Intensification of Instantaneous Heterogeneous Reaction by Simple Salts and Charged Microphase

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The mass-transfer rate for the instantaneous heterogeneous reaction between N,N-diethylaniline (organic phase) and HCl in the aqueous phase was determined in the presence of a number of supporting electrolytes, that is, NaCl, $SrCl_2$, $AlCl_3$, and cetyltrimethyl ammonium bromide surfactant micelle. Both the simple salts and the cationic surfactant enhance the mass transfer of the reactive H^+ ion, the effectiveness being in the order of CTAB > $AlCl_3$ > $SrCl_2$ > NaCl. The experimentally observed enhancement factor for the reaction in the presence of the supporting electrolytes ranges from 1.3 to 6. This enhancement is explained on the basis of the "ion-coupling" effect that augments the diffusive fluxes of the more mobile ionic species in a multi-ion system. The film-theory approximation is used to obtain theoretical estimates of the enhancement factor, and these are found to be in reasonably good agreement with the experimentally obtained values.

Introduction

Mass transfer with chemical reactions is a widely encountered phenomenon in the chemical industry. In such situations, transfer of one or more reactants may occur across a gas–liquid (Astarita, 1967; Danckwerts, 1970; Cornelisse et al., 1980; Trambouze, 1981; Charpentier, 1981; Decoursey and Thring, 1989; Glasscock and Rochelle, 1989; Littel et al., 1991), a liquid–liquid, or a solid–liquid interface (Sherwood and Wei, 1955; Brian et al., 1964; Bunton et al., 1976; Janakiraman and Sharma, 1982, 1985; Littel et al., 1994). Several theoretical treatments and experimental studies of the phenomenon of mass transfer with chemical reactions have appeared in the literature, beginning with the pioneering work of Hatta (1929–1932) and continuing to the recent works of Doraiswamy and Sharma (1984). These include the well-known film theory, Higbie's penetration theory, and Danckwerts surface-renewal theory, as well as other lesser known theories (Doraiswamy and Sharma, 1984). In general, most of the theoretical approaches to modeling such heterogeneous reactions consider that the mass-transfer occurs by molecular diffusion through a laminar boundary layer at the interface between the two phases. In situations where the two phases exist in a turbulent state, mass transfer occurs through eddy-diffusion (King, 1966; Glasscock and Rochelle, 1989).

Many of the heterogeneous reactions with slow, medium, or fast kinetics can be intensified considerably through the use of a variety of microphases such as micelles, emulsions, hydrotopes, and suspended particles (Janakiraman and Sharma, 1982, 1985; Mehra, 1988; Littel et al., 1994). Using the penetration and the surface-renewal models, Mehra (1988) has proposed a general theory to explain the experimentally observed enhancement in specific reaction rates in the presence of microphase. It has been shown that a microphase may increase the mass-transfer rates by either preferentially solubilizing the sparingly soluble solute or by directly enhancing the reaction rate by providing a more favorable locale for the reaction. However, Mehra's treatment predicts that no enhancement in specific rate of mass transfer in the case of instantaneous heterogeneous reactions is possible using a microphase, except under extreme circumstances that are normally not attainable in practice. A similar conclusion was drawn by Janakiraman and Sharma (1982) from their theoretical study on instantaneous heterogeneous reactions using the film theory.

In contrast to the prediction of the preceding theories, the principal experimental findings of the present work suggest that the overall rate of a typical instantaneous heterogeneous

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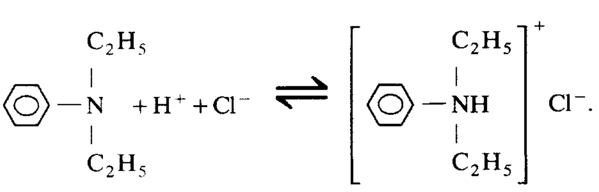
reaction between *N,N*-diethylaniline (DEA) (organic phase) and HCl (aqueous phase) can be enhanced significantly in the presence of charged microphase as well as in the presence of simple inert salts. The scheme of the reaction is as follows:


(1)

N, N-diethylaniline (DEA)

DEA hydrochloride salt

The observed rate of this reaction is found to be enhanced by a factor of 3–6 in the presence of cationic micellar species of the surfactant cetyltrimethylammonium bromide (CTAB), and by a factor of 1.4–2 in the presence of simple salts such as NaCl, $SrCl_2$, and $AlCl_3$. Both the micelle of CTAB and the salts are present in the aqueous phase as what is called "supporting electrolytes." A supporting electrolyte is defined as a nonreactive (or inert) electrolyte initially present at uniform concentration throughout a system in which diffusion of reactive ionic species occurs (Dean, 1945).

According to the film-theory representation, the instantaneous reaction (Eq. 1) between H^+ ion and the free amine *N,N*-diethylaniline (DEA) can be considered to occur at a reaction plane within the Nernst diffusion film of thickness, δ(Figure 1). The organic (nonelectrolyte) molecule, DEA, diffuses through the region of thickness, λ, and its flux is counterbalanced by the diffusion of H^+ ions in the $\lambda < x < \delta$ region. The concentrations of these two species are reduced to zero at the λ-plane (the reaction plane). The product of the reaction, the hydrochloride salt of the amine ($DEAH^+Cl^-$), being negligibly soluble in the nonaqueous phase, diffuse toward the bulk solution.

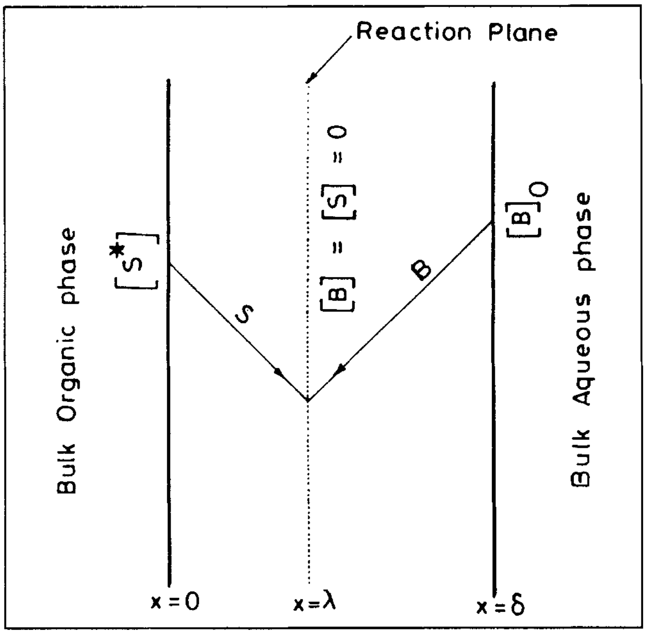


Figure 1. Film theory representation of an instantaneous heterogeneous reaction.

