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INTENSIFICATION OF MULTIPHASE REACTIONS THROUGH THE USE OF A MICROPHASE—II. EXPERIMENTAL

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Abstract—The specific rates of alkaline hydrolysis of solid esters—2,4-dichlorophenyl benzoate, *p*-chlorophenyl benzoate and phenyl benzoate—in the presence of a second emulsified liquid phase were measured in a 67 mm i.d. mechanically agitated contactor. For 2,4-dichlorophenyl benzoate the above study was also carried out in microemulsions and allied micellar media. Significant enhancements in the specific rates of hydrolysis, as high as 29, were observed. The above data on solid–liquid systems, along with those of absorption of gases, namely, isobutylene, but-1-ene and propylene into emulsions of an additional liquid phase in aqueous sulfuric acid as well as microemulsions and various micellar solutions, published earlier, have been analysed with the unsteady state theory developed in Part I of this study. In some of the cases, where bulk concentration of the sparingly soluble reactant was finite, it was necessary to modify the original theory. The predicted values of the enhancement factor, for systems where macroemulsions were used, were found to be in good agreement with the experimental values of the enhancement in the specific rate. For the other cases, where *a priori* prediction was not possible the model equations provided a reasonable basis for correlation of data. The analysis of experimental data brings out clearly the importance of time dependent phenomenon like accumulation within the microphase and demonstrates the necessity of models based on unsteady state formulations for such cases.

INTRODUCTION

In the first part of this study a comprehensive theory of 'catalysis', through the use of a microphase, to enhance the rates of multiphase reactions, was presented. We will now use this theory to analyse experimental data obtained in the present work as well as published earlier for a variety of reaction systems where macroemulsions/microemulsions/micellar solutions constituted the microheterogeneous media.

The use of an emulsified second liquid phase in order to enhance the specific rates of gas absorption was first suggested by Sharma (1983). Subsequently this strategy was probed by Mehra and Sharma (1985) wherein the absorption of various unsaturated hydrocarbon gases, namely, isobutylene, but-1-ene and propylene, into emulsions of chlorobenzene in aqueous solutions of sulfuric acid was studied. Absorption data were correlated by the use of a simple model based on the film theory of mass transfer. However, in the light of a more appropriate theory, developed in the first part of this study, it will be seen that the data need to be reanalysed whereby it becomes possible to predict the specific rate of absorption *a priori*, unlike the film theory model which could only provide a limited basis to correlate data.

The general applicability of this strategy will be shown, by its extension to the alkaline hydrolysis of solid esters, namely, 2,4-dichlorophenyl benzoate (2,4-DCPB), *p*-chlorophenylbenzoate (PCPB) and phenyl benzoate (PB) in emulsions of chlorobenzene in aqueous solutions of potassium hydroxide. Alkaline hydrolysis of these esters have served as model systems in several contexts. Janakiraman (1984) has shown that the rates of hydrolysis of PB can be enhanced by a factor of 2-14 in the presence of anionic micelles. Bhagwat and Sharma (1988) have studied the specific rates of alkaline hydrolysis of 2,4-DCPB and PB in microemulsion media containing anionic surfactant and found the enhancement in the specific rates to range from 2 to 50.

In a very recent communication Mehra and Sharma (1986) have reported significant enhancements in the specific rates of absorption of but-1-ene and propylene, into microemulsions constituted by an oil, a non-ionic surfactant, co-surfactant and aqueous solutions of sulfuric acid. The alkaline hydrolysis of 2,4-DCPB in similarly constituted microemulsions (the aqueous phase being a KOH solution in this case) was also carried out and a substantial increase in the rate of hydrolysis was observed. The results of these studies, involving non-ionic surfactants, have been analysed in the present paper.

Each of the following sections (except the section on 'materials') in this paper are divided into two parts, the first dealing with macroemulsions and the second with microemulsions and allied micellar media.

MATERIALS

2,4-DCPB, PCPB and PB were made in the laboratory by the Schotten–Bauman reaction (Vogel, 1962) and purified by crystallization from ethanol. All other materials were obtained from reputed firms like Fluka, Aldrich, HICO, SISCO etc.

The average particle size of finely ground ester powder was obtained by sieve analysis. These values were confirmed by visual examination under a microscope. The average particle size was found to be 235, 195 and 120 μm for 2,4-DCPB, PCPB and PB, respectively.

EXPERIMENTAL

Macroemulsions

The specific rates of gas absorption were studied in a stirred cell and the volumetric rates of absorption were measured by the uptake method. Further details regarding the set-up, procedure and emulsification have been reported earlier (Mehra and Sharma, 1985).

Some runs were also carried out in a fully baffled, 92 mm diameter mechanically-agitated contactor equipped with a 30 mm diameter, six bladed, glass turbine impeller. The gas was introduced through a sparger just below the agitator and it was ensured that the volumetric flow rate of the outgoing gas stream was at least 80% of the inlet stream so that the extent of absorption had an insignificant effect on the gas–liquid interfacial area. The volumetric rate of absorption was estimated from the differences in the flow rates at the inlet and the outlet.

