply by allowing sufficient time for the dark reaction to run to completion (*9* to *11*). Another disadvantage is that the reaction is also sensitized by light emitted from fluorescent lamps in the laboratory. Proper shielding of equipment in which reactant is contained eliminates this problem.

The reactor configuration chosen was designed to approximate as closely as possible to the system described earlier. It consisted of a tubular reactor surrounded by a thin annulus through which water was passed to maintain temperature control. The cylindrical reactor was located at one focus of an ellipsoidal reflector with a slender ultraviolet light source located at the other focus. This arrangement permitted essentially uniform irradiation of the reactor tube surface. Such a device represents an approximation to a truly radially irradiated reactor vessel, deviating from the ideal model since both the reactor and light source are finite in size rather than line elements and the lamp emits some nonradial radiation. However this was felt to be a reasonable approximation and perhaps as close to ideality as one might expect an industrial installation to come.

A sketch of the reactor assembly is shown in Figure 1. The reflector used was 18 in. in length, with the elliptical base having major and minor diameters of 10 and 9 5/32 in., respectively. In this configuration the foci are 4 in. apart. The reflector was made of polished aluminum lighting sheet (20 gauge, Alzak treated), which reflected 80 to 85% of the incident radiation in the ultraviolet region (*12*). The elliptical shape was supported by a wooden frame (*10*). End pieces for the reflector were made of ¾ in. Transite which provided adequate heat resistance.

The ultraviolet light source used was a General Electric UA-11-Uviarc lamp. This is a 1,200 w. lamp with an 18 in. arc, with approximately a 250 w. output in the ultraviolet range (2,200 to 4,000 Å.). Since the lamp generated a considerable amount of heat, it was necessary to provide cooling to the reactor as well as to the reflector assembly. For the latter purpose, air was passed through the device by a small blower. Some experimentation was required to find a suitable air rate which would permit temperature control and yet allow the lamp to reach its operating temperature and rated output.

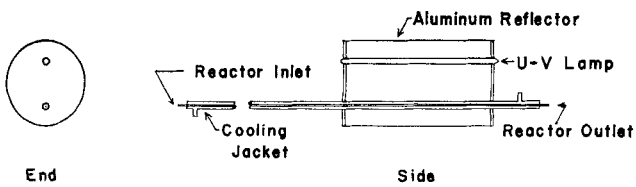

Fig. 1. Reactor configuration.

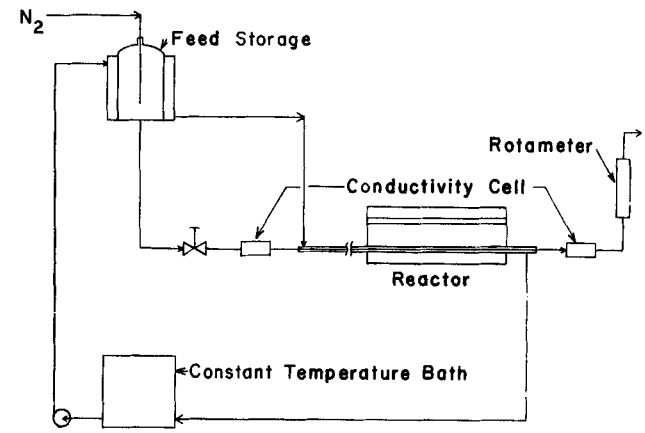

Fig. 2. Flow system.

Both the reactor tube and the cooling jacket tube were fused quartz with 1 mm. walls. This material transmitted 90 to 95% of the ultraviolet radiation (*12*). The tubes were obtained in 4 ft. lengths and used in their full lengths. This provided adequate entrance sections for the reactor. Two different central reactor tubes with diameters of 5 and 10 mm., respectively, were used. The water jacket had an inside diameter of 20 mm. Distilled water from a constant temperature batch was circulated through the annular region to maintain temperature at a fixed level. Since distilled water is an excellent transmitter of ultraviolet light (*12*), the net effect of the water jacket was a 10 to 15% maximum attenuation of the incident radiation. The absorption figures quoted above apply to short wavelengths (2,200 Å.). Figures for the longer wavelengths, and therefore for the average transmission, would probably be significantly higher than these values.