Heterogeneous reactions are usually limited by the diffusion of a sparingly soluble solute in the phase in which reaction occurs. In such situations the essential role of a microphase is to interact with the diffusing solute near the interface—formed by the original phases—in such a way as to remove it from the vicinity of the interface either by reaction or by facilitating its transport from the bulk of the phase in which the solute is sparingly soluble and wherein the diffusional limitations to transfer lie. Under the conditions used in the present work, however, such an effect of enhanced solubilization of the organic solute (DEA) by the cationic micellar microphase cannot satisfactorily explain the extent of observed rate enhancement of the reaction studied.

The general explanation offered by Janakiraman and Sharma (1982) on the improbability of surfactant micelles (acting as the microphase) having any effect on an instantaneous reaction is as follows: in the absence of organic reactant S (DEA molecule) (Figure 1), all the micelles are initially saturated with respect to the bulk aqueous phase reactant B(H^+ in the present case). Once S is brought in contact with the aqueous phase, concentrations of S and B fall to zero at the reaction plane. In the region $0 < x < \lambda$, the concentration of B is zero, and since the micelles in this region have no other source to pick up B, once the initially present B in the micelles in this region is consumed, these micelles no longer contribute to the reaction rate. Furthermore, in the region $\lambda < x < \delta$, no S is present and the micelles therein will not have any access to this reactant. Since the micellar volume fraction used is generally small, the amount of B initially present in the micelles is consumed very rapidly ($\approx 10^{-4}$ s). As a consequence the micellar contribution to mass-transport enhancement would be expected to be negligible for such reactions. Mehra (1988) has shown that in systems such as those just discussed the absolute enhancement factor is dependent upon a term $q = (D_B/D_s)^{1/2}$ ($[B]_0/[S^*]$) and m_s, where D_B and D_S are the diffusivities of B and S, respectively; $[B]_0$ is the bulk concentration of B and $[S^*]$ is the concentration of S at the interface; and m_s is the partition coefficient of S in the micellar phase relative to the aqueous phase. Further, it is argued that no enhancement is expected except for low values of $q(<8)$ and high values of $m_s(>1{,}000)$. In the present system, the values of q and m_s are 9 and 175, respectively. Under these conditions, the rate enhancement predicted by the preceding considerations is therefore negligible, and the observed rate enhancement cannot be explained on the basis of micellar solubilization.

Further, it is also not feasible to explain the observed intensification by invoking the phenomenon of micellar catalysis of reactions. Surfactant micelles are known to catalyze a variety of slow to moderately fast liquid–liquid reactions (Menger et al:, 1975; Fendler and Fendler, 1975; Bunton and Romsted, 1982; Bonan et al., 1990). In general, the effect of the presence of the micellar phase may range from enhancement to inhibition of the reaction. Most of the results on the kinetics of such reactions have been interpreted either by using the pseudophase kinetic model (Menger and Portnoy, 1967; Bunton, 1979), which treats micelle as a separate phase, or by a mass-action model (Martinek et al., 1973), or by an ion-exchange equilibrium model (Romsted, 1977). The last type of model is used to describe the distribution of reactive and nonreactive counterions between the micellar and the aqueous phases.

A cationic micelle that has a positively charged surface may catalyze a reaction between a nucleophilic anion and a neutral substrate by delocalizing the negative charge developed during the transition state of the reaction. This reduces the energy of activation of the reactions, thereby facilitating the conversion of reactants to the products. It may also catalyze the reaction by concentrating the nucleophile anion at the vicinity of the micelle–water interface. The instantaneous heterogeneous reaction studied in the present work involves the reaction between the H^+ ion and the neutral DEA molecule. Any DEA solubilized within such a cationic micellar core (CTAB micelle in the present work) is not likely to be accessible to H^+ ions, which will be largely excluded from the vicinity of the positively charged micellar surface. Therefore, the conventional mechanism of micellar catalysis, too, is an unlikely reason behind the rate enhancement observed in the present study.

The effect of charged microphases on the rate of instantaneous heterogeneous reactions is not a well-investigated phenomenon, and the present authors are not aware of any other comprehensive attempts to study it except for the works of Janakiraman and Sharma (1982) and Mehra (1988). Nevertheless, since instantaneous heterogeneous reactions constitute an industrially important class of reactions (Doraiswamy and Sharma, 1984), the effect of a nonreactive microphase on such reactions is of considerable technological interest. As indicated earlier, in the present work positively charged CTAB micelles constitute the inert microphase in a reactive system comprising an organic molecule (DEA) and ionic reactant (H^+). Since such a reaction primarily occurs within a small "diffusion film" close to the actual physical interface between the organic and aqueous phases, for the reaction to be intensified by an ionic micellar microphase (or by simple salts as supporting electrolytes), the latter must, in effect, increase the flux of H^+ ions from the bulk phase to the reaction plane by a mechanism other than those described in the foregoing paragraphs.

It has long been known that the ionic diffusion in the mixed electrolyte systems is governed by the electrical potential generated due to the movement of ions of unequal mobilities (Vinograd and McBain, 1941; Dean, 1945; Leaist and Lyson, 1980; Mills et al., 1985). The more mobile ion that migrates at higher rate "drags" the ion of opposite charge with it. Such mutual interactions of ions, the so-called "ion-coupling effect," alter the mass-transfer rate of individual ionic species considerably in a multi-ion system. In general, the strongest ion-coupling effect obtains when ions of opposite sign diffuse in the same direction. The presence of additional electrolytes can cause the decoupling of the diffusion of the more mobile ionic species from that of the less mobile one, and at sufficiently high concentration of inert electrolytes each ionic species may move at its intrinsic mobility.

Several authors (Vinograd and McBain, 1941; Sherwood and Wei, 1955; Sherwood and Ryan, 1959) have investigated such coupled diffusion effects in neutralization reactions between sodium hydroxide and acetic acid (or hydrochloric acid) within the framework of the film theory. They have shown that the enhancement in the diffusion of reactive ions in such systems is largely governed by the ion-coupling phenomenon. Similar studies have been conducted by Brian et al. (1964), who have used the penetration theory to explain the increase in reaction rates of fast heterogeneous reactions.

The present authors think that the observed intensification of the ionic reaction between the DEA molecule and the H^+ ion can be explained using similar principles. It is proposed that the cationic micelle induces intensification of this reaction due to two factors. First, since the valence of micelle is very high (each micelle carries about 12 units of positive charge), it can cause a strong ion-coupling effect during its diffusion along with the other ions in the system. Second, ion diffusion may be accompanied by counterion binding on the micellar surface (Quina and Chaimovich, 1979). This may alter the amount of free counterions available for diffusion under a concentration gradient. Both these effects are considered in the present work in formulating a general theory to describe the effect of the presence of an inert ionic microphase on instantaneous heterogeneous ionic reactions.

