

New Model of Micromixing in Chemical Reactors. 2. Application to a Stirred Tank Reactor

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A new model of micromixing based on the spectral interpretation of turbulent mixing in the liquid phase, presented in the first part of this series, is used here in the case of a stirred tank reactor with a flat blade turbine. The model also gives a relation between the "mixing time" and micromixing parameters. Experiments carried out for baffled vessels, operated in a semicontinuous and batch manner, confirmed the validity of theoretical analysis. The results calculated using the model are in good agreement with the experimental results obtained by other authors.

Introduction

Although stirred vessels are widely used in chemical technology, the existing micromixing models are not very helpful in evaluating the course of chemical reaction in such reactors from first principles.

In the first part of this series (Pohorecki and Baldyga, 1983) we have described a new model of micromixing based on the spectral interpretation of mixing in an isotropic, homogeneous turbulent field.

The model assumes that the content of the reactor consists of two zones: the zone of complete segregation and the zone of molecular dissipation.

The influence of the intensity of mixing on the volume of the completely segregated zone is given by eq 1 and 2

$$-\frac{dV_s}{dt} = \frac{V_s}{t_{ms}} \quad (1)$$

$$t_{ms} = \frac{\pi^{1/2}\Gamma(1/3)C_\gamma}{2\Gamma(5/6)}k_{oc}^{-2/3}\epsilon^{-1/3} \quad (2)$$

The course of chemical reaction in the completely segregated zone may be evaluated from the classical Danckwerts (1958) theory; in the unpremixed feed case in which reactants have not been contacted before the reactor, the reaction does not occur in this zone.

The rate of mixing in the molecular dissipation zone is described by

$$-\frac{d(c'_i)_2}{dt} = \frac{(c'_i)_2}{t_{md}} \quad (3)$$

with time constant

$$t_{md} = 3.08(\nu/\epsilon)^{1/2}[\ln(Sc) - 1.27] \quad (4)$$

To describe the process of mixing with chemical reaction in the molecular dissipation zone a suitable micromixing model must be used together with eq 3 and 4. To this end we have used the micromixing equation as proposed by Costa and Trevissoi (1972)

$$-\frac{dc_i}{dt} = k_{md}(c_i - \bar{c}_i) + R_i \quad (5)$$

Using eq 3, 4, and 5, it is possible to evaluate k_{md} as

$$k_{md} = \frac{1}{2t_{md}} = 0.162(\epsilon/\nu)^{1/2}[\ln(Sc) - 1.27]^{-1} \quad (6)$$

Of course, micromixing models other than eq 5 may also be used together with eq 3 and 4. For example, application of the statistical Toora's (1969) approach is presented in

the last paragraph of this paper. The above equations can only be applied provided that the necessary condition for the existence of inertial-convective subrange of the spectrum is fulfilled, i.e., when

$$Re_\lambda^{3/4} \gg 1 \quad (7)$$

where

$$Re_\lambda = \frac{u'_i \lambda_g}{\nu} \quad (8)$$

The presented theory will only be useful in practice for stirred tank reactors if we are able to estimate the values of the Reynolds number, Re_λ , the micromixing parameter, k_{md} , and the time constant for completely segregated zone, t_{ms} , from the working conditions of the stirred tank reactor. In this paper we attempt to obtain these relations.

The Criterion of Sufficient Intensity of Mixing in Stirred Tank Reactors

In order to specify more precisely the condition (7) for the existence of the inertial subrange of the Kolmogoroff type in the stirred tank reactor we consider the reactor as a turbulent isotropic mixer.

The velocity fluctuation component u'_i in such a mixer is given by Schwartzberg and Treybal (1968) as

$$u'_i = \frac{0.67NL^2}{D_t^{2/3}H^{1/3}} \quad (9)$$

In order to estimate the microscale of turbulence λ_g we make use of the expressions

$$\epsilon = 15\nu[(u'_i)^2/\lambda_g^2] \quad (10)$$

(valid for isotropic, homogeneous turbulence—see, for example Hinze, 1959) and

$$\epsilon = \frac{4\Phi N^3 L^5}{\pi D_t^2 H} \quad (11)$$

(for stirred tanks). In eq 11 the rate of energy dissipation ϵ is expressed using power number Φ . According to (9), (10), and (11) we obtain

$$\lambda_g = 2.3\Phi^{1/2}\nu^{1/2}N^{-1/2}L^{-1/2}D_t^{1/3}H^{1/6} \quad (12)$$

and thus

$$Re_\lambda = \frac{1.54\Phi^{1/2}N^{1/2}L^{3/2}}{H^{1/6}D_t^{1/3}\nu^{1/2}} \quad (13)$$

The Reynolds number for a mechanically stirred mixer is equal to

$$Re = NL^2/\nu \quad (14)$$

and therefore

$$Re_\lambda = 1.54\Phi^{1/2}Re^{1/2}(H/L)^{-1/6}(D_t/L)^{-1/3} \quad (15)$$

Using eq 15, we can express condition (7) in the form

$$1.4\Phi^{3/8}Re^{3/8}(H/L)^{-1/8}(D_t/L)^{-1/4} \gg 1 \quad (16)$$

Condition (16) may be used for reactors operated in the continuous, semicontinuous, and batch manner.

The condition for ideal mixing on a macroscale given by Burghardt and Lipowska (1972) is by far less strict than (16), so if (16) is valid we can assume that the tank content is also ideally mixed on a macroscale.