For the hydrolysis (solid–liquid) studies a 67 mm i.d. fully baffled mechanically-agitated contactor made of glass was used as the reactor and a 23 mm diameter six bladed glass turbine impeller was used as the agitator. Stable emulsions were obtained as has been described by Mehra and Sharma (1985) except that in place of sulfuric acid solutions, the continuous phase consisted of aqueous solutions of potassium hydroxide. For every run powdered ester was used at a loading of 40 kg/m^3 of the total liquid phase volume. All experiments were carried out at 301 K. The speed of agitation was fixed at 20 rps. The batch time was manipulated to maintain nearly the same level of conversion. The conversion levels for the alkaline hydrolysis of 2,4-DCPB, PCPB and PB were around 20%, 23% and 38%, respectively. The corresponding average concentrations of potassium hydroxide were 0.47, 0.46 and 0.42 kmol/m^3 aq., respectively (the initial concentration in all cases being 0.5 kmol/m^3 aq.). At the end of a run, the reaction was followed by the loss of weight method for solid esters and changes in the concentration of the aqueous phase by extraction of components, after acidification, into a polar organic solvent and subsequent analysis by gas–liquid chromatography.

The hold-up of chlorobenzene (emulsified) in the liquid phase was varied from 0.005 to 0.20 (v/v of total liquid phase).

Microemulsions and micellar media

Varieties of microemulsion formulations were used in the absorption studies. The surfactant used was a non-ionic, namely, ethoxylated lauryl alcohol (7 moles of ethylene oxide per mole of alcohol); co-surfactants included *n*-butanol, *n*-pentanol, *n*-hexanol and 2-ethyl hexanol; the oil phase was chlorobenzene. The continuous phase was an aqueous solution of sulfuric acid. Some runs were carried out in the absence of an oil phase—a formulation more appropriately referred to as a swollen micellar solution (Holt, 1980). Micellar solutions of the dissolved surfactant in aqueous sulfuric acid were also used for some runs in order to be able to assess and quantify the effect of the surfactant alone, on the absorption rates.

For the hydrolysis studies, aqueous potassium hydroxide was used as the continuous phase; the co-surfactant used was usually isopropanol and for some runs *n*-propanol. The oil phase was chlorobenzene for most runs except for a few where cycloexane was used.

Microemulsions (and swollen micellar solutions), in all cases, were prepared by the addition of the desired components, in any order and stirring mildly. As a precaution these formulations were left overnight, so that any phase separation that might occur could be detected and further that the system reach its final thermodynamic configuration. All microemulsions (and swollen micellar solutions) thus obtained were absolutely transparent and generally ranged in color from the pale yellow to reddish orange.

Before the commencement of an absorption run the microemulsions were shaken thoroughly to nullify the effects of creaming which may have taken place during the long storage period. It was further ensured that no bubbles or foam remained at the gas–liquid interface during a run. A typical run lasted over a period of 900–1500 s. The specific rates of absorption remained constant over a fairly long period often exceeding 400 s. Successive runs gave reasonable reproducibility.

The ester hydrolysis as well as gas absorption runs were carried out in a manner identical to that described for macroemulsions.

RESULTS AND DISCUSSIONS

Microemulsions

(I) *Alkaline hydrolysis of* 2,4-*DCPB*, *PCPB and PB*, *respectively*, *in emulsions of chlorobenzene in aqueous solutions of potassium hydroxide.* Tables 1, 2 and 3 present the results for the enhancements in the specific rates of reaction for each of the above esters, respectively, along with the pertinent experimental conditions.

Experimental data clearly show that the specific rate of reaction (hydrolysis) goes up substantially with the suggested strategy. The extent of enhancement increases with an increase in the hold-up of the emulsified liquid phase in the range of 0.005 to 0.20 (v/v of total liquid phase).

Experiments with aqueous alkaline solutions containing the emulsifier—ethoxylated lauryl alcohol (6 moles of ethylene oxide per mole of alcohol)—alone showed an increase in the specific rate of reaction compared to that in the aqueous solution alone, thus indicating the existence of micellar effects.

The last two columns in Tables 1 and 2 indicate the theoretically predicted values of enhancement factor, using Danckwerts' and Higbie's approach, respectively (for the hydrolysis of 2,4-DCPB and PCPB). The last six columns of Table 3 give the theoretically predicted values of the enhancement factor, ϕ_A, along with the values of the bulk concentration of PB using both the above-mentioned approaches and a transient analysis.