A modified version of the general (film-theory) mechanism of simultaneous mass-transfer with chemical reactions as outlined by Hatta (1929) is used in this work to derive the ionic flux expressions. Although the rigorous penetration theory or the surface-renewal theory would in principle offer an improvement over the film theory, it has been shown that the maximum deviation between the results predicted by the ionic penetration theory and the film theory is generally less than 4% (Brian et al., 1964).

Experimental Studies

Measurement of the solubility of DEA in the aqueous phase

The solubility of DEA in the aqueous phase (in the presence of a supporting electrolyte) was estimated by determining the DEA-HCl content using a precalibrated UV spectrophotometer (UV Atlas). The organic phase and the aqueous phase (with an added supporting electrolyte) were shaken thoroughly and the mixture was allowed to settle. The DEA dissolved in the aqueous phase was completely converted into the organic salt by adding excess HCl. UV absorption spectra of DEA-HCl salt, which shows a peak at 254 nm (Fendler and Fendler, 1975), was found to remain unaffected in the presence of the surfactant CTAB or simple salts used in this work. The solubility of DEA in 100 $\text{mol}\cdot\text{m}^{-3}$ NaCl solution at 298 K was found to be 35 $\text{mol}\cdot\text{m}^{-3}$.

Measurement of the critical micelle concentration

The critical micelle concentration (CMC) of the CTAB was determined by surface-tension measurements of the surfactant solution using Fisher Surface Tensiomat (Model No. 21). Surface tension was plotted against the logarithm of molar concentration of CTAB solution and was used to estimate a CMC value of 0.721 $\text{mol}\cdot\text{m}^{-3}$ in a 100 $\text{mol}\cdot\text{m}^{-3}$ HCl solution. This value concurs well with those reported by others (Sepulveda and Cortes, 1985, Pardes et al., 1984).

Measurement of overall reaction rate

The cationic surfactant CTAB and simple salts NaCl, $SrCl_2$, and $AlCl_3$ were used as the supporting electrolytes. CTAB was purchased from Merck and was used after recrystallization from the ethanol–ether mixture. The salts were obtained from reputable firms. Batch reactions between DEA and HCl were carried out in a 0.5-dm^3 glass reactor (internal diameter = 0.079 m). A 0.25-dm^3 volume of HCl solution with a known concentration of the supporting electrolyte was contacted with the pure organic phase in the reactor provided with a paddle stirrer. Vertical strips of Teflon fixed to the side of the reactor acted as baffles, promoting better mixing and preventing a large central vortex. Special care was taken while placing the organic phase above the aqueous phase. Since the reaction starts immediately after contact between the two phases, it is desired that the addition of the organic phase be quick. For this reason, the organic phase was kept in a funnel and was injected onto the wall of the container and allowed to settle down on the aqueous phase by gravity flow. The flow rate was adjusted to ensure rapid spread of the organic layer over the cross-sectional area of the reactor. The injector used for this purpose was placed at an appropriate distance above the aqueous-phase solution to prevent any deep penetration of the organic liquid jet into the aqueous phase. The time taken to spread the organic layer thus was less than a few seconds. The stirrer was positioned near the actual physical interface between the two phases so as to minimize the liquid-film resistance. The rpm was adjusted at 60 to avoid interfacial disturbance.

During each experimental run the concentration of H$^+$ ions in the aqueous phase (the solution pH) was measured using an ORION pH electrode (Ag-Sureflow Electrode) that was connected to an ORION pH meter (E-940 model). The pH of the solution was continuously monitored and the accuracy of the measurement was within ± 0.001. The reactor containing the solution, stirrer, and electrode was surrounded by a water-thermostat for maintaining the system temperature at 298 ± 0.02 K.

The experiment just outlined, was also carried out in the absence of any supporting electrolyte in the aqueous phase. The rate of mass transfer of the reactive H$^+$ ion under such a condition provided the basal rate over which any enhancement in the corresponding mass-transfer rates in the presence of a supporting electrolyte was measured. In all experimental runs the initial HCl concentration in the aqueous solution was 100 mol·m^{-3}. The concentration of NaCl ranges from 40 to 150 mol·m^{-3}, whereas for SrCl$_2$ and AlCl$_3$ the concentration was 100 mol·m^{-3} each. For CTAB as the microphase, the concentration varies from 2.9 mol·m^{-3} to 13 mol·m^{-3}.

Theory

As mentioned earlier, the film-theory representation of the instantaneous reaction (Eq. 1) studied in the present work corresponds to that shown in Figure 1. The nonionic molecule, DEA, diffuses through the region $0 < x < \lambda$, and is counterbalanced by the diffusion of H$^+$ ions in the $\lambda < x < \delta$ region. The concentrations of these two species become zero at the λ-plane (the reaction plane). The product of the reaction, the hydrochloride salt of the amine (DEAH$^+$Cl$^-$) being ionic in nature, is likely to be negligibly soluble in the nonaqueous phase; it is therefore assumed that it diffuses toward the bulk solution. The reaction being instantaneous, no H$^+$ ions exist in the region between the λ-plane and the interface (i.e., between $x = 0$ and $x = \lambda$). Similarly, no amine exists beyond the reaction plane (i.e., between $x = \lambda$ and $x = \delta$). It may be assumed that the mass-transfer resistance in the organic phase is negligible, which implies that the concentration of DEA at the phase boundary is constant over the entire period of contact between the two phases. It is further assumed that the presence of a supporting electrolyte in the aqueous phase does not affect the solubility of DEA in water to any appreciable extent.

Case I: Reactive system without supporting electrolyte

Diffusion in the Region, $0 < x < \lambda$. In this region (see Figure 1) only DEA (here designated as S) diffuses. The flux of the DEA molecule is given by Fick's law:

$$J_S = -D_S \frac{d[S]}{dx}. \tag{2}$$

A quasi steady state is assumed to exist in this region, which allows us to write

$$\frac{dJ_s}{dx} = 0 \tag{3}$$

Integration of the preceding equation is carried out using the following boundary conditions

$$\text{at } x = 0 \quad [S] = [S^*] \tag{4}$$

$$\text{at } x = \lambda \quad [S] = 0 \tag{5}$$

to yield the linear concentration profile of DEA in the film:

$$[S] = \left(1 - \frac{x}{\lambda}\right)[S^*], \tag{6}$$

where $[S^*]$ is the equilibrium solubility of DEA in the aqueous phase.