Relation between the Model Parameters and Working Parameters of the Reactor

In order to express the micromixing parameter, k_{md} , as a function of the geometry and working parameters of the stirred tank reactor, we make use of eq 6 and 11. Substituting (11) into (6) we obtain

$$k_{md} = 0.183 \frac{\Phi^{1/2}NR^{1/2}}{(D_t/L)(H/L)^{1/2}[\ln(Sc) - 1.27]} \quad (17)$$

Estimation of the time constant for the completely segregated zone, t_{ms} , is much more difficult; the value of the time constant is related not only to the energy dissipation rate but also to the characteristic wave number for large scale-eddies, k_{oc} .

The value of k_{oc} may be evaluated from Cutter's (1966) results. Cutter has shown experimentally that the integral scale of turbulence in a stirred tank is approximately proportional to the impeller diameter L . Therefore we have

$$\Lambda_\gamma = \text{constant } L$$

and

$$k_{oc} = \frac{0.75}{\Lambda_\gamma} = \frac{\text{constant}}{L} = \frac{C_L}{L} \quad (18)$$

where C_L is constant for a given mixer; generally, it should be a function of the reactor geometry

$$C_L = f\left(\frac{D_t}{L}, \frac{H}{L}, \frac{w}{L}, \frac{h}{L}\right) \quad (19)$$

Substituting (11), (18), and (19) into (2), we have obtained

$$t_{ms} = \frac{\pi^{1/2}\Gamma(1/3)C_\gamma}{2\Gamma(5/6)} k_{oc}^{-2/3} \epsilon^{-1/3} = \text{constant } f\left(\frac{D_t}{L}, \frac{H}{L}, \frac{w}{L}, \frac{h}{L}\right)^{-2/3} \left(\frac{D_t}{L}\right)^{2/3} \left(\frac{H}{L}\right)^{1/3} N^{-1}\Phi^{-1/3} \quad (20)$$

The form of the function $f(D_t/L, H/L, w/L, h/L)$ is unknown.

In order to establish the form of this function one needs extensive experimental data. Luckily, many of such data have already been described in the literature; we shall use for our purposes the results of measurements of the "mixing time" carried out for stirred tank mixers by chemical methods.

Relation between the "Mixing Time" and the Micromixing Parameters

The "mixing time" is a measure of the effectiveness of mixing in the stirred tank mixers used for single liquid phases. The "mixing time" is defined as the time required

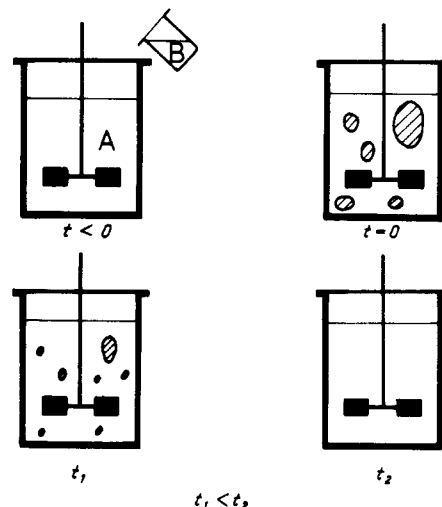


Figure 1. Scheme of the mixing time measurements in a stirred tank mixer (the completely segregated zone is hatched).

to obtain a given level of homogeneity of initially nonhomogeneous mixture, the level of homogeneity being measured by physical or chemical criteria. We are interested here in the chemical criterion consisting of the neutralization of a strong alkali present in the vessel by a portion of a strong acid added in the form of a short, small pulse. The acid is added in small stoichiometric excess, and the course of reaction is followed either visually with an indicator (the "mixing time" is then equal to the time of decoloration of the indicator) or by the electrical conductivity method.

The decoloration method is usually considered to be better. It gives the possibility of visual observation of the mixing in the whole content of the mixer without using any probe.

The above-described new model of micromixing shall now be used for the interpretation of the "mixing time" measurements. To this end we have to consider the process of mixing with chemical reaction taking place in a stirred tank reactor operated in a batch manner. Such a system, generally used for the mixing time measurements, is shown in Figure 1. Let us assume that the neutralization reaction



may be regarded as irreversible and instantaneous.

A small volume V_{OB} of the concentrated solution of reagent B (acid) having initial concentration C_{B0} is suddenly discharged into the vessel containing a volume V_{OA} of the dilute solution of reagent A (alkali) having initial concentration C_{A0} .

Both solutions contain an indicator, so that the alkaline fluid is colored. The volume of acid pulse V_{OB} is much smaller than the initial volume of alkaline fluid

$$V_{OB} \ll V_{OA} \quad (22)$$

and the quantity of acid is in excess in comparison to the quantity of the alkali

$$V_{OB}C_{B0} > V_{OA}C_{A0} \quad (23)$$

The completely segregated volume of the acid solution decreases according to eq 24.

$$\begin{aligned} -\frac{dV_{SB}(t)}{dt} &= \frac{V_{SB}(t)}{t_{ms}} \\ V_{SB}(0) &= V_{OB} \end{aligned} \quad (24)$$

The instantaneous value of the completely segregated

volume of the acid solution ($C_B = C_{B0}$) is therefore obtained by integration of (24)

$$V_{SB}(t) = V_{0B}e^{-t/t_{ms}} \quad (25)$$

In the zone of molecular dissipation of concentration fluctuations the reagents are being mixed and react according to eq 5 and 21. To find the relation between the initial concentrations, the mixing time, and the parameters of micromixing model, one has to consider the behavior of "points" containing initially only the base. Concentration changes in these "points" can be described by the equations of micromixing with chemical reaction

$$-\frac{dC_A}{dt} = k_{md}(C_A - \bar{C}_A) + R_A \quad (26)$$

$$-\frac{dC_B}{dt} = k_{md}(C_B - \bar{C}_B) + R_B \quad (27)$$

with the initial conditions $C_A(0) = C_{A0}$ and $C_B(0) = 0$. The values \bar{C}_A and \bar{C}_B in eq 26 and 27 are the mean concentrations of the reagents in the zone of molecular mixing (ideally mixed on the macroscale).

