

# Diffusion accompanied by chemical reaction in water-in-oil media

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*Water-in-oil emulsions represent microheterogeneous media where the dispersed phase constituent size is much less than the diffusional length scales for a typical solute. Such formulations, when tailored out of the right components and employed in heterogeneous, reactive systems, in lieu of a true liquid phase, may provide intensification in the specific rate of reaction (interphase flux) and even desirable modifications with respect to selectivity and product distribution. A theory of mass transfer (accompanied by chemical reaction) in such media, incorporating transient effects, is presented here.*

THE investigation of diffusion/reaction characteristics of chemical systems in (micro) heterogeneous media in comparison with truly homogeneous phases is an area of considerable importance in chemical reaction engineering where multiphase reaction systems are frequently encountered.

## *What are multiphase reactions?*

In the simplest instance, when two chemical species which reside in different physical phases, are brought together in order that these may react with each other, we obtain a two-phase reaction system. At least one of the reactants must be transferred from its original phase of residence to the other where the reaction occurs. The rates of such multiphase reactions are normally influenced by the diffusional speed of the sparingly soluble (transferred) species in the phase in which reaction occurs, the intrinsic reaction velocity and the interfacial area of contact between the physical phases. A familiar example would be the bubbling of carbon dioxide gas (absorption) into lime water where the gas diffuses into the aqueous solution and also reacts with the hydroxyl ion.

In actual practice, very complex multiphase systems may be encountered owing to factors such as multiple reactants and products, more than two physical phases, and of course intricate reaction schemes.

## *What are some significant objectives associated with reactive systems?*

It is obvious that chemical reactions provide the route

by which raw materials (reactants) may be transformed into useful end-products or intermediates (products). From a reaction engineer's point of view these reactions must be conducted in such a manner that the overall rate of transformation as well as the overall yield of the desired product are maximized. These objectives are important in that the size (volume) of the reactor and the downstream purification costs involved in separating the desired product from the undesired species are minimized.

One simple way of increasing the overall rate of reaction is to physically increase the interfacial area of contact between the reactant-bearing phases (for instance by using an emulsifying agent or special type of agitating arrangements). Since the interface area per unit volume of the contacting equipment is increased the total volume required for achieving a given throughput is decreased. Yet another, but more difficult strategy, is to somehow intensify the specific rate of interphase mass transfer (in other words, the rate per unit interface area). Microheterogeneous media play an important role in achieving this aim of obtaining higher specific rates.

## *What are microheterogeneous media?*

Figure 1 shows a schematic sketch of the typical two-phase situation. Species A diffuses from phase  $\alpha$  into phase  $\beta$  (which contains the non-volatile reactant B) where it simultaneously undergoes chemical reaction with species B. In the simple scenario considered here there are no diffusional gradients of A in its original phase ( $\alpha$ ) and no B can leave its own phase ( $\beta$ ). We may now replace the homogeneous phase  $\beta$  by an emulsified media wherein an oil phase (o), which has a markedly higher affinity for the species A compared to the phase  $\beta$ , is microdispersed in the original phase  $\beta$  (this therefore will become the continuous phase of the