Table 1. Enhancement factors for the alkaline hydrolysis of 2,4-dichlorophenyl benzoate in emulsions of chlorobenzene in aqueous potassium hydroxide solution

l_0 (v/v)	$[S]$ (%w/w)†	R_A (kmol/m^2 s) × 10^9	$\phi_{A,\mathrm{exp}}$	$\phi_{A,\mathrm{th}}$ (Danckwerts)	$\phi_{A,\mathrm{th}}$ (Higbie)
—	—	0.695	—	—	—
0.005	0.024	1.40	2.00	1.98	1.90
0.01	0.048	2.00	2.88	2.60	2.55
0.02	0.095	2.78	4.00	3.54	3.45
0.03	0.143	3.33	4.80	4.27	4.15
0.04	0.190	3.90	5.65	4.89	4.75
0.05	0.237	4.67	6.73	5.45	5.70
0.10	0.465	6.30	9.10	7.62	8.00
0.20	0.930	8.35	12.00	10.76	11.25

†Of total liquid phase.

Speed of stirring = 20 rps, $T = 301$ K, $D_A = 5.9 \times 10^{-10}$ m^2/s, $k_L = 9.8 \times 10^{-6}$ m/s, $[A^*] = 3.59 \times 10^{-5}$ kmol/m^3 cont., $m_A = 8890$ (kmol/m^3 mic.)/(kmol/m^3 cont.), $d_p = 3.5$ μm, $k_1 = 0.58$ s^{-1}.

Table 2. Enhancement factors for the alkaline hydrolysis of *p*-chlorophenyl benzoate in emulsions of chlorobenzene in aqueous potassium hydroxide solution

l_0 (v/v)	$[S]$ (%w/w)†	R_A (kmol/m^2 s) × 10^9	$\phi_{A,\mathrm{exp}}$	$\phi_{A,\mathrm{th}}$ (Danckwerts)	$\phi_{A,\mathrm{th}}$ (Higbie)
—	—	1.26	—	—	—
0.005	0.024	2.10	1.66	2.10	2.16
0.01	0.048	2.90	2.30	2.78	2.90
0.02	0.095	4.25	3.35	3.80	4.00
0.03	0.143	5.20	4.15	4.60	4.80
0.04	0.190	5.98	4.75	5.27	5.50
0.05	0.237	7.45	5.90	5.88	6.20
0.10	0.465	10.20	8.10	8.25	8.70
0.20	0.930	13.00	10.30	11.62	12.25

†Of total liquid phase.

Speed of stirring = 20 rps, $T = 301$ K, $D_A = 6.1 \times 10^{-10}$ m^2/s, $k_L = 1 \times 10^{-5}$ m/s, $[A^*] = 7.06 \times 10^{-5}$ kmol/m^3 cont., $m_A = 7085$ (kmol/m^3 mic.)/(kmol/m^3 cont.), $d_p = 3.5$ μm, $k_1 = 0.45$ s^{-1}.

Table 3. Enhancement factors for the alkaline hydrolysis of phenyl benzoate in emulsions of chlorobenzene in aqueous potassium hydroxide solution

t_B (s)	l_0 (v/v)	$[S]$ (%w/w)†	R_A (kmol/m^2 s) × 10^9	$\phi_{A,\mathrm{exp}}$	$[A_{bm}]/[A^*]$	$\phi_{A,\mathrm{th}}$	$[A_{bm}]/[A^*]$	$\phi_{A,\mathrm{th}}$	$[A_{bm}]/[A^*]$	$\phi_{A,\mathrm{th}}$
					(Higbie)		(Danckwerts)		(Transient)	
12,600	—	—	4.37	—	0.245	—	0.25	—	0.25	—
5100	0.01	0.048	10.90	2.5	0.395	3.25	0.41	3.06	0.548	2.36
3600	0.02	0.095	15.40	3.5	0.396	4.63	0.41	4.25	0.549	3.26
3000	0.03	0.143	17.50	4.0	0.384	5.75	0.391	5.34	0.541	4.27
2700	0.04	0.190	20.95	4.8	0.370	6.78	0.370	6.35	0.476	5.30
2400	0.05	0.237	25.35	5.8	0.356	7.73	0.353	7.28	0.432	6.40
1500	0.10	0.465	33.00	7.55	0.277	12.23	0.273	11.54	0.259	11.51

†Of total liquid phase.

Speed of stirring = 20 rps, $T = 301$ K, $D_A = 6.4 \times 10^{-10}$ m^2/s, $k_L = 1.2 \times 10^{-5}$ m/s, $[A^*] = 4.47 \times 10^{-4}$ kmol/m^3 cont., $m_A = 5170$ (kmol/m^3 mic.)/(kmol/m^3 cont.), $d_p = 3.5$ μm, $k_1 = 0.038$ s^{-1}, $a/V = 1418$ m^2/m^3 tot.

As can be seen these values of the enhancement factor match extremely well with the experimentally observed values. Also the predicted values of the enhancement factor from both the models are in close agreement.