The neutralization reaction is regarded as irreversible and instantaneous, therefore in "points" containing initially only alkali the acid concentration before neutralization is equal to zero ($C_B = 0$ and $dC_B/dt = 0$). According to the above remark, eq 27 assumes the form

$$R_B = k_{md}\bar{C}_B \quad (28)$$

and, by the condition of stoichiometry

$$R_A = R_B = k_{md}\bar{C}_B \quad (29)$$

Substituting (29) into (26) we have

$$-\frac{dC_A}{dt} = k_{md}C_A + k_{md}(\bar{C}_B - \bar{C}_A) \quad (30)$$

with initial condition $C_A(0) = C_{A0}$.

The value of $(\bar{C}_B - \bar{C}_A)$ in eq 30 may be easily calculated from the balance of reagents in the molecular dissipation zone.

Using eq 24 and 25 to obtain the rate of supply of acid to the molecular dissipation zone, we have

$$\bar{C}_B - \bar{C}_A = \frac{V_{0B}(1 - e^{-t/t_{ms}})C_{B0} - V_{0A}C_{A0}}{V_{0A} + V_{0B}(1 - e^{-t/t_{ms}})} \quad (31)$$

But, according to condition (22), $V \approx V_{0A}$, and thus we can write (31) in the simplified form

$$\bar{C}_B - \bar{C}_A = \Delta C_0 - \bar{C}_{B0}e^{-t/t_{ms}} \quad (32)$$

where

$$\Delta C_0 = \frac{V_{0B}C_{B0} - V_{0A}C_{A0}}{V} \quad (33)$$

and

$$\bar{C}_{B0} = \frac{V_{0B}C_{B0}}{V} \quad (34)$$

Upon integration of eq 30 with the term $(\bar{C}_B - \bar{C}_A)$ substituted by eq 32, we obtain the concentration of alkali as a function of time.

$$C_A = \left(C_{A0} - C_{B0} \frac{k_{md}t_{ms}}{k_{md}t_{ms} - 1} + \Delta C_0 \right) e^{-k_{md}t} + \frac{k_{md}t_{ms}}{k_{md}t_{ms} - 1} \bar{C}_{B0} e^{-t/t_{ms}} - \Delta C_0 \quad (35)$$

As the mixing time, t_M , is the time required to obtain

decoloration, thus for $t = t_M$ the concentration of alkali C_A must be very small ($C_A \ll \Delta C_0$ and may be practically taken as equal to zero ($C_A \cong 0$) (for example, phenolphthalein is decoloring at alkali concentration $C_A = 10^{-9}$ mol/m³). Substituting $t = t_M$ and $C_A = 0$ in eq 35 we obtain the relation of interest

$$\left(C_{A0} - C_{B0} \frac{k_{md}t_{ms}}{k_{md}t_{ms} - 1} + \Delta C_0 \right) e^{-k_{md}t_M} + \frac{k_{md}t_{ms}}{k_{md}t_{ms} - 1} \bar{C}_{B0} e^{-t_M/t_{ms}} - \Delta C_0 = 0 \quad (36)$$

The above relationship shows that the mixing time is related to the quantities of alkali and acid (volumes and concentrations), the micromixing parameter for molecular dissipation zone, k_{md} , and the time constant for completely segregated region, t_{ms} .

However, this equation is not fully consistent with the experimental results obtained for the "mixing time" using chemical methods (Fox and Gex, 1956; Norwood and Metzner, 1960; Brennan and Lehrer, 1976). From the experimental data it follows that the mixing time, t_M , is practically independent of the molecular properties of the liquid.

Brennan and Lehrer (1976) considered the "mixing time" as the sum of the "turbulent mixing time" and the "molecular mixing time", the latter being much smaller.

Neither the experimental results obtained using the electric conductivity method did exhibit any relation between the mixing time and molecular properties of the liquid (Kramers et al., 1953; Holmes et al., 1964; Prochazka and Landau, 1961; Biggs, 1963; van de Vusse, 1955).

In the theory described here (eq 36) only the micromixing parameter, k_{md} , is related to the molecular properties of the liquid.

It results from eq 36 that the mixing time may be independent of the micromixing parameter, k_{md} , only for large values of the latter. Consequently, we assume that for stirred tank mixers usually

$$t_{ms} \gg \frac{1}{k_{md}} \quad (37)$$

and the relation (36) may be simplified to a form not containing k_{md}

$$t_M = t_{ms} \ln \frac{\Delta C_0}{\bar{C}_{B0}} \quad (38)$$

Condition (37) shall be confirmed experimentally in the experimental part of this work.

Estimation of the Mixing Time Constant for the Completely Segregated Zone

Equation 38 may now be used to calculate the mixing time constant for the completely segregated zone, t_{ms}

$$t_{ms} = t_M \frac{1}{\ln(\Delta C_0/\bar{C}_{B0})} \quad (39)$$

Unfortunately, eq 39 may only be used in a simplified form, because, as a rule, other authors did not state precisely what excess of acid was used (Fox and Gex, 1956; Brennan and Lehrer, 1976).