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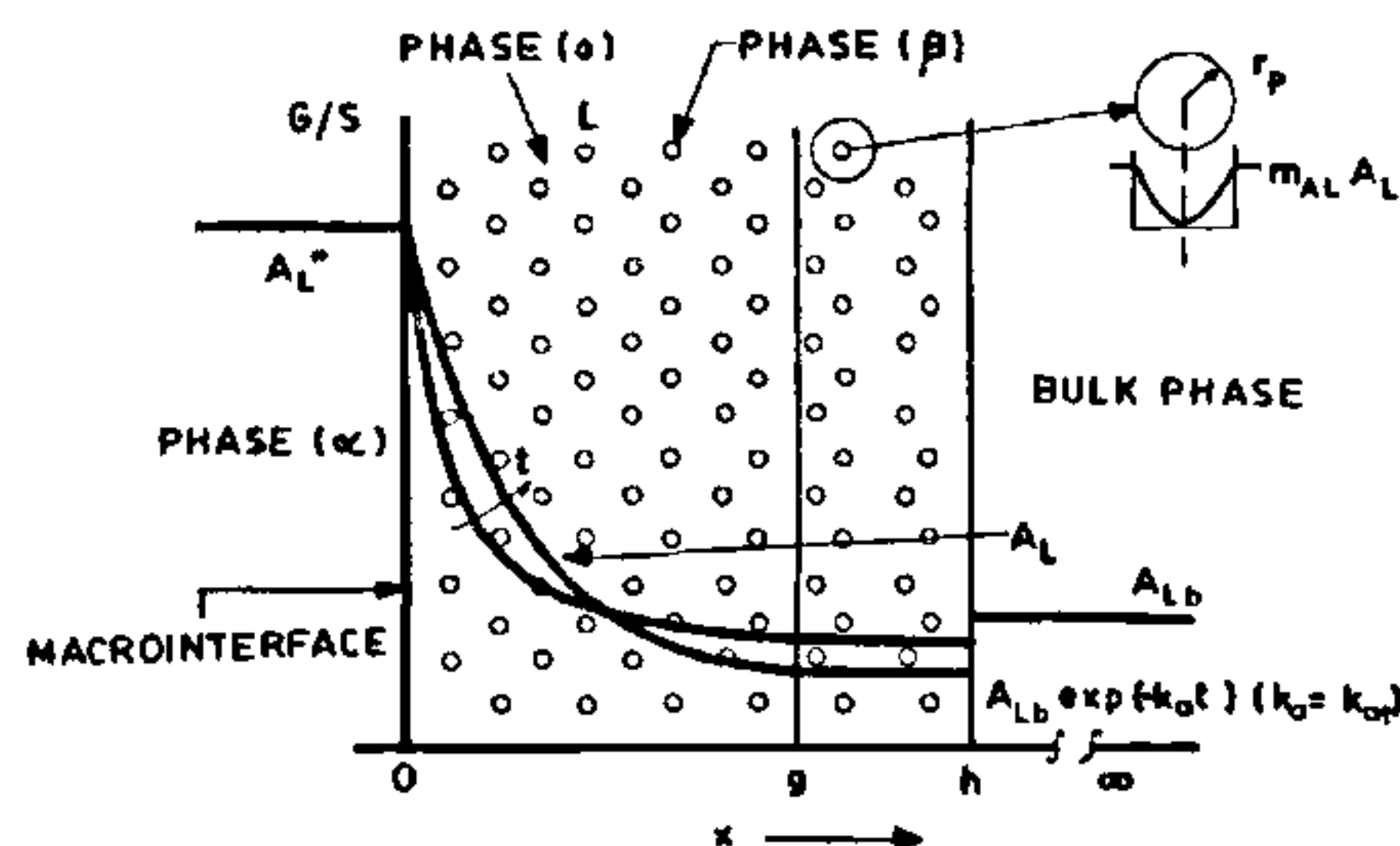


Figure 1. Physical picture for mass transfer in water-in-oil media.

emulsion media). Alternatively, we may microdisperse phase  $\beta$  (containing reactant B) in the oil ( $\alpha$ ) phase; given that phase  $\beta$  is usually aqueous, microdispersing the  $\beta$  phase would require the formation of a water-in-oil emulsion. Such systems are dealt with in this article<sup>1</sup>.

#### How do microheterogeneous media work?

From the point of view of mass transfer, the size of the microdispersed constituents should be less than the diffusional length scales of solute A in the continuous phase. The basic action of these microconstituents is to remove the diffusing species, by interacting with it via solubilization/adsorption/reaction (reversible or irreversible), from near the interface (also known as the macrointerface) formed by phase  $\alpha$  and the microheterogeneous (emulsion) media. This causes the concentration gradients near the macrointerface to become steeper leading to an enhanced interphase flux of A. In the specific case of water-in-oil type of systems, the oil phase, which possesses a high capacity for the solute A, provides an A-rich reservoir around the microdrops of the reactive phase  $\beta$ . The extremely high interfacial area between the microdispersed and the continuous phases, on account of the very small size of the microdrops, allows for rapid transfer of A into these tiny micro-reactors. In comparison, the specific rate in the original system composed only of the phases  $\alpha$  and  $\beta$ , is much smaller since it is limited by diffusion of A in phase  $\beta$ , where it is (relative to the oil phase ( $\alpha$ )) sparingly soluble; the overall rate is of course further limited by the low interface area between these phases ( $\alpha$  and  $\beta$ ) compared to the microdispersed-continuous phases. Thus a water-in-oil emulsion succeeds in pairing a high-capacity (for A) phase ( $\alpha$ ) with low interfacial area ( $\alpha$  to  $\alpha$  phase) on the one hand, and a low-capacity phase ( $\beta$ ) with high interfacial area ( $\alpha$  to  $\beta$  phase) on the other, thereby intensifying the specific rate of reaction between A and B.

