Imperfect Mixing and Dead-Zone Effects in Nonlinear Dynamics: Law of Mass Action Revisited

A. K. Dutt*,†,‡ and Avijit Datta*,‡,§

National Chemical Laboratory, Pune 411008, India, and Ghanarajpur (Jalapara), Dhaniakhali, Hooghly, WB 712302, India

Received: June 15, 1998

The law of mass action has been extended to include imperfect mixing and dead-zone effects in nonlinear chemical systems. It is concluded that if there is more concentration difference between two homogeneous layers in an incompletely mixed inhomogeneous solution obeying nonlinear kinetic laws, the reaction rate also is increased compared to that calculated on the basis of average reactant concentrations for homogeneous mixing. The presence of an unmixed dead-zone enhances this effect further.

The law of mass action[1] was proposed on the basis of the assumption that the chemically reacting components have uniform concentrations throughout the solution. During kinetic measurements the reaction vessel is normally stirred continuously with the belief that it would make the solution homogeneous. However, experiments in the recent past indicate that in at least some highly nonlinear kinetic systems exhibiting bistability or sustained oscillations, significant concentration gradients persist despite vigorous stirring of the solution. Spatial heterogeneities may well nucleate in a poorly stirred region, either in a batch reactor or in a continuous flow stirred tank reactor (CSTR).

Mixing is accomplished in two stages, macromixing and micromixing. Macromixing is the formation of macroscopic heterogeneities and their breakdown into tiny segregated liquid parcels. The segregations then either mix into the bulk by molecular diffusion (micromixing) or escape through the outlet, thus producing an effective "dead-zone" volume inside the reactor, where mixing is very much inefficient. Stirring effects become prominent whenever the micromixing time is comparable or longer than the shortest chemical relaxation time.

Roux et al.[2] obtained the dramatic effect of imperfect mixing for the bistable chlorite−iodide reaction where the hysteresis limits (as a function of the flow rate of the feed chemicals) vary significantly with stirring rate. Menzinger and Dutt[3] reported quantitative measurements of macroscopic concentration gradients in the same system carried out in a CSTR. They obtained concentration differences up to 800% between poorly and strongly stirred regions. Dutt et al.[4,5] obtained stirring induced bistability in the minimal bromate oscillator (MBO) and Belousov−Zhabotinskii (BZ) reaction using gallic acid as the organic substrate in CSTR experiments. Gyorgyi and Field[6] reproduced the experimental results of stirring and mixing effects on MBO system in numerical simulation using a micromixing model.[7a] Several other models[7b,c] of imperfect mixing in a CSTR have been proposed in the past to explain stirring and mixing effects in nonlinear dynamics. The Kumpinsky and Epstein[7b] model (KE) divides the reactor into active and dead

zones. All material enters and leaves the reactor through the "active zone", which is treated by the perfect mixing model. The dead zone is also treated as perfectly mixed, and the interchange between the two zones is reversible. The effect of imperfect mixing seems to be a real phenomenon associated with chemical systems obeying nonlinear kinetic laws. Imperfect mixing may well increase the overall reaction rate compared to that calculated from an average homogeneous concentration, which was pointed out by Epstein.[8] In the present paper, we have built up a general theory to extend the law of mass action to include the effect of incomplete mixing in nonlinear dynamics on the basis of a kinetic model, which has the following features different from those of the KE[7b] model: The "reactive zone" follows inhomogeneous kinetics, and the "dead-zone" volume is assumed nonreactive due to no mixing.

We consider a CSTR of volume V having $\bar{c}$ (moles/liter), the average concentration of the species X, whose concentration shows a spatial gradient in a real experiment due to the nonlinear kinetic effect of the chemical processes. Since our reactor is inhomogeneous due to imperfect mixing, the total volume V is assumed to be divided into two regions, namely, (1) a dead zone (V_d) of volume xV ($0 < x \ll 1$) and (2) a reactive zone (V_r) subdivided into a large number of small volumes v_i, such that the homogeneous concentration of X in the ith compartment (X_i) is given by $\bar{c}(1 + \alpha_i \delta c)$, where δc is a hypothetical quantity of small value, less than or equal to the reciprocal $\bar{c}$ times the maximum deviation of X_i in the ith compartment from the average value $\bar{c}$, and α_i is a real number such that mod(α_i) ≥ 0. M denotes the molecular weight of X. Therefore, we have

$$(1 - x)V = \sum_i v_i \qquad (1)$$

$$\frac{(1 - x)MV\bar{c}}{1000} = \frac{M\bar{c}}{1000} \sum_i v_i(1 + \alpha_i \delta c) \qquad \text{or}$$

$$(1 - x)V = \sum_i v_i + \delta c \sum_i \alpha_i v_i \quad (2)$$

Using eq 1, one obtains from eq 2

$$\sum_i \alpha_i v_i = 0 \qquad (3)$$

* Address correspondence to the authors at: Ghanarajpur (Jalapara).
† National Chemical Laboratory.
‡ Ghanarajpur (Jalapara).
§ Present address: Materials Science Theory Group, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India.