Assuming that the excess ΔC_0 was constant (though unknown) in each of the considered works, we can set

$$t_{ms} \sim t_M \quad (40)$$

Analyzing the influence of geometry of a stirred tank vessel with a flat blade disk turbine on the values of "mixing time", t_M , exhibited by the results presented by Fox and

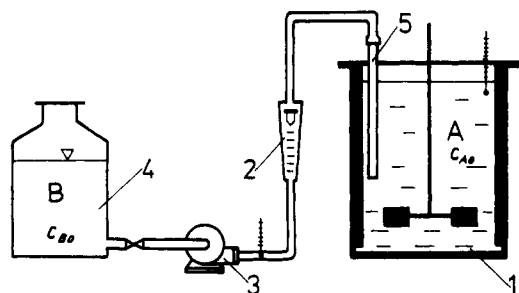


Figure 2. The experimental setup (semicontinuous glass reactor): 1, reactor vessel; 2, rotameter; 3, pump; 4, acid solution storage; 5, feed tube.

Gex (1956), Norwood and Metzner (1960), Kramers et al. (1953), Holmes et al. (1964), Prochazka and Landau (1961), and Biggs (1963), we arrive at the following relation for a Rushton type mixer

$$t_M \sim \left(\frac{D_t}{L}\right)^2 \left(\frac{H}{L}\right)^{1/2} N^{-1} \quad (41)$$

and, according to Brennan and Lehrer (1976), for a general geometry stirred vessel mixer

$$t_M \sim \frac{\left(\frac{z}{L}\right)^2 \left(\frac{D_t}{L}\right)^2}{N \Phi^{1/3} \left(\frac{D_t}{L} - 1\right)^{1/3} \left(\frac{H}{L}\right)^{1/3}} \quad (42)$$

where $z = H - h - w/2$ for $h < H/2$ and $z = h + w/2$ for $h > H/2$. Substituting (41) and (42) into (40), we have obtained: for a Rushton type mixer

$$t_{ms} = \frac{C_{mI} \left(\frac{D_t}{L}\right)^2 \left(\frac{H}{L}\right)^{1/2}}{\Phi^{1/3} N} \quad (43)$$

For a general geometry mixer

$$t_{ms} = \frac{C_{mII} \left(\frac{z}{L}\right)^2 \left(\frac{D_t}{L}\right)^2}{\Phi^{1/3} N \left(\frac{D_t}{L} - 1\right)^{1/3} \left(\frac{H}{L}\right)^{1/3}} \quad (44)$$

This means, that in the first case

$$f\left(\frac{D_t}{L}, \frac{H}{L}, \frac{w}{L}, \frac{h}{L}\right) = \text{constant} \left(\frac{D_t}{L}\right)^{-2} \left(\frac{H}{L}\right)^{-1/4} \quad (45)$$

and in the second case

$$f\left(\frac{D_t}{L}, \frac{H}{L}, \frac{w}{L}, \frac{h}{L}\right) = \text{constant} \left(\frac{D_t}{L}\right)^{-2} \left(\frac{H}{L}\right) \left(\frac{D_t}{L} - 1\right)^{1/2} z^{-3} \quad (46)$$

In order to verify the above predictions, to confirm the validity of condition (37), and to determine the values of constants C_{mI} and C_{mII} , the following experimental program has been carried out.

Experimental Verification of the Model

Semicontinuous Neutralization in a Baffled Vessel. The experiments were carried out in a semicontinuous manner, for very rapid reactions, using the systems (NaOH

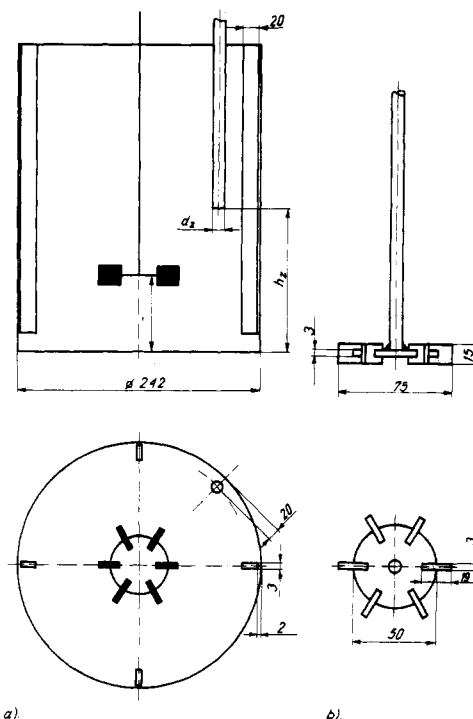


Figure 3. Reactor vessel and impeller.

+ HCl) and (NaOH + CH₃COOH) and the experimental setup shown in Figure 2.

The Rushton-type baffled stirred vessel with six-blade turbine shown in Figure 3 was used as the reactor. The reactor vessel was made of glass to permit visual observations. The experimental procedure was as follows.

About 9 dm³ of an aqueous solution of NaOH ($C_{A0} = 0.025$ N) containing phenolphthalein as an indicator was placed in the stirred vessel.

The acid solution (HCl or CH₃COOH), also containing phenolphthalein, was then added in a semicontinuous manner through a tube of diameter d_z , the feeding point being placed at height h_z from the reactor bottom.

The concentration of acid was 8–12 times greater than that of the alkali; the volume of liquid at the moment of decoloration was thus about 10 dm³. At the moment of decoloration the flow of acid was stopped.

In the case of a baffled vessel the decoloration of liquid took place suddenly and simultaneously in the whole vessel volume (very good mixing on the macroscale). Variable ranges in the experiments were as follows: impeller speed, 1 rps $< N < 9$ rps; volumetric feed rate, 0.5×10^{-5} m³/s $< q < 10^{-5}$ m³/s; liquid viscosity, 1000 kg/m s $< \mu < 10000$ kg/m s (glycerol was added to the solution to increase the viscosity); feed concentration ratio, $0.08 < C_{A0}/C_{B0} < 0.15$; feed tube diameter, 2×10^{-3} m $\leq d_z \leq 8 \times 10^{-3}$ m; vertical clearance between the bottom of vessel and the feeding point, 2×10^{-2} m $\leq h_z \leq 20 \times 10^{-2}$ m; temperature, $T = 293.2 \pm 0.1$ K. The impeller speed was measured by means of a stroboscope, the feed rate volumetrically, and the height of the liquid head in the vessel (before and after neutralization) with a cathetometer.