Diffusion in the region, $\lambda < x < \delta$. In the following equations, the species DEAH$^+$ (reaction product), H$^+$ and Cl$^-$ are designated as A, B, and X respectively.

The electroneutrality condition in this region requires that

$$[A] + [B] = [X] \tag{7}$$

Further, the no-current condition is given by

$$J_A + J_B = J_X \tag{8}$$

The fluxes of ions in the film are represented by the Nernst–Planck equations;

$$J_i = -D_i \left[\frac{d[i]}{dx} + [i]\frac{\mathfrak{F}}{RT}\frac{d\psi}{dx}\right] \qquad i = A, B \tag{9}$$

$$J_x = -D_x\left[\frac{d[X]}{dx} - [X]\frac{\mathfrak{F}}{RT}\frac{d\psi}{dx}\right], \tag{10}$$

where ψ represents the electrical potential generated by local deviations from electroneutrality owing to the different mobilities of the ions in the system. Since the Cl^- ion does not enter into the chemical reaction, no net diffusion of this ion is expected. Thus, at any point in this region

$$J_X = 0. \tag{11}$$

The following expression for J_B can be derived through Eqs. 7–9 and 11:

$$J_B = -D_B\left[1 - \frac{(D_B - D_A)[B]}{(D_B - D_A)[B] + 2D_A[X]}\right]\frac{d[B]}{dx}. \tag{12}$$

A relationship between $[X]$ and $[B]$ is obtained by making use of Eqs. 10 and 11, and by eliminating $d\psi/dx$ from the resulting expression. This yields the following equation:

$$\frac{d}{dx}\ln[X] = -\frac{d}{dx}\ln(D_B[B] + D_A[A]) \tag{13}$$

Integrating the preceding equation and substituting for $[A]$ from Eq. 7, we get

$$[X](D_A[X] + (D_B - D_A)[B]) = C \tag{14}$$

The integration constant C in the preceding equation can be evaluated using the electroneutrality condition for the bulk solution as:

$$[A]_0 + [B]_0 = [X]_0 \tag{15}$$

$$[X]_0 = [B]_i, \tag{16}$$

where $[B]_i$ is the initial concentration of ion B in the bulk. The subscript 0 is used to represent bulk-phase concentrations.

Equation 14 is now solved for $[X]$ and substituted in Eq. 12. The resulting expression is

$$J_B = -D_B\left[1 - \frac{(D_B - D_A)[B]}{\left\{(D_B - D_A)^2[B]^2 + 4D_A C\right\}^{1/2}}\right]\frac{d[B]}{dx}. \tag{17}$$

The quasi-steady-state condition is assumed to exist in the film; for the continuity of B in the region $\lambda < x < \delta$, one may write

$$\frac{dJ_B}{dx} = 0. \tag{18}$$

Substituting the expression for J_B from Eq. 17 into Eq. 18 and integrating with the help of the following boundary conditions

$$\text{at } x = \lambda \quad [B] = 0 \tag{19}$$

$$\text{at } x = \delta \quad [B] = [B]_0 \tag{20}$$

the concentration profile of ion B in the region $\lambda < x < \delta$ is obtained as follows:

$$[B] - \sqrt{[B]^2 + m^2} = \frac{1}{\delta - \lambda}\left[\left([B]_0 - \sqrt{[B]_0^2 + m^2}\right)(x - \lambda) - (\delta - x)m\right] \tag{21}$$

where

$$m^2 = \frac{4D_A C}{(D_B - D_A)^2}.$$

At $x = \lambda$, the flux of dissolved solute S (i.e., DEA) is equal to that of reactive ionic species B (i.e., H^+ ion)

$$J_S|_{x=\lambda} = -J_B|_{x=\lambda}. \tag{22}$$

Substituting the expressions for J_B and J_S from Eqs. 17 and 2, respectively, in Eq. 22 and simplifying with the help of Eqs. 6 and 21, the movement of the λ-plane over time can be obtained as

$$\frac{\delta}{\lambda} = 1 + \frac{D_B}{D_S[S^*]}\left[[B]_0 - \sqrt{[B]_0^2 + m^2} + m\right]. \tag{23}$$

The change in bulk solution concentration of ion B with time is given by the material balance equation

$$-V\frac{d[B]_0}{dt} = aJ_B|_{x=\lambda} \tag{24}$$

where V is the aqueous solution volume and a is the area of the interface between the two phases. Using Eqs. 2, 6, and 23, Eq. 24 may be written as:

$$\frac{d[B]_0}{dt} = -\frac{aD_s[S^*]}{V\delta}\left\{1 + \frac{D_B}{D_S[S^*]}\left[[B]_0 - \sqrt{[B]_0^2 + m^2} + m\right]\right\}. \tag{25}$$

The preceding equation is integrated with the initial condition

$$\text{at } t = 0 \quad [B]_0 = [B]_i. \tag{26}$$

Case II: Reactive system with supporting electrolyte

Although the ions of the supporting electrolyte do not take part in the reaction, they can significantly influence the rate of mass transfer of the reactive species (i.e, DEAH$^+$ and H$^+$ ions) by altering their diffusion coefficients. As the reaction begins, the product, DEAH$^+$ ions, will diffuse toward the bulk phase. This diffusion is accompanied by counter diffusion of H$^+$ ions. This mutual diffusion of ions generates an electrical potential gradient in the region $\lambda < x < \delta$, which in turn induces a gradient in the concentration of ions of the supporting electrolyte. However, since the latter are nonreactive, their fluxes are expected to be zero, and therefore their concentration profiles will be independent of their ionic self-diffusion coefficients. Consequently, in mathematical terms it is possible to group the concentration of the monovalent anion of the supporting electrolyte with that of the Cl$^-$ ion. Thus, the total concentration of the anionic species will be the sum of the concentrations of added anions and that of the Cl$^-$ ion. In all the cases where the surfactant CTAB is present above its CMC, the monomer concentration of the surfactant will be approximately equal to CMC; which can also be grouped with that of Cl$^-$ ion.