#### What are mass transfer models?

To quantify the effects discussed above we need to choose a framework within which to express the species balance equations. It is well known that the concept of a mass transfer coefficient is used to describe the interphase flux of any species in a multiphase situation, such that the mass transfer coefficient multiplied by a suitable concentration difference (driving force) is equal to the appropriate flux. For most practical situations this coefficient is measured experimentally and correlated to the operating parameters; this approach is preferred in comparison to the often, extremely complicated theoretical task of formulating the diffusion-convection equations which expectedly are very tedious to solve for the relevant fluxes.

The mass transfer coefficient, however, can be interpreted with the help of simple models which represent a grossly simplified picture of the generic mass transfer problem. One such unsteady state model, which we will use here, has been proposed by Danckwerts<sup>2</sup>. In this visualization the solute transfer occurs by transient diffusion into fluid elements which make up the interface and the simultaneous transit of these 'loaded' elements into the 'bulk' of the relevant phase where the elements lose their identity; fresh (unloaded) elements arrive from the bulk at the interface to make up for the departing fluid. The fraction of the interface having an age between  $t$  and  $t + dt$  is further assumed to be given by  $s \cdot \exp(-st) \cdot dt$  (minimum age = 0, and maximum age =  $\infty$ ) where  $s$  is called the surface renewal frequency and can be related to the mass transfer coefficient through the equation

$$k_L = (D_A s)^{1/2}. \quad (1)$$

Figure 1 represents the processes inside a typical surface element including the situation when the microdispersed phase is present. Here, we have a 'composite' surface element consisting of the emulsion medium rather than a truly homogeneous phase.

#### Theoretical development

##### Physical scenario

Consider the case where a reactant A (which is originally a gas or a solid, phase  $\alpha$ ), which is sparingly soluble in the aqueous phase ( $\beta$ ) and can react with a species B (irreversibly) present in it, is brought into contact with a water-in-oil emulsion. The oil phase ( $\alpha$ ) is expected to show a high degree of affinity for the solute A vis-a-vis the aqueous phase, but no reaction of A occurs in this oil phase.

Basic mechanism

The basic mechanism of transport and reaction that may be constructed thus consists of the diffusion of A into the oil phase and simultaneous diffusion (uptake) and reaction of A in the aqueous microdispersed phase (which is uniformly and isotropically dispersed in the oil phase), near the macrointerface. For this situation, the uptake is likely to be controlled by the transport resistance residing in the internal phase since this is the low-solubility phase.

Species balances and solutions

A species balance on A in the surface element, comprising the continuous oil phase and a microdispersed reactive aqueous phase (spherical constituents), is written as

$$D_{AL} \frac{\partial^2 A_L}{\partial x^2} = (1 - l_a) \frac{\partial A_L}{\partial t} + l_a a_{LL} D_A (\partial A / \partial r)|_{r=d_p/2}, \quad (2)$$

the last term representing the mass flux into the aqueous phase microdroplets. The above equation is rigorously valid for low hold-ups of the microdispersed phase, and is based on the assumption that the diffusion coefficient of A has a negligibly weak dependence on the concentration of A in the oil phase.

The initial and boundary conditions for the above balance are

IC:  $t=0 \ A_L = A_{Lb}$ , all  $x$   
 BCs:  $t>0 \ A_L = A_L^*$ , at  $x=0$  (3)

$$A_L = A_{Lb} \{ (k_a/k_{at}) \cdot \exp(-k_a t) + 1 - k_a/k_{at} \} \text{ at } x \rightarrow \infty,$$

where  $k_a$  and  $k_{at}$  are apparent first order rate constants (to be calculated later) accounting for the uptake by the aqueous droplets. The last boundary condition is based on the principle of a surface element towards the end of which diffusion may be neglected and is thus derived by setting the term associated with  $D_{AL}$  in eq. (2) to zero (i.e. this zone between  $g$  and  $h$  marked in Figure 1, behaves like a batch reactor)<sup>2</sup>.