A systematic application of the theory developed in Part I of this study can now be illustrated. (Equation references with the Roman I preceding the equation number indicate it is from Part I of this study.)

From the milky white appearance of the emulsion and other available data it can be inferred that the droplet size of emulsified chlorobenzene will lie between 1 and 10 μm (Becher, 1975). A microscopic examination of some emulsion samples shows the droplet size to lie in the range of 1–12 μm with a clustering around 3–4 μm.

The contact time may be calculated from the k_L and D_A values provided in Table 1, for instance,

$$t_c = 4D_A/\pi k_L^2 = 7.79 \text{ s}.$$

Condition (I.11) is indeed satisfied, i.e.

$$d_p \ll 4\sqrt{D_A t_c}.$$
$$(3.5\ \mu\text{m}) \quad (271\ \mu\text{m})$$

Considering a microdroplet size of 3.5 μm,

$$a_{LL} = 6/d_p = 1.714 \times 10^6 \text{ m}^{-1} \quad [\text{eq. (I.9)}]$$

and

$$K_0 = \frac{12 D_A}{d_p^2} = 578 \text{ s}^{-1} \quad [\text{eq. (I.10)}].$$

No reaction can occur in the emulsified microphase since OH^- ion cannot penetrate into chlorobenzene, so $k_{1org} = 0$; the particle is large enough so that D_p is low ($D_p \approx 1 \times 10^{-13}$ m²/s; Dickinson, 1985).

The relative solubility, m_A, values were determined by independent measurements wherein a fixed amount of ester was allowed to equilibrate with a mixture of chlorobenzene and water. The total weight lost by dissolution was found and the solubility of the ester in water (after phase separation) determined using a UV spectrophotometer. The value of m_A was then obtained by the following balance,

$$[A^*]_{tot} = (1 - l_0)[A^*]_w + l_0 m_A [A^*]_w. \tag{1}$$

For instance, for 2,4-DCPB, $m_A = 8890$ (Table 1).

Condition (I.19) is satisfied, i.e.

$$\frac{D_p}{D_A} \ll \frac{l_0 K_0 t_c}{(1 - l_0) m_A} \qquad (\text{for } l_0 = 0.01)$$
$$(1.7 \times 10^{-4}) \ll (0.051)$$

hence the droplets may be considered stationary. Also,

$$\frac{K_o t_c}{m_A} = 0.506 \qquad [\text{condition (I.33)}]$$

which is not much less than 1.

Therefore eqs (I.20) or (I.20a) apply and may be used for calculating the specific rate of absorption. The reactions involved in the system are first order with respect to the solute ester (*A*) and KOH (*B*), respectively. The reaction is fast enough to occur near the solid–liquid interface but still not fast enough to cause depletion of the hydroxide ion near the interface. Therefore, the pseudo first order reaction rate constant, k_1, may be estimated from the base case rate (equation I.18; $k_1 = 0.58 \text{ s}^{-1}$, Table 1). The calculated specific rate of absorption divided by the base rate is equal to the theoretical value of the enhancement factor, $\phi_{A,th}$.

The above outlined procedure and arguments apply to all entries in Tables 1 and 2, i.e. for 2,4-DCPB and PCPB, respectively. The alkaline hydrolysis of PB, however, provides an interesting variant of the general solution [eqs (I.20) and (I.20a)] since the base case rate itself overlaps the very slow, slow and fast reaction regimes, and therefore the bulk concentration of *A* is non-zero (Doraiswamy and Sharma, 1984). If the emulsified organic phase is indeed delivering *A* to the bulk of the liquid phase then the bulk concentration of *A* in the presence of the microphase should be even higher. The relevant theory for the case of finite bulk concentrations may be found in the Appendix. Table 3 illustrates this for the case of PB using Higbie's [eqs (A6) and (A8)] as well as Danckwerts' [eqs (A7) and (A9)] model and the transient analysis [eqs (A7) and (A16)]. As we can see, the predicted values of the enhancement factors match reasonably well with the experimentally observed values (except for 1 point). Also the predictions given by the transient analysis are somewhat better than those given by the approximate technique [eqs (A8) and (A9)].