The reactor was incorporated in a flow system as shown in Figure 2. The inlet and outlet were connected to flow types of electric conductivity cells which permitted the instantaneous measurement of the average solution conductivity entering and leaving the reactor. The reactor feed was supplied from a premixed solution placed in a jacketed feed bottle from which it was displaced by nitrogen under pressure. Flow control was achieved by the use of a valve and flow measurement by rotameters in the outlet line. During experiments the reactor and feed system temperatures were kept at 25°C. by circulating water. Maintenance of constant temperature was more important for standardization of electrical conductivity measurements than for the reaction control, since the reaction is apparently only slightly sensitive to temperature. Thermometers were located near each conductivity cell to permit continual check of the temperature of the fluid. All quartz and glass tubing outside the reaction zone were covered by rubber tubing or opaque plastic tape to exclude extraneous light.

Experiments were carried out in the two different reactor tubes with various exposed lengths. The lengths used were 18.00, 9.00, 4.50, 2.25, and 0.75 in. The short lengths were obtained by masking the 18 in. reaction zone either with black plastic tape or with aluminum foil, the inner surface of which was blackened with carbon to reduce reflection.

In general, the operation of this equipment was quite satisfactory. The only serious experimental problem encountered was the formation of a slight deposit of reaction product on the inside wall of the reaction tube. It is suspected that this was the slightly soluble platinum hydroxide indicated previously in Equation (27). The deposit appeared as a uniform film of yellowish-green material which was most intense at the entrance to the reaction zone and tapered off rapidly thereafter. It appeared that the deposit formed more quickly when the reactor was operating in the turbulent region. Since no suitable solvent was found to this deposit, it was removed mechanically by a long-handled test tube brush. In general, the deposit would have a noticeable effect on reactor conversion after several minutes operation, as determined by replicated experiments. Thus, it was necessary to brush out the reaction tube frequently. By careful attention to this point, it was possible to minimize the effect of this deposit on the results.

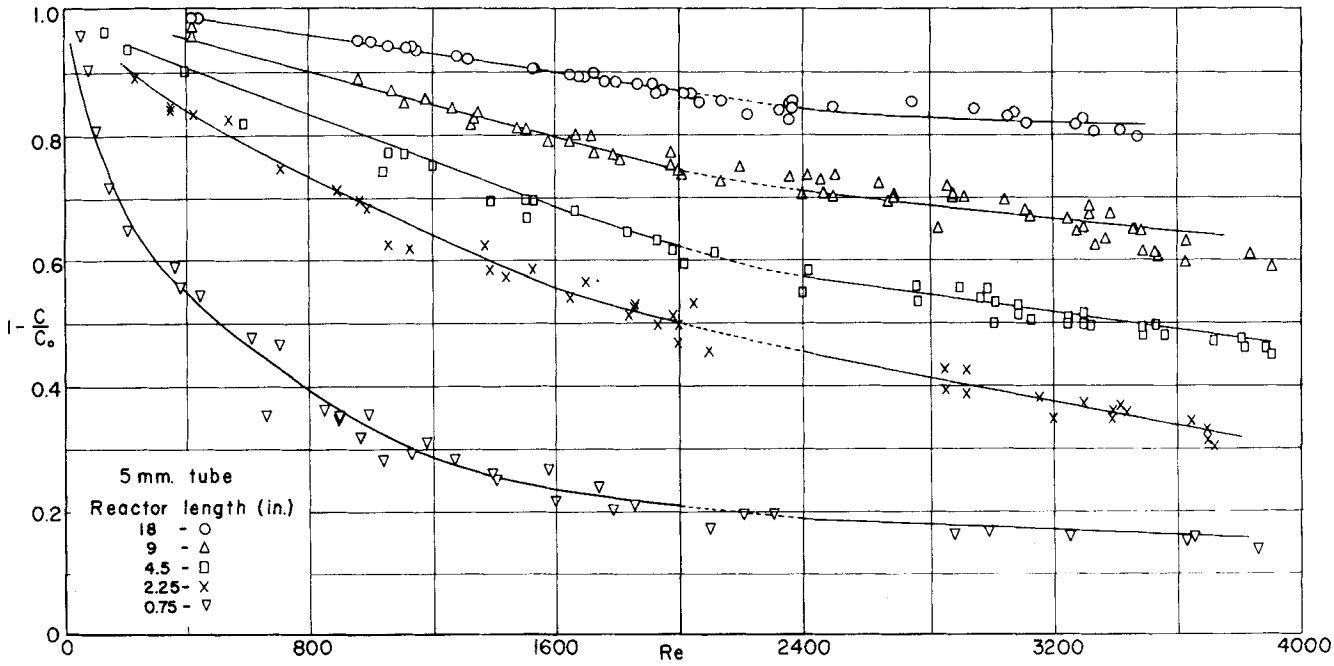

Fig. 3. Fractional conversion vs. Reynolds number.