On the further assumption of pseudo first order conditions within the microdispersed phase and that all B remains within it with no significant spatial distribution (within the microdroplet), the diffusion of A into the internal phase accompanied by chemical reaction can be described by

$$\frac{\partial A}{\partial t} = \frac{D_A}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial A}{\partial r} \right) - kA \quad (4)$$

the relevant conditions on eq. (4) being given by

IC:  $t=0 \ A = m_{AL} A_{Lb} \sinh(\phi(2r/d_p)) / [(2r/d_p) \sinh(\phi)]$

BCs:  $t>0 \ A = m_{AL} A_L$  at  $r = d_p/2$  (5)

$$\partial A / \partial r = 0, \text{ at } r = 0.$$

It is embodied in the above formulation that the time-scales of depletion of B within the droplets is much larger than the average surface element contact time ( $1/s$ ). The initial condition implies that all microdroplets in the bulk are in 'equilibrium' with the bulk concentration of A in the oil phase,  $A_{Lb}$ , i.e. within each one of them the steady-state profile with respect to the surface concentration  $m_{AL} A_{Lb}$  has been established. The boundary conditions similarly indicate that in a surface element each microdroplet is exposed to a surface concentration equivalent to the local concentration of A at the point of residence of the droplet in the oil phase. Here  $m_{AL}$  is the distribution coefficient of A between the aqueous and the oil phase.

The above style of writing the species balances is based on the assumption of *pseudo-homogeneity*, which means that in some respects (notably in the way we write eq. (2) and eq. (3)) we can 'pretend' that the emulsion media is a single, 'homogeneous' continuum. Furthermore, the diffusion within it can be approximated by diffusion in the continuous phase but more importantly this assumption implies that droplet-droplet interaction is neglected.

Transforming eqs. (2) to (4) by using the Laplace transform we obtain the solution

$$R_A = s \mathcal{L} \left\{ D_{AL} \frac{\partial A}{\partial x} \Big|_{x=0} \right\} = s \int_0^\infty \left\{ D_{AL} \frac{\partial A}{\partial x} \Big|_{x=0} \right\} \exp(-st) dt =$$

$$[(1 - l_a) D_{AL}]^\dagger \{ (A_L^*(s + k_{at})^\dagger - A_{Lb}(s + (k_{at} - k_a))/(s + k_{at})^\dagger \} \quad (6)$$

where  $k_{at} = 2 m_{AL} l_a a_{LL} \eta_i D_A / ((1 - l_a) d_p)$ ,  
 $k_a = 2 m_{AL} l_a a_{LL} \eta D_A / ((1 - l_a) d_p)$ ,  
 $\eta_i = \phi_i / \tanh(\phi_i) - 1$ ,  $\eta = \phi / \tanh(\phi) - 1$ ,  
 $\phi_i = (d_p/2) [(s + k) / D_A]^\dagger$ ,  
 $\phi = (d_p/2) (k / D_A)^\dagger$  and  $s = k_L^2 / D_A$  from eq. (1).

The interesting part in obtaining the above solution is that the definition of the Laplace transform of any property/quantity  $p(t)$  (here it is,  $-D_A \partial A / \partial x|_{x=0}$ ) and the *time-averaged* value of  $p(t)$ , as calculated from Danckwerts' surface element age distribution given earlier (see material preceding eq. (1)), differs only by the factor  $s$  (see first two parts of eq. (6)); in fact  $s$ , the Laplace domain variable, thereby becomes identical to the surface renewal frequency as given by eq. (1). The necessity of finding the inverse transform to calculate the *average* specific rate is thus obviated! It can also be shown that the choice of the age distribution does not influence the calculated values of the specific rate since

alternative distributions give answers which are nearly the same (the rate expressions are of course different)<sup>2</sup>. Danckwerts' distribution is therefore very convenient for attacking those mass transfer problems which can be handled by Laplace transforms.

**Experimental systems**

Table 1 shows the results of some relevant calculations. Typical systems which show values of parameters such as those used in Table 1 are represented by the absorption of carbonyl sulphide into emulsions of aqueous hydroxide in toluene, the absorption of oxygen into emulsions of aqueous sulphite solutions in perfluorocarbons and the absorption of olefinic gases in emulsions of aqueous sulphuric acid in chlorobenzene.