Using the letter M to designate the cationic species of the supporting electrolytes, the electroneutrality condition in the region $\lambda < x < \delta$ can be written as

$$[A]+[B]+Z_M[M]=[X]. \tag{27}$$

Zero current conditions in the region are expressed by

$$J_A+J_B=0 \tag{28}$$

$$Z_M J_M=0 \tag{29}$$

$$J_X=0. \tag{30}$$

The Nernst–Planck equations are used to represent the ionic fluxes:

$$J_i=-D_i\left[\frac{d[i]}{dx}+Z_i[i]\frac{\mathcal{F}}{RT}\frac{d\psi}{dx}\right] \quad i=A,B,M,\text{ and } X, \tag{31}$$

where Z_i is the valence of the respective ion. Using Eqs. 27 to 31, the following relations can be derived:

$$J_B=-\frac{D_A D_B(2[X]+Z_M(Z_M-1)[M])}{(D_B-D_A)[B]+D_A\{2[X]+Z_M(Z_M-1)[M]\}}\frac{d[B]}{dx} \tag{32}$$

$$\frac{d[M]}{dx}=\frac{Z_M(Z_M-1)(D_B-D_A)[M]}{(D_B-D_A)[B]+D_A\{2[X]+Z_M(Z_M-1)[M]\}}\frac{d[B]}{dx} \tag{33}$$

$$\frac{d[X]}{dx}=-\frac{(D_B-D_A)[X]}{(D_B-D_A)[B]+D_A\{2[X]+Z_M(Z_M-1)[M]\}}\frac{d[B]}{dx}. \tag{34}$$

Assuming that a quasi steady state exists in the film, we can write

$$\frac{dJ_B}{dx}=0. \tag{35}$$

Substituting for J_B from Eq. 32 into Eq. 35, and using Eqs. 33 and 34, we get

$$\frac{d^2[B]}{dx^2}-\frac{(D_B-D_A)}{(D_B-D_A)[B]+D_A\{2[X]+Z_M(Z_M-1)[M]\}}\left[1+\frac{2[X]-Z_M^2(Z_M-1)[M]}{2[X]+Z_M(Z_M-1)[M]}\right]\left(\frac{d[B]}{dx}\right)^2=0. \tag{36}$$

The following boundary conditions are needed for simultaneous solution of Eqs. 33, 34 and 36

$$\text{at} \quad x=\lambda \quad [B]=0 \tag{37}$$

$$\text{at} \quad x=\delta \quad \left.\begin{array}{l}[B]=[B]_0\\ [M]=[M]_i\\ [X]=[X]_i\end{array}\right\}. \tag{38}$$

The position of the λ-plane can be located by the fact that at $x=\lambda$ the fluxes of the reactive species must be equal, that is,

$$D_B\left.\frac{d[B]}{dx}\right|_{x=\lambda}=\frac{D_S[S^*]}{\lambda}. \tag{39}$$

The rate of change of the bulk solution concentration of ion B is described by the material balance Eq. 24. In this equation J_B is substituted from Eq. 32, and the resultant equation is integrated using the initial condition (Eq. 26) to obtain the bulk solution concentration $[B]_0$ as a function of time.

Definition of the enhancement factor (ϕ)

In the present work the relative enhancement factor (ϕ) is defined as the ratio of the flux of the reactive species S at the reaction plane in the presence of a supporting electrolyte in the aqueous phase to that in the absence of the supporting electrolyte. Mathematically, the enhancement factor may be expressed as

$$\phi=\frac{J_S}{J_S^W}, \tag{40}$$

where J_S and J_S^W are the fluxes of the reactive species S at $x=\lambda$ in presence and in absence of the inert or supporting electrolyte, respectively. Substituting the expressions for fluxes in the previous equation and simplifying, we get

$$\phi=\frac{\lambda^W}{\lambda}, \tag{41}$$

where λ^W is the corresponding thickness of the region $0 < x < \lambda$ in absence of a supporting electrolyte.

Numerical Procedure

For Case I, Eq. 25 is integrated using the Gear backward differentiation technique with the initial condition, Eq. 26. The diffusivities, D_A and D_B, and δ are regressed from the experimental data by minimizing the standard deviation between the experimentally measured values and the theoretical prediction of the concentration of H^+ ions in the bulk aqueous phase as a function of time. The Simplex method (Nelder and Mead, 1965) was used for optimization. The unweighted linear least-square method was used to estimate the standard deviation.

For Case II, where a supporting electrolyte is present, we integrate Eq. 24 using the fourth-order Runge-Kutta method in conjunction with Eqs. 33, 34 and 36 employing the boundary conditions given by Eqs. 37 and 38. Since in the experiment the value of $[B]_0$ varies with time, these equations are also solved for a set of $[B]_0$ obtained during each run. This essentially is a moving boundary-value problem (since the position of the reaction plane varies with time), and the well-known shooting method was employed to arrive at its solution. This technique involves the integration of the equations just mentioned using the Gear method along the x-axis from the bulk solution ($x = \delta$) to the reaction plane. The value of $[B]$ at $x = \lambda$ obtained by this numerical solution is matched with that given by Eq. 37 using the Newton–Raphson technique. Finally, the parameter λ is evaluated simultaneously using Eq. 39.

For the purpose of solution, the position of the reaction plane was fixed by the front-fixing method (Crank, 1984), for which the following transformation was needed:

$$\eta = \frac{x - \delta}{\lambda - \delta} \tag{42}$$

Using this transformation, the following identities can be written:

$$\frac{d[B]}{dx} = \frac{1}{\lambda - \delta}\frac{d[B]}{d\eta} \tag{43}$$

$$\frac{d^2[B]}{dx^2} = \frac{1}{(\lambda - \delta)^2}\frac{d^2[B]}{d\eta^2}. \tag{44}$$

These transformations when substituted in Eq. 39 give the following relation:

$$\frac{D_B}{\lambda - \delta}\frac{d[B]}{d\eta}\bigg|_{\eta = 1} = \frac{D_S[S^*]}{\lambda}, \tag{45}$$

which, after simplification, yields

$$\lambda = \frac{\delta}{1 - \dfrac{D_B}{D_S[S^*]}\dfrac{d[B]}{d\eta}\bigg|_{n = 1}}. \tag{46}$$

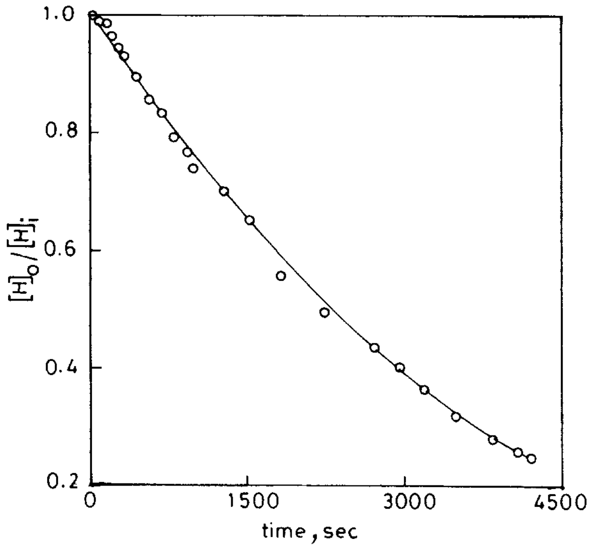


Figure 2. Bulk H^+ ion concentration vs. time in the absence of supporting electrolytes.