Though the micellar effects were detected when the specific rates were measured with surfactant alone, this contribution is likely to be negligible in the presence of chlorobenzene for the following reasons: a substantial fraction of the surfactant is likely to be adsorbed on the liquid–liquid interface in addition to that dissolved in chlorobenzene, all of which is therefore, not available for micelle formation. However, it may still be possible that the amount of surfactant residing in the aqueous phase is higher than the CMC value of relevant surfactant which is quite low (Fendler and Fendler, 1975), such that micelles are formed. A rigorous analysis will demonstrate that the contribution due to micelles, to the rate is insignificant. When non-reactive micelles are present along with an emulsified liquid phase, the specific rate of reaction is given by,

$$R_A = [A^*]\sqrt{D_A((1 - l_0 - l_m) + l_m m_{Am})}\, I/t_c \tag{3}$$

where *I* is defined as in eq. (I.20) after the values of the parameters involved have been reset as,

$$\begin{aligned}\alpha &= (1 - l_0 - l_m)k_1/[(1 - l_0 - l_m) + l_m m_{Am}] \\ &\quad + l_0 K_0/[(1 - l_0 - l_m) + l_m m_{Am}] + K_0/m_A \\ \beta &= [(1 - l_0 - l_m)k_1/(1 - l_0 - l_m) \\ &\quad + l_m m_{Am})] \cdot K_0/m_A \\ &(k_{1org} = 0).\end{aligned}$$

Corresponding to the last entry in Table 1 ($l_0 = 0.2$) the surfactant hold up, l_m, assuming all of it to have formed micelles is around 0.01 and the value of the distribution coefficient of ester with respect to the micellar phase, m_{Am}, as deduced from independent rate measurements, is around 1500. Using eq. (3) and the above values, $\phi_{A,th}$ is computed to be 11.40. On a more realistic basis, assuming, say 50% of the surfactant to be available for micelle formation, the value of $\phi_{A,th}$ obtained is 11.33 as compared to the value entered in Table 1, i.e. 11.25. Thus micelles affect the rate enhancement to a negligible extent when a second emulsified liquid phase is present.

Thus, it has been shown that accumulation of the ester in the emulsified phase is significant and the general solution [eq. (I.20) or (I.20a)] ought to be used for predicting the theoretical values of the specific rate of reaction.

Furthermore, if the bulk concentration of A is non-zero for the base case, the additional transfer of solute into the bulk via the emulsified second liquid phase raises the bulk concentration level of solute A. This has been demonstrated by making suitable modifications in the theory, presented in the first part of this study, and subsequent application to the analysis of experimental data on PB hydrolysis.

It has also been shown rigorously, that micelles, that may form due to the dissolution of some of the emulsifier in the continuous phase, do not affect the rate significantly in the presence of the emulsified second liquid phase.

(II) *Absorption of isobutylene, but-1-ene and propylene, respectively, into emulsions of chlorobenzene in aqueous solutions of sulfuric acid.* The experimentally observed enhancement factors for the specific rates of absorption with respect to the rates in only sulfuric acid were first reported by Mehra and Sharma (1985) for the above systems, along with a simple model based on the film theory. The theoretical expression used for correlating the rate data was essentially eq. (I.26).

Tables 4, 5 and 6 show some typical results. The extent of enhancement decreases sharply with an increase in sulfuric acid concentration which results in a marked increase in the rate constant for the reaction between the dissolved gas and sulfuric acid (Gehlawat and Sharma, 1968; Sankholkar, 1974; Deckwer, 1977). Other relevant observations have also been reported in the earlier communication (Mehra and Sharma, 1985).

Table 5. Enhancement factors for the absorption of isobutylene into emulsions of chlorobenzene in aqueous solutions of sulfuric acid in a mechanically agitated contactor

l_0 (v/v)	$\phi_{A,\mathrm{exp}}$	$\phi_{A,\mathrm{th}}$
0.025	1.8	1.8
0.05	3.2	2.3
0.10	5.0	3.0

$T = 300$ K, $P = 1.0132 \times 10^5$ Pa, speed of stirring $= 41.6$ rps, $\underline{a} = 1800$ m^2/m^3 tot., $V = 2 \times 10^{-4}$ m^3, $k_L = 1 \times 10^{-4}$ m/s, $[B_0] = 5.28$ kmol/m^3, $l_G \approx 40\%$ (v/v), Other data as in Table 4.

In order to apply the general theory developed in the first part of this study we need to know the relevant parameters, as has been outlined above for the case of hydrolysis studies.

A microscopic examination of emulsion samples revealed the size range of the droplets to be 1–12 μm when ethoxylated lauryl alcohol (6 moles of ethylene oxide per mole of alcohol) was used as emulsifier for the low acid strengths (used for isobutylene absorption) and just below 1 μm for the high acid strengths where dimethyl cocoamine was used as the emulsifying agent (used for but-1-ene and propylene absorption).