For the elementary reaction

$$nX \rightarrow \text{products} \qquad (4)$$

the reaction rate (R_{ac}) from average concentration $\bar{c}$ is given according to the law of mass action by

$$R_{ac} = k(\bar{c})^n \qquad (5)$$

where k and n are respectively the rate constant and order of the reaction. The overall rate from imperfect mixing (R_{im}) is given by

$$R_{im} = \frac{k}{V_r} \sum_i \nu_i (X_i)^n$$

$$= \frac{k}{V - V_d} \sum_i \nu_i (1 + \alpha_i \delta c)^n (\bar{c})^n \qquad (6)$$

In eq 6, we have imposed imperfect mixing, a nonlinear effect to the homogeneous kinetics, eq 5, in terms of α_i's and ν_i's. The ratio of the two reaction rates is given by

$$\text{Ratio} = \frac{R_{im}}{R_{ac}} = \frac{1}{V(1 - x)} \sum_i \nu_i (1 + \alpha_i \delta c)^n \qquad (7)$$

For first order reaction, one obtains from eqs 1, 3, and 7

$$\text{Ratio} = \frac{1}{V(1 - x)} \sum_i \nu_i (1 + \alpha_i \delta c) = \frac{1}{V(1 - x)} [V(1 - x) + \delta c \sum_i \alpha_i \nu_i] = 1 \quad (8)$$

Therefore, neither imperfect mixing nor the existence of a dead zone inside the solution has any effect on the reaction rate of first order reactions. For second order reactions, one obtains from eqs 1, 3, and 7

$$\text{Ratio} = \frac{1}{V(1 - x)} \sum_i \nu_i (1 + \alpha_i \delta c)^2 =$$

$$1 + \frac{1}{V(1 - x)} [(\delta c)^2 \sum_i \alpha_i^2 \nu_i + 2\delta c \sum_i \alpha_i \nu_i]$$

$$= 1 + \frac{1}{V(1 - x)} (\delta c)^2 \sum_i \alpha_i^2 \nu_i > 1 \qquad (9)$$

For third order reactions (this, of course, is a rare possibility), we have from eqs 1, 3, and 7

$$\text{Ratio} = \frac{1}{V(1 - x)} \sum_i \nu_i (1 + \alpha_i \delta c)^3 =$$

$$1 + \frac{1}{V(1 - x)} [(\delta c)^3 \sum_i \alpha_i^3 \nu_i + 3(\delta c)^2 \sum_i \alpha_i^2 \nu_i] \quad (10)$$
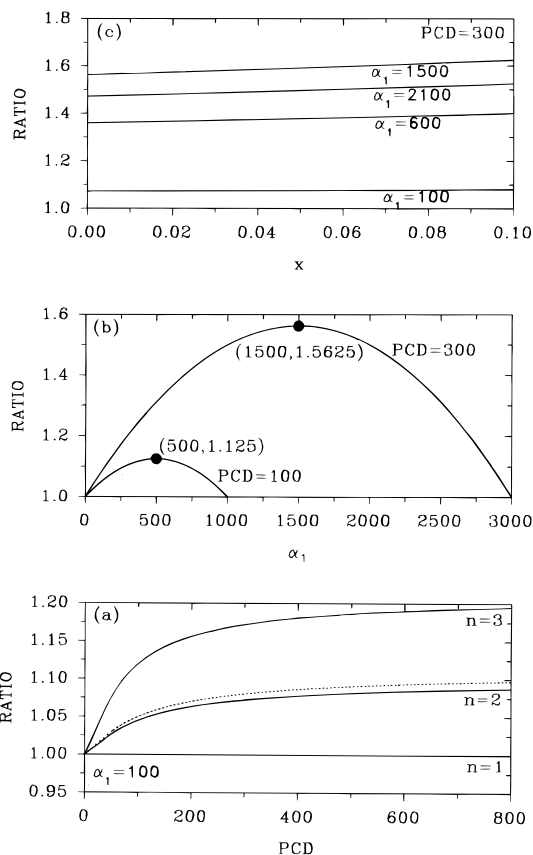
Figure 1. (a) Ratio versus percentage of concentration difference (PCD) between two homogeneous layers for first, second, and third order reactions on the basis of a two homogeneous compartment model of eq 7: δc, 10^{-3}; α_1, 100; x, 0; V, 1000 mL. The dotted line corresponds to $x = 0.1$ for the second order reaction. (b) Ratio as a function of α_1 for two different PCD values (300 and 100), for the second order reaction. The parameters are the same as those in a: $x = 0$. (c) Ratio as a function of x for different values of α_1 for the second order reaction: PCD = 300. The other parameters are the same as those in a.

The cubic terms on the right hand side of eq 10 are either positive or negative according to whether α_i is positive or negative. In this case in the algebraic calculation it does not help to have any idea about the value of the ratio. To resolve this, we computed numerically this ratio for first, second, and third order reactions from eq 7 using the constraints given by eqs 1 and 3.