RESULTS AND DISCUSSION

Approximately four hundred experimental runs were made with this equipment. The experimental conductivity readings were converted to fractional conversions based on the total possible change in conductivity for the given feed solutions. The latter was determined by allowing the feed to pass through the reactor at very slow flow rates. Experiments were made at a large number of different flow rates for each exposed reactor length with both the 5 and 10 mm. reactor tubes. Some of the data obtained for the 5 mm. tube are shown in Figure 3 in a plot of fractional conversion as a function of Reynolds number, with reactor length as a parameter. Similar data were obtained with the 10 mm. tube. The curves drawn through the data are indicated as dotted lines in the region of Reynolds number from 2,000 to about 2,400, corresponding to the normal transition zone from laminar to turbulent flow. Although the data appear to undergo a smooth transition from one range of Reynolds number to the other, actually it was found in the experiments that the conductivity fluctuated rapidly whenever the Reynolds number reached the 2,000 to 2,200 range. At lower or higher Reynolds numbers, the flow cells gave steady readings which were independent of flow rate. Therefore, it was assumed that the indicated fluctuations were produced by the transitional flow at these Reynolds numbers. It was not possible to ascertain the magnitude of the concentration fluctuations in this apparatus, but they were large enough to make it impossible to get accurate conductivity readings. In view of this fact, it is rather surprising that the data shown in Figure 3 exhibit no apparent discontinuity.

As noted above, the main experimental problem encountered was the formation of a deposit on the reactor wall. Despite the careful cleaning process used, this effect contributed to the scatter of the data about the mean curves, which were drawn in by inspection. It is felt, however, that this scatter is not excessive for such experiments.

It was desired to test the previous analysis by a correlation which would collapse these experimental data to a single curve. All the data for a given reactor tube size were obtained with the same feed concentration (10^{-4} molar) and the same light intensity. Thus the parameters based on the inlet concentration and incident light inten-

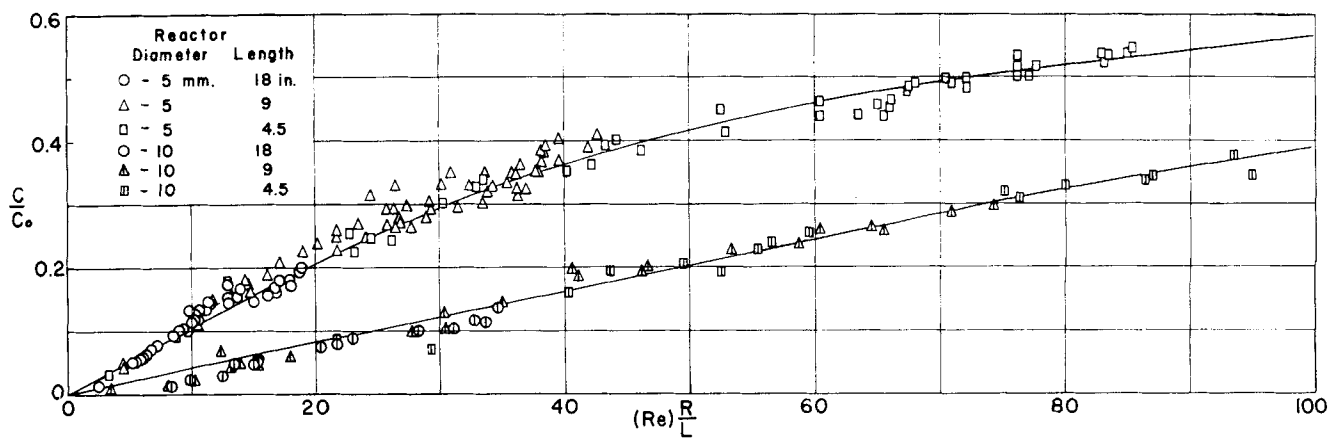

Fig. 4. Data correlation, low range.