**Some comments**

When the internal phase reaction time orders (1/k) are much smaller than the true scales of diffusion in the oil phase (1/s) the internal (microphase) profiles quickly reach a steady state and for  $k \gg s$ ,  $k_{at} = k_a$ .

The value of the apparent rate constant may be limited by the diffusion of A in the internal phase. As a limiting case when  $\phi$  tends to be small, it can be shown that  $2D_A a_{LL} \eta / dp \rightarrow k$ . Therefore, for the apparent rate constant we obtain,  $k_a = l_a m_{AL} k / (1 - l_a)$  which holds when  $d_p^2 k / 4D_A \ll 1$ . Such a situation is likely for very small droplet sizes.

**Table 1.** Calculated values of ratio of specific rates in emulsion media to that in pure  $\beta$  phase (water-in-oil emulsion).

Operating parameters	Microphase properties	Intermediate values	Ratio
$k_L = 5 \times 10^{-5} \text{ m s}^{-1}$ $k = 10 \text{ s}^{-1}$ $D_A = D_{AL} = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ $a = 100 \text{ m}^2 \text{ m}^{-3}$ $A_{Lb} = 0$ $s = 5 \text{ s}^{-1}$	$d_p = 15 \mu\text{m}$ $m_{AL} = 0.2$  $l_a = 0.3$	$\phi = 1.06$ $\phi_t = 1.30$  $\eta = 0.35$ $\eta_t = 0.51$ $k_a = 0.81 \text{ s}^{-1}$ $k_{at} = 1.16 \text{ s}^{-1}$	2.3
$k_L = 5 \times 10^{-5} \text{ m s}^{-1}$ $k = 100 \text{ s}^{-1}$ $D_A = D_{AL} = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ $a = 100 \text{ m}^2 \text{ m}^{-3}$ $A_{Lb} = 0$ $s = 5 \text{ s}^{-1}$	$d_p = 15 \mu\text{m}$ $m_{AL} = 0.02$  $l_a = 0.3$	$\phi = 3.35$ $\phi_t = \phi$  $\eta = 2.35$ $\eta_t = \eta$ $k_a = 0.54 \text{ s}^{-1}$ $k_{at} = k_a$	9.6
$k_L = 3 \times 10^{-5} \text{ m s}^{-1}$ $k = 100 \text{ s}^{-1}$ $D_A = D_{AL} = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ $a = 200 \text{ m}^2 \text{ m}^{-3}$ $A_{Lb} = 0$ $s = 0.9 \text{ s}^{-1}$	$d_p = 1 \mu\text{m}$ $m_{AL} = 1 \times 10^{-4}$  $l_a = 0.1$	$\phi = 0.16$ $\phi_t = \phi$  $\eta \rightarrow 0$ $\eta_t \rightarrow 0$ $k_a = 1 \times 10^{-3} \text{ s}^{-1}$ $k_{at} = k_a$	158

*a*, Macrointerface area ( $\alpha$  phase to emulsion phase).

In order to calculate the bulk concentration,  $A_{Lb}$ , a separate bulk balance is needed which may be found elsewhere<sup>2</sup>.

If our aim is to 'process' the same amount of aqueous phase per unit time as we would have in the absence of the oil phase, the reactor volume has to be incremented by a factor  $1/l_a$  and this effect may be offset only if the ratio of the specific rate in presence of the emulsion to that for the aqueous phase alone  $\gg 1/l_a$ . In case our primary intention is to process greater amounts of phase  $\alpha$ , for a fixed reactor volume, the above argument is not valid and clearly any ratio, referred to above, which is  $> 1$  is beneficial. For a continuous contacting equipment, where it may be possible to maintain low values of  $A_{Lb}$  even if pure oil were used for gas absorption, the use of water-in-oil media is to be preferred over oil alone, provided  $R_A/k_L A_{Lb}^* > 1$ .

For low values of  $k$  and high values of  $m_{AL}$  the surface renewal frequency,  $s$  and the apparent rate constants  $k_a$  and  $k_{at}$  are of similar order as well as  $k_a$  and  $k_{at}$  are substantially different. For higher values of  $k$  the transient effects become unimportant and  $k_a = k_{at}$ . When  $m_{AL}$  values are low the value of  $k_a$  may become negligible compared to that of  $s$  and eq. (6) simplifies further.