The contact time may be calculated as 4.79 s, for say entry 2, Table 4. Condition (I.11) is satisfied, i.e.

$$\underset{(2\ \mu\mathrm{m})}{d_p} \ll \underset{(296\ \mu\mathrm{m})}{4\sqrt{D_A t_c}}.$$

Table 4. Enhancement factors for the absorption of isobutylene into emulsions of chlorobenzene in aqueous sulfuric acid

$[B_0]$ [%w/w (kmol/m^3)]	l_0 (v/v)	$[S]$ (%w/w)†	R_A (kmol/m^2 s) $\times 10^7$	$\phi_{A,\mathrm{exp}}$	$\phi_{A,\mathrm{th}}$	$\phi_{A,\mathrm{L}}$
39.6 (5.28)	0.0	0.0	0.374	—	—	—
$k_1 = 0.321$ s^{-1}	0.01	0.08	0.791	2.11	2.85	2.94
	0.05	0.38	2.161	5.78	6.10	6.28
	0.20	0.47	4.110	11.00	12.10	12.45
42.0 (5.68)	0.0	0.0	0.614	—	—	—
$k_1 = 1.45$ s^{-1}	0.20	0.47	5.138	8.38	7.03	7.25
46.9 (6.53)	0.0	0.0	1.078	—	—	—
$k_1 = 4.86$ s^{-1}	0.05	0.37	2.029	1.88	2.19	2.26
	0.10	0.45	3.577	3.32	2.96	3.06
	0.20	0.45	5.660	5.25	3.96	4.22
49.5 (7.01)	0.0	0.0	1.700	—	—	—
$k_1 = 13$ s^{-1}	0.10	0.43	4.248	2.50	1.94	2.01
	0.20	0.44	6.576	3.87	2.59	2.69
55.4 (8.16)	0.0	0.0	3.485	—	—	—
$k_1 = 61$ s^{-1}	0.2	0.55	7.150	2.05	1.4	1.45

†Of total liquid phase.

$T = 300$ K, $P = 1.0132 \times 10^5$ Pa, speed of stirring $= 1$ rps, $a = 59.8 \times 10^{-4}$ m^2 (cell dia $= 92$ mm), $V = 2 \times 10^{-4}$ m^3, $k_{L,39.6\%} = 1.74 \times 10^{-5}$ m/s, $D_{A,39.6\%} = 1.14 \times 10^{-9}$ m^2/s, $[A^*] = 1.546 \times 10^{-3}$ kmol/m^3, $m_A = 1617 \dfrac{\text{kmol/m}^3\ \text{mic.}}{\text{kmol/m}^3\ \text{cont.}}$, $d_p = 2\ \mu$m.

Table 6. Enhancement factors for the absorption of but-1-ene into emulsions of chlorobenzene in aqueous solutions of sulfuric acid

$[B_0]$ [% w/w (kmol/m^3)]	l_0 (v/v)	$[S]$ (% w/w)†	R_A (kmol/m^2 s) × 10^7	$\phi_{A,\mathrm{exp}}$	$\phi_{A,\mathrm{th1}}$	$\phi_{A,\mathrm{th2}}$
65.5 (10.2)	0.0	0.0	0.152	—	—	—
$k^{\ddagger}_{1,1} = 0.248\ \mathrm{s}^{-1}$	0.02	0.24	1.111	7.29	7.92	—
	0.05	0.39	1.875	12.31	12.43	—
	0.10	0.48	2.739	17.98	17.51	—
	0.20	0.50	3.914	25.68	21.00	—
70.5 (11.5)	0.0	0.0	0.548	—	—	—
$k_{1,1} = 3.52\ \mathrm{s}^{-1}$	0.2	0.48	4.567	8.33	5.30	6.89
$k_{1,2} = 0.88\ \mathrm{s}^{-1}$						
73.8 (12.53)	0.0	0.0	1.133	—	—	—
$k_{1,1} = 22.94\ \mathrm{s}^{-1}$	0.2	0.47	5.034	4.44	2.24	3.04
$k_{1,2} = 5.76\ \mathrm{s}^{-1}$						
77.0 (13.43)	0.0	0.0	2.719	—	—	—
$k_{1,1} = 149.3\ \mathrm{s}^{-1}$	0.2	0.46	5.228	1.92	1.16	1.42
$k_{1,2} = 37.3\ \mathrm{s}^{-1}$						

†Of total liquid phase.

‡Value determined by extrapolating from other values of k_1 at higher concentrations.

$T = 300$ K, $P = 1.0132 \times 10^5$ Pa, speed of stirring = 1 rps, $a \doteq 59.8 \times 10^{-4}\ \mathrm{m}^2$ (cell dia = 92 mm), $V = 2 \times 10^{-4}\ \mathrm{m}^3$, $k_{\mathrm{L},65\%} = 1.267 \times 10^{-5}$ m/s, $D_{A,65\%} = 6.19 \times 10^{-10}\ \mathrm{m}^2/\mathrm{s}$, $[A^*]_1 = 1.33 \times 10^{-3}\ \mathrm{kmol/m}^3$, $[A^*]_2 = 0.665 \times 10^{-3}\ \mathrm{kmol/m}^3$, $m_{A1} = 2014$ (kmol/m^3 mic.)/(kmol/m^3 cont.), $m_{A2} = 1007$ (kmol/m^3 mic.)/kmol/m^3 cont.), $d_\mathrm{p} = 0.8\ \mu$m.