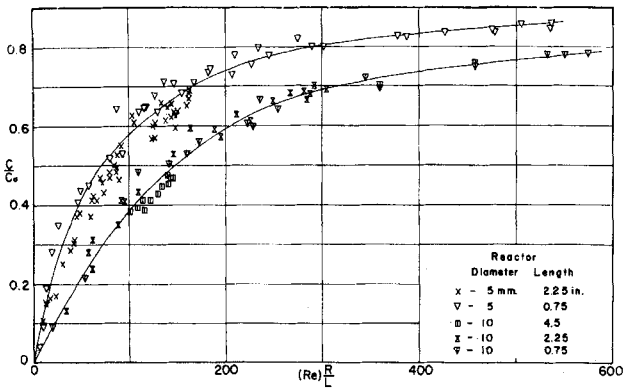

Fig. 5. Data correlation, high range.

sity were constant throughout the experiments, In fact, the only parameters which varied were reactor length and average fluid velocity. Equation (25) thus predicts that the dimensionless concentration data for a single reactor should correlate against (L/v_{avg}). A related plot of dimentionless concentration vs. the product of Reynolds number and the ratio of reactor radius to length is shown in Figure 4. The abscissa here is directly proportional to the inverse of (L/v_{avg}) and is a suitable parameter for this test. It was chosen because of the convenience of the resulting scale. Note that on this plot low dimensionless concentrations correspond to high conversions, while low values of the abscissa correspond to long reactors and low flow rates. Figure 5 shows additional data for higher values of the abscissa. No points have been repeated between these two figures, but the curves shown are duplicated on each plot. These curves represent a visual fit to the experimental data which cover a large range of flow rates and tube lengths, with Reynolds numbers ranging approximately from 100 to 4000. It is quite evident from these figures that this is an excellent method for correlating data from a single tube. There is, to be sure, some scatter of the data about the curves, but this is felt to be acceptable for the present experiments and does not detract from the obviously good correlation achieved. The scatter is somewhat worse for data corresponding to short reactor lengths. This is probably due to errors in effective reactor length resulting from improper masking of the reaction zone and/or the effect of the reaction product deposit.

Thus, these results confirm the prediction from dimensional considerations that average contact time (L/v_{avg}) should be a suitable correlating parameter when the rate controlling process is the primary photochemical reaction. Although this approach was used previously in the work of Gaertner and Kent and in part of the work of Huff and Walker, the present study is the first to give a dimensional basis for its success and to demonstrate its validity over a wide range of experimental conditions.

With respect to the failure of the laminar flow data of Huff and Walker to correlate in this way, it seems quite likely that postirradiation effects were significant in these data, thus violating one of the prime assumptions of the analysis. Under turbulent flow conditions, however, mixing was probably vigorous enough to cause the rapid consumption and/or deactivation of sensitized species in their work, thus eliminating the possibility of postirradiation effects and allowing the results to correlate as predicted. This behavior suggests caution in the application of the present technique to complex chain reactions for which mechanistic studies indicate secondary steps to be rate controlling.

It would, of course, be desirable to correlate the data for the two different reactor diameters used. However, consideration of the dimensionless parameters involved and the method by which these experiments were carried out precludes this possibility. If the same dimensionless concentration is to be achieved in two different experiments, the values for all dimensionless groups must be the same in both sets of experiments. This can only be achieved by varying simultaneously the reactant concentration as well as the incident light intensity, which was not possible in the present investigation.

In view of these results, it is concluded that the basic model proposed for a continuous photochemical reactor is sound. Although the validity of the dimensional analysis approach used has been confirmed partially, more extensive testing is indicated, especially with respect to changes in the new dimensionless groups A and P_o, in order to firmly establish its utility.

ACKNOWLEDGMENT

The authors wish to acknowledge with thanks fellowships from Northwestern University (to CAD) and Columbia University (to WJD), and a summer research grant from the Du Pont Company (to JSD) which have made this work possible.