The initial concentrations of reagents and the concentration of acid in the vessel after neutralization were determined by titration.

The molecular diffusivity of solutions with increased viscosity was calculated from the well-known relation

$$(D_v \mu)_{H_2O} = (D_v \mu)_{\text{solution}} \quad (47)$$

at $T = \text{constant}$. The power number Φ (Euler number for mixing) was calculated using the classical Rushton rela-

Table I. Typical Results Obtained for Semicontinuous Neutralization in Stirred Tank Reactor

no.	Re	Sc	$\Delta t, s$	$1/k_{md}, s$	t_{ms}, s	C_{mI}	C_{mII}
1	13 000	740	9.98	0.26	9.72	2.31	2.13
2	13 500	740	10.14	0.23	9.91	2.46	2.28
3	18 700	740	6.68	0.14	6.54	2.24	2.09
4	24 000	740	5.14	0.10	5.04	2.17	2.01
11	9 800	430	16.90	0.34	16.56	2.91	2.51
12	14 500	430	9.36	0.27	9.09	2.43	2.35
13	19 000	430	7.09	0.12	6.97	2.44	2.36
14	28 000	430	4.27	0.07	4.20	2.22	2.19
37	40 000	430	3.29	0.03	3.26	2.38	2.20
38	46 600	430	2.62	0.03	2.59	2.22	2.13
39	41 600	430	2.84	0.03	2.81	2.15	2.00
64	9 930	3 900	3.86	0.17	3.69	1.93	1.89
65	8 110	3 900	4.89	0.23	4.66	1.98	1.96
66	6 500	3 900	5.35	0.32	5.03	1.71	1.64
73	1 533	113 000	5.17	0.90	4.27	1.66	1.65
74	3 070	113 000	2.71	0.30	2.41	1.95	2.00
75	1 230	113 000	6.84	1.27	5.57	1.72	1.77

tions (Rushton et al., 1950a,b). The condition (16) for the existence of the inertial subrange of Kolmogoroff's type was fulfilled for all measurements.

It was also found that practically the whole amount of kinetic energy was supplied by impeller mixing, that is

$$\Phi N^3 L^5 \rho \gg \frac{8q^3 \rho}{\pi^2 d_z^4} \quad (48)$$

(The term on the right-hand side of eq 48 represents the kinetic energy supplied with the stream of acid solution.) The over-titration time, defined as the time interval from the moment at which the stoichiometric quantity of acid was added to the vessel to the moment of decoloration, was calculated from the simple acid balance

$$qC_{B0}\Delta t = V_k \bar{C}_B = N_a \quad (49)$$

where \bar{C}_B is the mean concentration of acid in the vessel at the moment of decoloration and V_k is the volume of liquid in the vessel at the same time.

Thus

$$\Delta t = \frac{V_k}{q} \frac{\bar{C}_B}{C_{B0}} \quad (50)$$

The whole quantity of free acid, N_a , present in the reactor at the moment of decoloration, must have remained segregated.

This amount of acid comprises the acid contained in the completely segregated zone, N_s , and the portion of acid remaining segregated in the molecular dissipation zone, N_d . Of course

$$N_a = N_s + N_d \quad (51)$$

Integrating eq 1 for the conditions of experiment one can show that the quantity of acid contained in the completely segregated zone is equal to

$$N_s = qC_{B0}t_{ms} \quad (52)$$

Integrating in turn eq 5 for the experimental conditions one can show that the quantity of acid remaining segregated in the molecular dissipation zone is equal to

$$N_d = \frac{qC_{B0}}{k_{md}} \quad (53)$$

Thus

$$t_{ms} + \frac{1}{k_{md}} = \Delta t \quad (54)$$

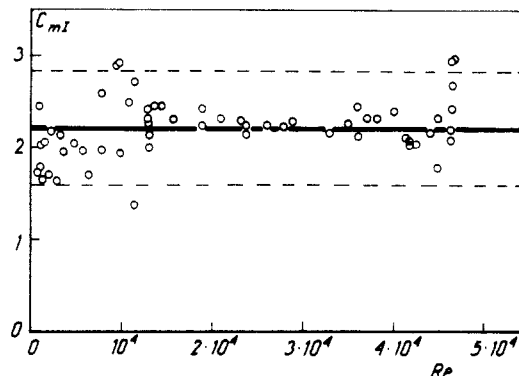


Figure 4. The values of C_{mI} calculated from experimental data for the baffled vessel.

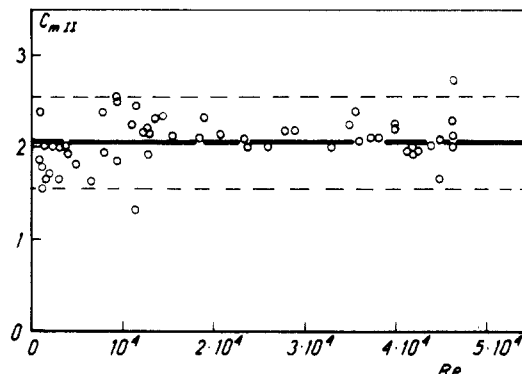


Figure 5. The values of C_{mII} calculated from experimental data for the baffled vessel.