During the numerical solution, the following parameteric values were used. The diffusivity of DEA in the aqueous phase was estimated at 5.43×10^{-10} $m^2 \cdot s^{-1}$ (Wilke and Chang, 1955). The micellar charge in CTAB micelle was calculated from the relation $Z = \alpha N$, where α is the degree of ionization of micellar head groups and N is the aggregation number. The values of N and α were taken to be 62 and 0.22, respectively (Sepulveda and Cortes, 1985).

Results and Discussion

A comparison of the rates of change of H^+ ion concentration in the aqueous phase in the absence and in the presence of a supporting electrolyte (comparing Figures 2 and 3), indicates that an enhancement of the overall reaction rate is achieved by the introduction of a supporting electrolyte in the aqueous phase. Theoretically, the relative enhancement factor for the reaction may be defined by either of Eqs. 40 or 41. However, defining an overall experimental enhancement

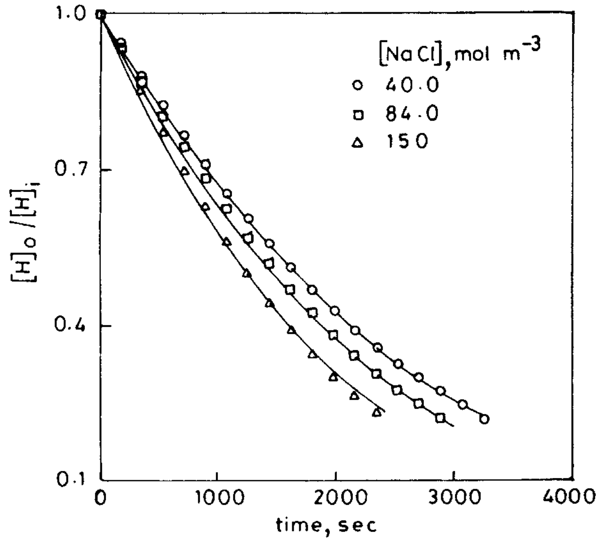


Figure 3. Bulk H^+ ion concentration vs. time in the presence of NaCL as supporting electrolyte.

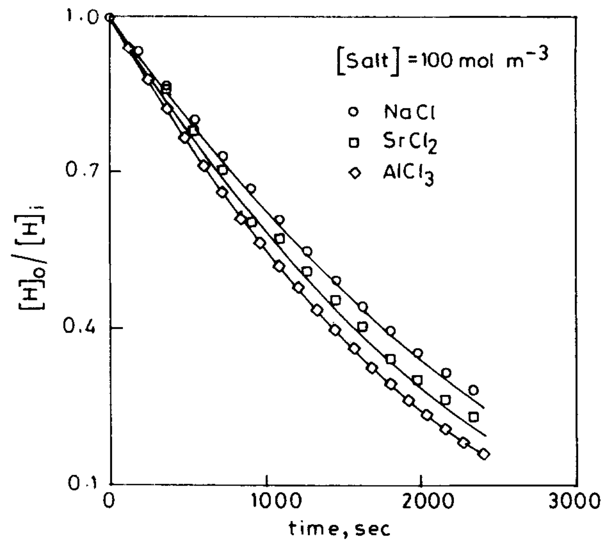


Figure 4. Bulk H$^+$ ion concentration vs. time with simple salts as supporting electrolytes.

factor (ϕ_{exp}) in this work is difficult, as the mass-transfer rates (with and without a supporting electrolyte) change with time due to change in bulk H$^+$ ion concentration. Moreover, ϕ_{exp} is also a function of the bulk concentration of the supporting electrolyte. However, this problem is overcome by the following approximation procedure. The relative enhancement factor is defined as the ratio of the slope (at $t = 0$) of a typical experimental curve of [H$^+$] vs. t in the presence of a supporting electrolyte (Figures 3 and 4) to the slope of the curve (at $t = 0$) in Figure 2, the latter representing a reaction without the supporting electrolyte. The estimated enhancement factors (ϕ_{model}) obtained from Eq. 41 are compared with those from experimental data (ϕ_{exp}) in Table 1. The accuracy of prediction is encouraging (maximum deviation 14%).

It can be seen that ϕ_{exp} increases with the concentration of the supporting electrolyte, as well as with the valency of its cation. Thus, for simple salts as supporting electrolytes, the ϕ_{exp} are 1.53, 1.64, and 1.73, respectively, when each is present at a concentration of 100 mol·m^{-3}. For CTAB as the supporting electrolyte, the ϕ_{exp} is higher (about 3–6) than that obtained using simple salts. The concentration of CTAB used in this study ranges over 2 to 14 times that of its CMC. For this range of concentration, CTAB molecules are expected to exist dominantly in the form of roughly spherical micellar aggregates. These micelles carry as many as twelve units of positive charge on the surface (Sepulveda and Cortes, 1985) due to the dissociation of the head groups of the surfactant molecules. In the present reactive system such aggregates are also likely to behave as cations of a supporting electrolyte. But because the micelle is in the nature of a polyelectrolyte, its effect is expected to be more pronounced compared to that of the cations of simple salts. The high values of ϕ_{exp} at a relatively low concentration of CTAB compared to that of simple salts therefore indicates that the valency of the cation of the supporting electrolyte is an important determinant of the enhancement factor.

Table 1. Comparison of Experimental and Computed Enhancement Factors

Supporting Electrolyte	Supporting Electrolyte Conc., mol·m^{-3}	ϕ_{exp}	ϕ_{model}
CTAB	2.91	2.91	3.27
	5.20	4.08	3.94
	8.00	4.67	4.43
	10.0	5.39	5.23
	13.0	6.28	6.12
NaCl	40.1	1.28	1.39
	70.0	1.39	1.45
	85.0	1.49	1.56
	100	1.53	1.73
	150	1.60	1.89
SrCl$_2$	100	1.64	1.86
AlCl$_3$	100	1.73	1.98

Upon dissociation the surfactant head groups at the CTAB micelle surface releases Br$^-$ ion as counterions. However, in the present experimental system, an additional counterion Cl$^-$ ion (from the HCl solution) is also present in the aqueous phase. Thus, to an extent, the Br$^-$ counterions bound to the micelle surface is likely to be exchanged for Cl$^-$ counterions, which will reduce the effective concentration of the latter that is available for diffusion or interaction with other ions in solution. Pardes et al. (1984) have shown that the relative strength of the binding of anions to the CTAB micelle surface lies in the order of Br$^-$ > NO$_3^-$ > Cl$^-$ > OH$^-$. Therefore, the Cl$^-$ counterions are unlikely to replace the bound Br$^-$ ions to any significant extent. Hence this effect is ignored in the present work. Moreover, since both Br$^-$ and Cl$^-$ are monovalent and since their mobilities are nearly identical (Robinson and Stokes, 1959), even a significant exchange of bound counterions at the micelle surface would not have any significant effect on the rate of mass transfer of the reactive species. This is because the inert ion diffusivities (i.e., those of Cl$^-$ and Br$^-$ ions) do not appear in the governing flux equations.