NOTATION

A = dimensionless absorption factor, $2R\mu_o$
c = reactant concentration, moles per volume
D = effective reactant diffusivity, length²/time
E = rate of energy absorption per unit volume, energy/(volume)(time)
f = frequency of radiation, time^{-1}
h = Planck's constant, energy/time
I = radiation intensity, energy/(area)(time)
L = reactor length, length
N_{Le} = dimensionless length ratio $2R/L$
N = Avogadro's number
P = rate of production of reactant by reaction, moles/(volume)(time)
P_o = dimensionless ratio of reaction rate at inlet condition to input molar flow rate of feed, $\dfrac{\mu_o\phi_o I_o L}{Nhf c_o v_{avg}}$
r = radial coordinate, length
R = reactor radius, length
N_{Re} = Reynolds number, $\dfrac{2R v_{avg}}{\nu}$
N_{Sc} = Schmidt number, ν/D
v_z = fluid velocity, length/time
v_{avg} = average fluid velocity, length/time
z = axial coordinate, length

Greek Letters

μ = extinction coefficient, length^{-1}
ν = kinematic viscosity, length²/time
ϕ = quantum efficiency, moles of reactant consumed/moles of quanta absorbed

Subscript

o = evaluated at inlet conditions

Superscripts

* = dimensionless quantity
$\bar{}$ = averaged quantity

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Manuscript received March 9, 1965; revision received July 10, 1965; paper accepted July 26, 1965. Paper presented at A.I.Ch.E. San Francisco meeting.

Diffusion Through the Liquid-Liquid Interface: Part II. Interfacial Resistance in Three-Component Systems

W. J. WARD and J. A. QUINN

University of Illinois, Urbana, Illinois

In an investigation of the transfer of solute molecules across the liquid-liquid interface, the transfer of acetic acid, benzoic acid, oleic acid, and cholesterol between benzene and water was measured. Experiments were carried out with a laminar jet apparatus wherein the organic phase was spread as a thin film on the surface of an aqueous jet. The results indicate that any interfacial resistance in these systems is negligibly small.

In an earlier publication (23) we considered some basic features of interphase mass transfer in binary systems. From experimental results for benzene and for toluene diffusing into water at contact times as small as 0.01 sec., it appears that in two-component systems chemical equilibrium is established rapidly at a freshly formed liquid-liquid interface and any interfacial resistance is vanishingly small. The present investigation is an extension of the previous study to the more significant case of transfer in three-component systems.

Most of the experimental work reported on diffusion of a solute through the liquid-liquid interface has been carried out with stationary systems (with or without mechanical stirring in the bulk phases) or transfer from droplets. [Pertinent literature has been summarized elsewhere (7, 16, 23).] The difficulties encountered in using stationary systems are (1) contact times are relatively long and therefore bulk resistances mask any interfacial resistances smaller than approximately 1,000 sec./cm. and (2) at long times attendant interfacial phenomena, such as the Marangoni effect, and contamination of the interface by ever-present surface-active impurities may further obscure the diffusion process. In studying transfer from droplets one must analyze the circulation within and around the droplet—a formidable problem involving flow in the bulk phases coupled with the rheological behavior of the interface.

To overcome the difficulties listed above it would appear that a suitable technique for studying diffusion across the liquid-liquid interface is a dynamic experiment, so that small contact times can be attained, with a well-defined flow field. Three such experiments have been reported recently (15 to 17), but none are applicable to three-component systems. In the present investigation a dynamic method has been developed for studying a wide range of three-component systems. The technique was previously tested by the authors on two binary systems (23). In the work reported here measurements have been made on four ternary systems.

THE EXPERIMENT

The two phases were contacted with a laminar jet apparatus with the organic phase spread as a thin film on the surface of an aqueous jet issuing from a circular nozzle. After falling some distance in contact, the phases were separated at a specially designed receiver. The resulting average concentration of solute in either of the phases could then be measured. In one system studied (benzene–acetic acid–water) there was a net transfer of solute between the phases. All other studies were carried out with a radioactive solute which exchanged between chemically equilibrated phases so that there was no net transfer.

The apparatus and the operation of the jet were described previously (23); only minor changes were made for the three-component experiments. All the experiments were performed in a constant temperature room maintained at 25°C. To collect the organic solution flowing off the jet a small Teflon reservoir was mounted on the outside of the receiver, 0.5 cm. below the point at which the phases separated. A

W. J. Ward is with General Electric Research Laboratory, Schenectady, New York.