A droplet size of 2 μm gives,

$$K_0 = \frac{12 D_A}{d_\mathrm{p}^2} = 3420\ \mathrm{s}^{-1} \quad \text{[eq. (I.10)]}.$$

Since no reaction can occur in the emulsified phase, as the H^+ ion cannot enter chlorobenzene, $k_{1\mathrm{org}}$ is set to zero. The calculated D_p value is, from Stokes–Einstein equation (Dickinson, 1985) about $1 \times 10^{-13}\ \mathrm{m}^2/\mathrm{s}$.

The relative solubility, m_A, values may be approximated by the ratio of the solubilities of the solute gas in the emulsified phase (chlorobenzene) to that in the aqueous acid phase (Glasstone, 1956). With respect to water (instead of acid) the m_A values are 539, 671 and 132 kmol/m^3 mic./m^3 aq. for isobutylene, but-1-ene and propylene, respectively (the last value for propylene has been revised as compared to our earlier reported one of 98 (Mehra and Sharma, 1985) since the present value of solubility of propylene in water, on whose basis the m_A value is calculated, has been taken from Tiwari (1976) and is consistent with the experimental diffusivity data provided by him which also has been used in this work. Also, some of the sources of these physico-chemical data have been provided therein.) However, the estimation of m_A values for acid solutions is somewhat problematic since the salting in/out behaviour of aqueous solutions of sulfuric acid at high acid concentrations is reasonably complex. Sankholkar (1974), Tiwari (1976), Gehlawat and Sharma (1968) and Deckwer (1976, 1977) have all used the logarithmic relationship as given by

$$\log_{10} \frac{[A^*]}{[A^*]_\mathrm{w}} = k_s I_s \tag{4}$$

to estimate the solubility values in aqueous solutions of sulfuric acid as a function of its ionic strength, where k_s values were estimated from low acid strength (negligible reaction) solubility measurements. However, Friedrich *et al.* (1981) have shown that for a variety of gases, the estimation of solubility in aqueous solutions of sulfuric acid, eq. (10) can be applied only till a strength of about 4 kmol/m^3 ($\sim$ 30% w/w). Beyond this concentration till about an acid concentration of 7 kmol/m^3 ($\sim$ 50% w/w) the solubility remains essentially constant, at a level of about one-third of that in water. Sanders (1985) suggests that salting in effects begin to occur after this limit ($\sim$ 60% w/w) and at substantially high acid concentrations the solubility values may even exceed those in water in a marked way. Therefore, using the hypothesis offerred by Friedrich *et al.* the m_A value for isobutylene may be estimated as 1617 and is expected to remain independent of the acid concentration, for the range of acid concentration covered.

Condition (I.19) is satisfied, i.e.

$$\frac{D_\mathrm{p}}{D_A} \ll \frac{l_0 K_0 t_\mathrm{c}}{(1 - l_0) m_A} \qquad (\text{for } l_0 = 0.01)$$

$$(9 \times 10^{-5}) \quad (0.1) \quad \text{and}$$

$$\frac{K_0 t_\mathrm{c}}{m_A} = 10 \qquad (\text{condition I.34})$$

which is greater than 1. Therefore we may use eq. (I.29) [or equivalently eq. (I.29a)] to compute the theoretical values of the specific absorption rates in the presence of the microphase. The column marked $\phi_{A,\mathrm{L}}$ in Table 4 shows enhancement factors calculated on the basis of the above rates. Enhancement factors shown in the column marked $\phi_{A,\mathrm{th}}$ have been computed on the basis of the more general eq. (I.20) [or equivalently eq. (I.20a)]. Notice that the values in both the columns are only marginally different from each other.

It can be seen from Table 4 that the predicted and the experimentally observed values for the enhancement factor, in the specific rate of absorption (ratio of specific rates in presence of microphase to that in its absence) for isobutylene agree reasonably well, at least for the lower acid concentrations.

It is necessary to point out that the values of the pseudo first order rate constant, k_1, as reported in Table 4 are different from those indicated in Table 1 of our earlier communication (Mehra and Sharma, 1985) and reported by Gehlawat and Sharma (1968) and Deckwer (1977) because of the different solubility value for isobutylene, used by us, in aqueous sulfuric acid solutions. In fact, it can be shown that using the conventional salting out relationship used by the earlier investigators [eq. (4)] the theoretical values of the specific rates of absorption, in the presence of the emulsified phase, are considerably under-predicted.

The k_1 values were computed, as usual, from the base rates [eq. (I.18)].

Table 5 shows the results for isobutylene absorption in a mechanically agitated contactor. The purpose of these runs was to study the effect of k_L on the enhancement factor. The theoretical values of the enhancement factor; $\phi_{A,\mathrm{th}}$ have been computed assuming reasonable k_L and $\underline{a}$ values subject to the constraint that the base case rate value is satisfied. At large k_L and $\underline{a}$ values the base case rate is expected to lie in between the slow and the fast reaction regimes. Therefore, eq. (A6) has been used for computing the specific absorption rates. The predicted values of the enhancement factor, ϕ_A in Table 5, are somewhat lower than the experimental ones, partly due to the approximations in the calculations and partly due to the effect of the emulsifier on the surface tension and hence on the gas–liquid area.