To estimate C_{mI} and C_{mII} one must calculate: Δt from eq 50; k_{md} from eq 17; t_{ms} from eq 54 using estimated values of Δt and k_{md} ; C_{mI} and C_{mII} from eq 43 and 44. Some typical results are presented in Table I. The results obtained confirm the validity of the previous assumption (37).

The values of C_{mI} and C_{mII} calculated from the experimental data are presented in Figures 4 and 5. As can be seen, the values of C_{mI} and C_{mII} are independent of the intensity of mixing as required by the presented theory.

The mean values of the constants are: $C_{mI} = 2.22$ and $C_{mII} = 2.07$. Equation 44 with $C_{mII} = 2.07$ is somewhat better than eq 43 because the scatter of C_{mI} values is greater. Equation 44 with $C_{mII} = 2.07$ is therefore recommended for calculations.

Equations 17 and 44 used for calculation of micromixing parameters k_{md} and t_{ms} suggest that these parameters are independent of the way the vessel is fed. The results

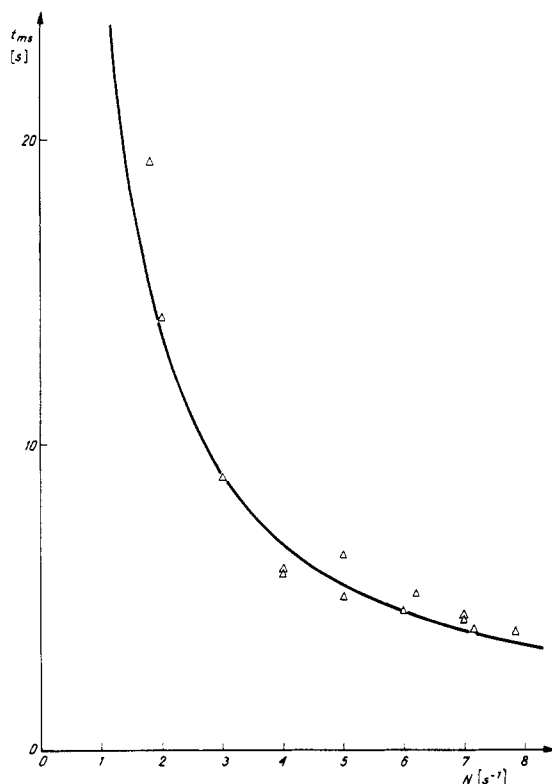


Figure 6. Experimental results obtained in the batch system (points) and results of calculations based on eq 44 (solid line).

obtained for different values of h_z and d_z and presented in Figures 4 and 5 confirm this conclusion for the case of a semicontinuous system.

According to the above presented theory, eq 17 and 44 may be used for the systems operated in a batch and continuous manner as well as for the system operated in a semicontinuous way. This conclusion is supported by the experimental results obtained for the batch system.

Investigations in the Batch System (Baffled Vessel). The vessel was filled with 11 dm³ of HCl solution of 0.007 N concentration, and after a few minutes of mixing a pulse of NaOH solution ($V = 200$ mL, $C_{B0} = 0.385$ N) was introduced near the liquid surface with the agitator running. The progress of the reaction was followed with the help of electric conductivity measurements.

Equation 35 for a stoichiometric system and for $1/k_{md} \ll t_{ms}$ may be written in the form

$$C_A = \frac{k_{md} t_{ms}}{k_{md} t_{ms} - 1} \bar{C}_{B0} e^{-t/t_{ms}} \quad (55)$$

For a batch system the starting time of the reaction is not very well established, as the time of introduction of the pulse is about 0.5–1 s.

In the same time the turbulence field is strongly disturbed by the liquid added. To circumvent this difficulty, we have used eq 55 for two instants t_1 and t_2 , sufficiently remote from the moment of introduction of the pulse.

$$C_A(t_1) = \frac{k_{md} t_{ms}}{k_{md} t_{ms} - 1} \bar{C}_{B0} e^{-t_1/t_{ms}} \quad (56)$$

$$C_A(t_2) = \frac{k_{md} t_{ms}}{k_{md} t_{ms} - 1} \bar{C}_{B0} e^{-t_2/t_{ms}} \quad (57)$$

The ratio of concentrations at t_1 and t_2 is

$$\frac{C_A(t_1)}{C_A(t_2)} = e^{(t_2 - t_1)/t_{ms}} \quad (58)$$

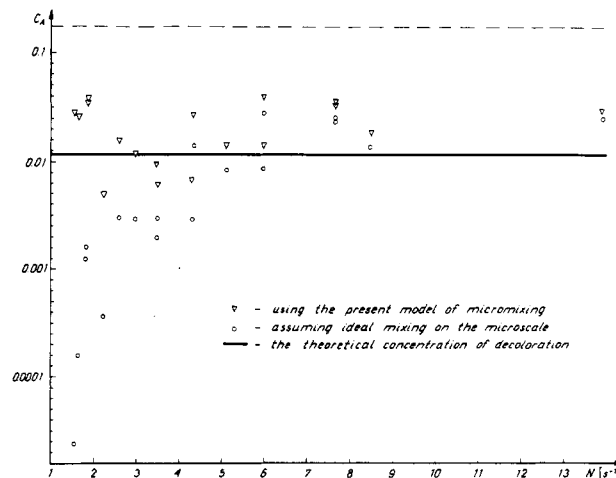


Figure 7. The values of alkali concentration calculated for the measured time of decoloration: (▽) using the present model of micromixing; (○) assuming ideal mixing on the microscale.

and is equal to the ratio of conductivities. The experimental values of t_{ms} have been calculated from eq 58 with the conditions $t_2 - t_1 = 2.5$ s and 2 s $< t_1 < 3$ s. The experimental values of t_{ms} , as well as those calculated from eq 44, are presented in Figure 6. As can be seen, the agreement between theory and experiment is very good.