Figure 1a is the plot of the ratio versus percentage of concentration difference (PCD) between two homogeneous layers for first, second, and third order reactions, assuming that the reactor contains only two homogeneous compartments due to imperfect mixing, i having only two values, 1 and 2. The bold lines assume the absence of any dead zone in the reactor, and the dotted line is for the effect of the dead zone for the second order reaction. Figure 1a shows that for the third order reaction, the contribution from the cubic term in eq 10 is less than that from the quadratic term, which ensures that the ratio is greater than 1. For second order reactions, this ratio is also greater than 1, as is evident from the analytical and numerical calculations (vide eq 9 and Figure 1a), though the value is less compared to that in the third order reaction. The presence of a dead zone with a second order reaction increases the ratio further, which should be noted with interest. For a first order reaction, the ratio is 1, both analytically (eq 8) and numerically (Figure 1a).

Mixing and Dead-Zone Effects in Nonlinear Dynamics

J. Phys. Chem. A, Vol. 102, No. 41, 1998 **7983**

Figure 1b is a plot of the ratio for the second order reaction as a function of α_1 at two different PCD values, 300 and 100 in the absence of a dead zone. Since ν_i is inversely proportional to mod(α_i) for a two compartment model (vide eq 3), $\alpha_1 =$ zero corresponds to $\nu_1(\nu_2) = V(0)$, and the ratio becomes 1 for the parameters in the figure caption. As α_1 is increased, the ratio gradually increases (ν_1 decreases, ν_2 increases) to make ν_1 equal to ν_2 at α_1, 600 (ratio, 1.36) for PCD, 300. The ratio attains the maximum value (1.56) at α_1, 1500 (ν_1, $^1/_5V$; ν_2, $^4/_5V$). With a further increase of α_1, the ratio starts to decrease (ν_1 decreases further and ν_2 increases) and at α_1, 3000 (ν_1, 0; ν_2, V), the ratio becomes 1 again. Therefore, for PCD, 300, the effect of imperfect mixing is maximum if $\nu_1:\nu_2 = 1:4$. The effect becomes less pronounced if a lower PCD value of 100 is considered, for which the maximum effect (ratio, 1.12) is observed at α_1, 500, for which $\nu_1:\nu_2 = 1:2$.

Figure 1c is a plot of the ratio as a function of x for different values of α_1 at a constant PCD value, 300, illustrating the dead-zone effect in second order chemical kinetics. The plots in Figure 1c are according to what is expected from Figure 1b with a gradual increase of α_1 for PCD, 300. It is clear from Figure 1c that, for all of the plots, the ratio is increased further with an increase in the volume of the dead zone in the reactor.

For $i > 2$, it is necessary to find out α_i's and ν_i's from quantitative measurements which must satisfy the constraints given by eqs 1 and 3. For a general reaction of the type

$$a\text{A} + b\text{B} \rightarrow \text{products} \qquad (11)$$

which is assumed to exhibit the phenomenon of imperfect mixing, R_{ac}, R_{im}, and the ratio are given accordingly in the following expressions.

$$R_{ac} = k|\bar{A}|^a|\bar{B}|^b \qquad (12)$$

$$R_{im} = \frac{k}{V(1-x)}|\bar{A}|^a|\bar{B}|^b\sum_i \nu_i(1 + \alpha_{iA}\delta A)^a(1 + \alpha_{iB}\delta B)^b \qquad (13)$$

$$\text{ratio} = \frac{1}{V(1-x)}\sum_i \nu_i(1 + \alpha_{iA}\delta A)^a(1 + \alpha_{iB}\delta B)^b \geq 1 \qquad (14)$$

The theory presented here has incorporated the nonlinear effect of imperfect mixing to the law of mass action to derive that, the greater the concentration difference between two layers in an inhomogeneous solution, the more is the overall reaction rate compared to that calculated on the basis of average homogeneous concentration. The presence of dead zone enhances the effect further, which is a result of great interest. Our result conforms to the comment of Epstein[8] on the basis of simple calculations on an incompletely mixed second order kinetic system.

References and Notes

(1) Guldberg; Waage, Etudes sur les affinites chimiques, Christiania, 1867.

(2) Roux, J. C.; Kepper, P. de; Boissonade, J. *Phys. Lett.* **1983**, *97A*, 168.

(3) Menzinger, M.; Dutt, A. K. *J. Phys. Chem.* **1990**, *94*, 4510.

(4) Dutt, A. K.; Menzinger, M. *J. Phys. Chem.* **1990**, *94*, 4867.

(5) Dutt, A. K.; Muller, S. C. *J. Phys. Chem.* **1993**, *97*, 10059.

(6) Gyorgyi, L.; Field, R. J. *J. Phys. Chem.* **1992**, *96*, 1220.

(7) (a) Villermaux, J. In Spatial Inhomogeneities and Transient Behavior in Chemical Kinetics; Gray, P., Nicolis, G., Baras, F., Borckmans, P., Scott, S. K., Eds.; Manchester University Press: Manchester, U.K., 1990; p 119. (b) Kumpinsky, E.; Epstein, I. R. *J. Chem. Phys.* **1985**, *82*, 53. (c) Bar-Eli, K.; Noyes, R. M. *J. Chem. Phys.* **1986**, *85*, 3251.

(8) Epstein, I. *Nature* **1990**, *346*, 16.