The possible use of such emulsion media in separating (gas) mixtures can also be contemplated<sup>1</sup>. If the specific rate for components  $A_1$  and  $A_2$  is given by a simplified form of eq. (6), (and  $A_{Lb}$  taken to be zero) which is

$$R_{A_i} = (1 - l_a)^{\frac{1}{2}} k_L A_{L_i}^* \quad (i = 1, 2) \tag{7}$$

then the point selectivity ratio is given by

$$S = (A_{L_1}^* / A_{L_2}^*) = (m_{A_1} / m_{A_2}) / (k_1 / k_2)^{\frac{1}{2}} \tag{8}$$

**Concluding remarks**

In a philosophical vein, the model developed here represents a combination of mirror images! The small particles are reactors where reaction is retarded by internal diffusion whereas in the oil phase the diffusion flux is enhanced by the reaction in the droplets.

Preliminary experiments on the absorption of butene-1 in emulsions of aqueous sulphuric acid in 2-ethyl hexanol have indicated intensification ratios in the specific rates up to 5. It needs to be emphasized here that the analogous theory for diffusion-reaction in oil-in-water type of emulsions has been reported elaborately and has also been well tested by experiments on model gas-liquid and solid-liquid systems, the details of which may be found in refs. 3, 4.

In the perspective of developing a *feasible technology* which utilizes the strategy of replacing homogeneous phases by microheterogeneous media, the gain in rates, lower costs of smaller reactors, etc. have to be

compared with the costs that have to be incurred in preparing and handling these media, downstream costs of breaking the media to obtain the original phases as well as those involved in the recovery of special agents such as emulsifiers etc.

**Nomenclature**

$A$	Concentration of A in the $\beta$ phase, $\text{kmol m}^{-3}$
$A_L$	Concentration of A in the $\alpha$ phase, $\text{kmol m}^{-3}$
$A_{Lb}$	Concentration of A in the $\alpha$ bulk phase, $\text{kmol m}^{-3}$
$A_o^*$	Solubility of A in the $\alpha$ phase, $\text{kmol m}^{-3}$
$a_{iL}$	Specific interfacial area between $\beta$ and $\alpha$ phase, $\text{m}^2 \text{m}^{-3}$
$B_o$	Concentration of B in the $\beta$ phase, $\text{kmol m}^{-3}$
$D_A$	Diffusivity of A in the $\beta$ phase, $\text{m}^2 \text{s}^{-1}$
$D_{AL}$	Diffusivity of A in the $\alpha$ phase, $\text{m}^2 \text{s}^{-1}$
$d$	Diameter of the microdispersed constituent, m
$k^p$	Pseudo first order reaction rate constant in $\beta$ phase ( $=k_{20}B_o$ ), $\text{s}^{-1}$
$k_a$	Apparent first order rate constant in emulsion media, $\text{s}^{-1}$
$k_{at}$	Apparent first order rate constant, including transient effects, in emulsion media, $\text{s}^{-1}$
$k_L$	Mass transfer coefficient, $\text{m s}^{-1}$
$k_{20}$	Second order rate constant for reaction between A and B, $\text{s m}^3 \text{kmol}^{-1}$

$l_a$	Fractional hold-up of the microdispersed phase [ $\beta/(o+\beta)$ ], dimensionless
$m_{AL}$	Distribution coefficient for solute A ( $\beta/o$ ), dimensionless
$m_A$	Reciprocal of $m_{AL}$ , dimensionless
$R_A$	Specific rate of reaction, $\text{kmol m}^{-2} \text{s}^{-1}$
$r$	Radial space coordinate inside spherical microdroplet, m
$t$	Time, s
$x$	Distance from macrointerface in the emulsion, m
$z$	Stoichiometric factor for reaction between A and B, dimensionless
$\alpha$	Phase containing A
$\beta$	Phase containing B
$\eta$	Constant in eq. (6), dimensionless
$\eta_1$	Constant in eq. (6), dimensionless
$o$	Oil phase
$s$	Surface renewal frequency, $\text{s}^{-1}$

Subscript 1 refers to solute 1  
Subscript 2 refers to solute 2

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