Semicontinuous Hydrolysis of $\text{CH}_2\text{ClCOOC}_2\text{H}_5$ by NaOH in the Baffled Vessel. To check the validity of the presented theory in the case of a slower reaction, further experiments were carried out with the $\text{CH}_2\text{ClCOOC}_2\text{H}_5$ hydrolysis reaction. In these experiments, an aqueous solution of NaOH colored by thymolphthalein was initially present in the reactor ($V_0 = 9$ dm³, $C_{A0} = 0.00123$ M) and an aqueous solution of $\text{CH}_2\text{ClCOOC}_2\text{H}_5$ ($C_{B0} = 0.07 - 0.1$ M) was added to it in a semicontinuous manner.

Upon decoloration of the indicator, the supply of $\text{CH}_2\text{ClCOOC}_2\text{H}_5$ was stopped, the time of decoloration was measured, and the excess of ester was determined by titration after 60 min. The concentration of OH^- ions at the moment of decoloration was then calculated from the experimental value of the time of decoloration.

The kinetic constant of the reaction was taken $k_2 = 23$ dm³/mol s (Takao et al., 1978). The results of calculations are presented in Figure 7.

The values obtained using the presented model (triangles) are compared in Figure 7 with the values obtained on assumption of ideal mixing on microscale (circles). The theoretical concentration of decoloration is denoted by the solid line. It can be seen that the assumption of ideal molecular mixing may give very large errors, especially for smaller intensities of mixing, even though there is ideal mixing on the macroscale.

Micromixing and Complex Reactions; Comparison with the Literature Data

It is well-known that mixing may affect strongly the selectivities of complex reactions for unpremixed feed systems. Bourne et al. (1977) reported a large influence of the agitator speed and of the viscosity of liquid on the product distribution for diazo coupling reactions. These authors investigated the diazo coupling between 1-naphthol and diazotized sulphanilic acid in alkaline aqueous solution.

The reactions occurring are well described by the series parallel scheme

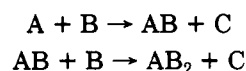


Table II. Influence of the Feeding Rate and the Stirrer Speed on Product Distribution x_s

$\bar{C}_{AO} = \bar{C}_{BO}$, mol/m ³ q, m ³ /min	0.1				0.091				
	0.0016		0.0008		0.0004		0.00077		
N , s ⁻¹	6	12.5	6	12.5	6	12.5	6	12.5	16.7
x_s , measd	0.206	0.120	0.213	0.124	0.208	0.132	0.170	0.135	0.011
x_s , calcd	0.191	0.115	0.194	0.117	0.195	0.118	0.185	0.112	0.091

where A is the ionic form of 1-naphthol, B is the diazonium ion, and AB and AB₂ are primary and secondary products of coupling. The kinetics is given by the overall equations

$$\frac{dC_A}{dt} = -k_{21}C_AC_B \quad (59)$$

$$\frac{dC_{AB}}{dt} = k_{21}C_AC_B - k_{22}C_{AB}C_B \quad (60)$$

$$\frac{dC_{AB_2}}{dt} = k_{22}C_{AB}C_B \quad (61)$$

$$\frac{dC_B}{dt} = -k_{21}C_AC_B - k_{22}C_{AB}C_B \quad (62)$$

The values of the kinetic reaction constants, as reported by Angst et al. (1979) are

$$k_{21} = 7.3 \times 10^3 \text{ m}^3/\text{mol s}$$

$$k_{22} = 3.5 \text{ m}^3/\text{mol s}$$

Experiments were carried out in the unpremixed feed continuous stirred tank reactor.

In order to calculate the product distribution one can use the model of micromixing proposed here together with Toor's (1969) method of description of second-order reactions in unpremixed feed systems.

For a simple, rapid, second-order reaction, $A + bB \rightarrow$ products, Mao and Toor (1971) gave the following equation for the time-averaged reaction rate (for an isothermal reaction)

$$\bar{R}_i = k_2[\bar{C}_A\bar{C}_B - d^2\bar{C}_{A0}\bar{C}_{B0}] \quad (63)$$

where

$$d^2 = \frac{(C_i')^2}{[(C_i')^2]_0} \quad (64)$$

d^2 in eq 64 defines the decay law for the concentration fluctuations in the reactor, and in Toor's method must be measured using tracers.

Using our model the d^2 value may be easily calculated. In the completely segregated zone molecular mixing does not occur and $d^2 = 1$.

From the balance of "unmixedness" in the dissipation zone for a nonreacting, continuously operated system, using eq 3 for the rate of dissipation of "unmixedness"

$$[(C_i')^2]_0 q = (C_i')^2 q + \frac{(C_i')^2}{t_{md}} V \quad (65)$$

we obtain

$$d^2 = \frac{(C_i')^2}{[(C_i')^2]_0} = \frac{1}{1 + \frac{\tau}{t_{md}}} = \frac{1}{1 + 2k_{md}\tau} \quad (66)$$

Let us return to the series parallel scheme.