The predicted variation of H$^+$ ion concentration in the bulk is also shown in Figures 2 to 5. The fit of the model to the experimental data is seen to be good. The regressed values of the diffusion coefficients of the reactive ionic species

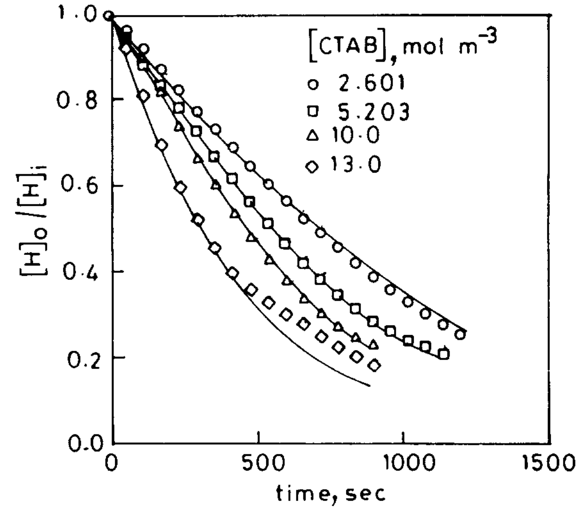


Figure 5. Bulk H$^+$ ion concentration vs. time with CTAB as supporting electrolyte.

Table 2. List of Estimated Parameters

Supporting Electrolyte	Supporting Electrolyte Conc., $\mathrm{mol \cdot m^{-3}}$	D_B/D_B^W	D_A/D_A^W	δ μm	σ $\times 10^2$
None	—	1.00	1.00	56.0	3.31
CTAB	2.91	2.83	3.56	56.1	1.39
	5.20	3.58	4.18	57.8	3.0
	8.00	3.83	4.67	54.4	0.884
	10.0	4.03	4.76	56.6	1.06
	13.0	4.57	5.51	57.2	0.977
NaCl	40.1	1.03	1.01	56.5	0.771
	70.0	1.04	1.11	55.9	1.06
	85.0	1.06	1.16	53.2	1.06
	100	1.14	1.24	53.8	1.15
	150	1.20	1.46	56.8	1.44
$SrCl_2$	100	1.17	1.69	56.2	1.49
$AlCl_3$	100	1.20	2.00	55.1	1.40

$D_A^W = 0.986 \times 10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$, $D_B^W = 1.80 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} \{[B_0^{\exp}](i) - [B_0^{\text{model}}](i)\}^2}{n-1}}, \quad n = \text{number of data points.}$$

(H^+ and $DEAH^+$ ions) and that of the diffusion film thickness (δ) are reported in Table 2. The standard deviations (σ) between the experimental rate data (i.e., the concentration of H^+ ion in the bulk solution) and theoretical predictions are also listed, the average value being less than about 3%. It can be noted that the film thickness is constant for all cases. This is not surprising, since the hydrodynamic conditions were kept the same for all the experiments.

It can also be seen from Table 2 that the diffusion coefficients of the reactive ions are influenced by both the cationic valency of the supporting electrolyte and its concentration. The ion-diffusion coefficients increase (i) with the increasing concentration of a given supporting electrolyte, and (ii) with the cationic valency for the given supporting electrolyte concentration. The effect of valence on diffusion coefficients is on the order of $CTAB^{n+} > Al^{3+} > Sr^{2+} > Na^+$.

A comparison of Tables 1 and 2 also shows that the increase in the concentration of the supporting electrolyte leads to an increase in the diffusion coefficients of the reactive species which, in turn, is manifested as an increase in the observed enhancement factor. These observations suggest that the presence of a supporting electrolyte tends to enhance the mass-transfer rate by altering the diffusivities of the two reactive species, H^+ and $DEAH^+$. This is in agreement with the fact that the addition of an inert salt enables ions of the same charge to diffuse at their own diffusivity in a situation when they are moving in the opposite direction. As noted earlier, this phenomenon of ion transport in a multi-ion system has also been observed by others (Vinograd and McBain, 1941; Sherwood and Wei, 1955; Brian et al., 1964) as well.

Concentration profiles of ionic species in the diffusion film

The simulated concentration profiles of the ionic species H^+, $DEAH^+$, Na^+ and Cl^- as functions of the distance in the region $\lambda < x < \delta$ are shown in Figure 6. Here the supporting electrolyte (NaCl) concentration is 100 $\mathrm{mol \cdot m^{-3}}$.

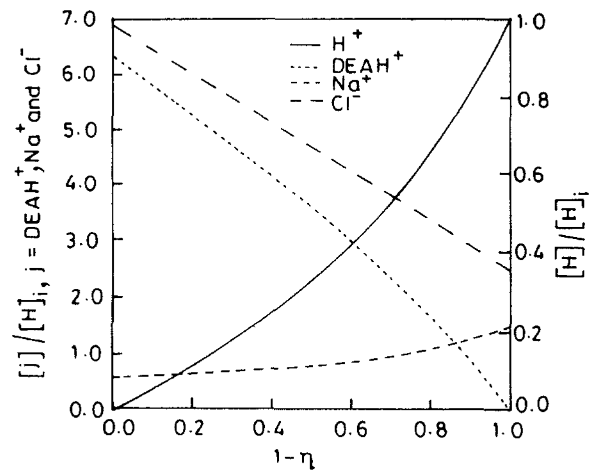


Figure 6. Concentration profiles of ionic species with $[NaCl] = 150\ mol \cdot m^{-3}$.

These concentration profiles are computed very soon after the commencement of the reaction. Although the electroneutrality is maintained throughout the $\lambda < x < \delta$ region, this does not necessarily imply that all ionic species diffuse at the same rate. It may also be noted that there is only a small gradient in Na^+ ion profile.