In the completely segregated zone the reaction does not occur. The component balances over the molecular mixing zone of the stirred tank reactor, using eq 63 and 66 for the

reaction rate, yield for the considered series-parallel scheme of reactions

$$\frac{\bar{C}_{A0} - \bar{C}_A}{\tau} = k_{21}(\bar{C}_A\bar{C}_B - \bar{C}_{A0}\bar{C}_{B0}d^2) \quad (67)$$

$$\frac{\bar{C}_{B0} - \bar{C}_B}{\tau} = k_{21}(\bar{C}_A\bar{C}_B - \bar{C}_{A0}\bar{C}_{B0}d^2) + k_{22}\bar{C}_B\bar{C}_{AB} \quad (68)$$

$$\frac{\bar{C}_{AB}}{\tau} = k_{21}(\bar{C}_A\bar{C}_B - \bar{C}_{A0}\bar{C}_{B0}d^2) - k_{22}\bar{C}_B\bar{C}_{AB} \quad (69)$$

$$\frac{\bar{C}_{AB_2}}{\tau} = k_{22}\bar{C}_B\bar{C}_{AB} \quad (70)$$

with

$$d^2 = \frac{1}{1 + 2k_{md}\tau}$$

Equations 68, 69, and 70 have been obtained using simplifications according to qualitative criteria of Bourne and Toor (1977). The experimental results obtained by Bourne et al. (1977) and the results of our calculations are presented in Table II.

The product distribution is characterized by the fraction of the diazonium ion which reacted to bisazo dyestuff.

$$x_s = \frac{2C_{AB_2}}{C_{AB} + 2C_{AB_2}} \quad (71)$$

The agreement between the calculated and the experimental values may be considered to be very good.

Conclusion

The proposed model of micromixing may be used for description of mixing with reaction for stirred tank reactors operated in a batch, semicontinuous, and continuous manner.

The model provides means for determination of the influence of mixing on conversion and selectivity in such reactors. The model gives a theoretical interpretation of the mixing time measurements.

The experimental results obtained for instantaneous and rapid reactions confirm the validity of the model. Results of calculations based on the proposed model are in good agreement with the experimental results of other authors.

Nomenclature

- C_i = concentration of component "i" in a "point"
- \bar{C}_i = concentration of component "i" in the environment of the "point" or mean concentration
- C_{i0} = feed concentration
- \bar{C}_{i0} = mean feed concentration
- C_i' = root-mean-square fluctuation of concentration
- ΔC_0 = see eq 33
- $C_\gamma, C_{mI}, C_{mII}$ = constants
- d = decay law of concentration fluctuations
- d_z = feed tube diameter
- D_t = stirred tank reactor diameter
- D_v = molecular diffusivity
- h = vertical clearance between the bottom of vessel and impeller blade
- h_z = vertical clearance between the bottom of vessel and feed point

H = height of liquid head in the vessel
 k_{md} = micromixing parameter
 k_{oc} = characteristic wave number for large-scale eddies
 L = turbine diameter
 N = impeller rotational speed
 N_a = quantity of acid segregated
 N_s = quantity of acid completely segregated
 N_d = quantity of acid segregated in the molecular mixing zone
 q = volumetric feed rate
 $Re = NL^2/\nu$ = Reynolds number for mechanically stirred mixer
 $Re_\lambda = u'_i \lambda_g / \nu$ = Reynolds number of turbulence
 R_i = reaction rate
 Sc = Schmidt number
 t = time
 t_{ms} = complete segregation time constant
 t_M = mixing time
 Δt = overtitration time
 V_{oi} = initial volume of reagent "i"
 V = total volume of liquid in vessel
 V_s, V_{s_i} = completely segregated volume
 w = height of blades
 z = see eq 42
Greek Letters
 ϵ = rate of energy dissipation by turbulence per unit mass of the fluid
 Φ = power number
 Γ = gamma function
 λ_g = Taylor's microscale of turbulence
 Λ_γ = macroscale of turbulence for concentration field
 μ = viscosity

ν = kinematic viscosity
 ρ = density

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Received for review May 17, 1982

Revised manuscript received May 3, 1983

Accepted May 27, 1983

Laminar Film Flow over a Sphere

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An asymptotic solution is developed for laminar film flow over a sphere. This solution establishes bounds on the approximate solution for very thin film flow and gives the first-order corrections to the latter solution due to neglected higher order viscous, inertia, and surface tension terms. The results are of particular value to investigators employing wetted-sphere or multiple-sphere laboratory absorbers to characterize commercial scale absorbers, and to those interested in studying the hydrodynamic stability of this diverging-converging flow. For conditions appropriate to laboratory studies using wetted-sphere and multiple sphere absorbers, this analysis indicates that the zeroth-order thin liquid film flow solution used to analyze data from these devices can be significantly in error.

The hydrodynamics of liquid film flow over a sphere figure prominently in a variety of coating operations and in the performance of gas-liquid contacting equipment such as packed columns, trickling filters, and high precision wetted-sphere and multiple-sphere laboratory absorbers. Indeed, a desirable feature of a laboratory scale absorber used to simulate the performance of commercial scale equipment is that its hydrodynamics be well understood. The wetted-sphere and multiple-sphere absorbers offer an advantage in this respect over the laboratory scale wetted-wall column, since they eliminate the rippling and end effects which complicate the hydrodynamics in the latter. However, Danckwerts (1970, p 84) has pointed out that the interpretation of absorption rate data from wetted-sphere absorbers can also be complicated by the diver-

gent-convergent flow in such devices. Clearly a detailed knowledge of the hydrodynamics of film flow over a sphere is needed.

Liquid film flow over a sphere is also of interest because it provides an ideal flow geometry for studying the hydrodynamic stability of a divergent-convergent nonparallel film flow. Indeed, there has been only one analysis reported in the literature for the stability of a nonparallel film flow which does not invoke the questionable quasi-parallel flow approximation. This analysis of Zollars and Krantz (1980) is a linear stability analysis of decelerating nonparallel film flow down a right-circular cone. Prerequisite to developing a stability analysis for film flow over a sphere is the need to develop a systematic solution to the unperturbed basic flow which incorporates the effects