The increase in the diffusion coefficients of the reactive species (Table 2) by ion-coupling may explain the observed reaction-rate enhancements observed in the present work. In effect, the more mobile reactive cation H^+ is "allowed" to diffuse out toward the physical interface at a higher rate as the less mobile cation (the mobility decreasing on the order of $Na^+ > Sr^{2+} > Al^{3+} > CTAB^{n+}$) contributes to the preservation of local electroneutrality with the common anion Cl^- in the region $\lambda < x < \delta$ (Figure 1). This situation is also reflected in the typical concentration profiles shown in Figure 6, where the H^+ ion concentration falls—as one moves from the bulk phase to the reaction plane—much more rapidly compared to that of the inert cation Na^+. The increased mobility of the H^+ ion creates an increased diffusion potential which, in turn, augments the flux of $DEAH^+$ in the reverse direction. In Figure 7, the concentration profiles of the various ionic species are shown for the case of CTAB as the supporting electrolyte. Here the concentration gradient of the $DEAH^+$ ion becomes sharper than in the case where simple salts are present.

Movement of the reaction plane

The movement of the λ-plane is governed by the balance of fluxes of H^+ ion from the bulk of the solution and of DEA from the actual physical interface. The concentrations of both H^+ *ion and DEA molecules are zero at this plane.* Since the organic phase is always in excess, the concentration $[S^*]$ in the aqueous phase is assumed to be constant for all time. It is also assumed that the diffusion coefficient of DEA is not affected by the presence of ions in the solution. The bulk H^+ ion concentration is depleted due to the reaction, and therefore the flux of H^+ ion also decreases with time. Along with the decreasing flux of H^+ ion, the DEA flux at the reaction plane must also decrease with time, primarily

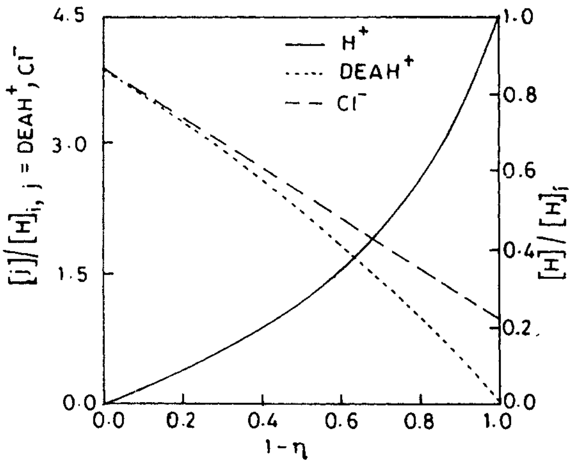


Figure 7. Concentration profiles of ionic species with [CTAB] = 13 mol·m^{-3}.

through the reduction of its concentration gradient. This, in turn, may only be achieved if the reaction plane progressively shifts away from the physical interface toward the bulk aqueous phase (the total film thickness δ being fixed).

As shown in Figure 8, this expected physical behavior is also replicated by theoretical estimates of the position of the reaction plane with time, both in the absence and in the presence of simple salts as supporting electrolytes. As is evident, the location of the λ-plane remains close to the physical interface ($x = 0$) for most of the reaction. The corresponding variation of the location of λ-plane in the presence of CTAB as the supporting electrolyte is shown in Figure 9. It can be seen that at any given time the ratio δ/λ increases with increasing CTAB concentration in the aqueous phase. This is because with higher CTAB concentration, the H$^+$ flux at the λ-plane is correspondingly higher for any given time. The concurrent DEA flux must also be identically higher, which according to the reason provided in the last paragraph, may be obtained only if the reaction plane is correspondingly closer to the interface.

An additional feature of Figures 8 and 9 is that the shift of the λ-plane toward the bulk aqueous phase becomes virtually independent of the concentration or of the type of supporting electrolyte when the bulk H$^+$ ion concentration has dropped to very low values. This is probably due to the fact that at such concentrations the diffusion potentials that drive H$^+$ ion flux toward the λ-plane is reduced to extremely low values, and the net flux is virtually reduced to zero. Thereafter the plane shifts at a rate that is negligibly small.

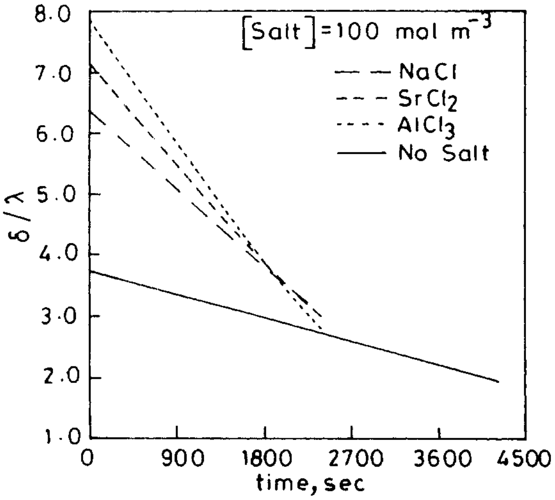


Figure 8. Shift of the reaction plane with time.

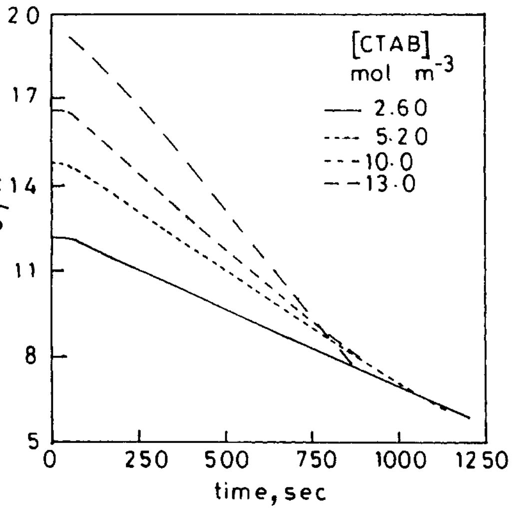


Figure 9. Shift of the reaction plane with time.

Conclusions

The present work demonstrates that the film-theory approximation along with the ion-coupling phenomenon can reasonably well describe the observed intensification of the instantaneous heterogeneous reaction in the presence of a supporting electrolyte. This study suggests that the role of a micellar microphase in the intensification of an instantaneous heterogeneous reaction may not only be in the form of conventional micellar catalysis. Indeed when such a mechanism is not dominant, an ionic micelle may still enhance an instantaneous ionic reaction by the mechanism of coupled ionic diffusion.

Notation

$[A]$ = concentration of A, mol·m^{-3}
$[B]$ = concentration of B, mol·m^{-3}
$\mathfrak{F}$ = Faraday constant, C·mol^{-1}
J = diffusion flux of ion, mol·m^{-2}·s^{-1}
$[M]$ = concentration of M, mol·m^{-3}
R = universal gas constant, J·K^{-1}·mol^{-1}
t = time, s
T = temperature, K
x = axial direction, m
$[X]$ = concentration of X, mol·m^{-3}
λ = distance of the reaction plane from the interface, m
η = dimensionless axial distance

Superscripts

$*$ = interfacial

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