For the case of but-1-ene and propylene absorption, the probelm of solubility estimation becomes more complicated since the salting-in data at high acid concentrations are not available. Tables 6 and 7 show a comparison between the experimental and predicted values [eq. (I.20) was used] of the enhancement factor for each of the above gases, respectively. $\phi_{A,\mathrm{th1}}$ is calculated on the assumption that the solubility remains constant at about one-third of that in water, as was the case for isobutylene. It can be seen that the agreement is poor between $\phi_{A,\mathrm{exp}}$ and $\phi_{A,\mathrm{th1}}$ for the higher acid concentrations. If a salting-in error of 100% is assumed (i.e. the value of solubility doubled and that of m_A halved, for these acid strengths) the agreement is improved as indicated by the column marked $\phi_{A,\mathrm{th2}}$.

The ratio of the specific rates of absorption of but-1-ene to propylene in identical strengths of sulfuric acid, in the presence of the emulsified liquid, phase, is predicted fairly well from theory (compare equivalent entries from Tables 6 and 7).

The rate constants have been computed from the base rates [eq. (I.18)], as for the previous analyses and the values are different from those reported earlier (Mehra and Sharma, 1985) on account of the different solubility values. The rate constant value for 65% acid for but-1-ene is only approximate since the system lies almost completely in the mass transfer controlled regime. A value may, however, be estimated from the limiting conditions for this regime (the actual value does not affect the rate in the presence or absence of the microphase as it is too small to contribute significantly).

Thus a more rigorous and conceptually sound reanalysis of the experimental data published earlier (Mehra and Sharma, 1985) has been presented. The variation of the enhancement factor with acid strength, i.e. rate constant, can be explained more clearly unlike as in our earlier work wherein it was tentatively stated to be due to variation in K_0 due to small changes in microdroplet size.

It has also been shown that for the conditions obtained in the above absorption studies it is possible to use the simpler forms of rate equations [eqs (I.29) or (I.29a)] which indicate that accumulation of the solute A in the microphase is significant and hence steady state models should not be applied.

The applicability of the theory, developed in the first

Table 7. Enhancement factors for the absorption of propylene into emulsions of chlorobenzene in aqueous solutions of sulfuric acid

$[B_0]$ [% w/w (kmol/m^3)]	l_0 (v/v)	$[S]$ (w/w)$^+$	R_A (kmol/m^2 s) $\times 10^7$	$\phi_{A,\mathrm{exp}}$	$\phi_{A,\mathrm{th1}}$	$\phi_{A,\mathrm{th2}}$
73.8 (12.53)	0.0	0.0	0.971	—	—	—
$k_{1,1} = 14.55\ \mathrm{s}^{-1}$	0.20	0.47	2.265	2.33	1.44	1.86
$k_{1,2} = 3.63\ \mathrm{s}^{-1}$						
77.0 (13.43)	0.0	0.0	1.618	—	—	—
$k_{1,1} = 83.76\ \mathrm{s}^{-1}$	0.20	0.46	2.470	1.53	1.06	1.26
$k_{1,2} = 20.90\ \mathrm{s}^{-1}$						

$^+$Of total liquid phase.

$T = 300$ K, $P = 1.0132 \times 10^5$ Pa, speed of stirring = 1 rps, $a = 59.8 \times 10^{-4}\ \mathrm{m}^2$ (cell dia = 92 mm); $V = 2 \times 10^{-4}\ \mathrm{m}^3$, $k_{L,73.8\%} = 8.67 \times 10^{-6}$ m/s, $D_{A,73.8\%} = 2.82 \times 10^{-10}\ \mathrm{m}^2/\mathrm{s}$, $[A^*]_1 = 1.516 \times 10^{-3}\ \mathrm{kmol/m}^3$, $m_{A,1} = 396$ (kmol/m^3 mic.)/(kmol/m^3 cont.), $[A^*]_2 = 0.758 \times 10^{-3}\ \mathrm{kmol/m}^3$, $m_{A,2} = 198$ (kmol/m^3 mic.)/(kmol/m^3 cont.), $d_p = 0.8\ \mu$m.

part of this study, has been demonstrated for higher mass transfer coefficient and gas–liquid interfacial area values, as encountered in a mechanically agitated contactor.

Microemulsions/swollen micelles/micelles

(I) *Alkaline hydrolysis of 2,4-DCPB in microemulsion/micellar media.* Table 8 presents some typical results for the hydrolysis of 2,4-DCPB in varieties of formulations.

Experimental data clearly show that the rate of reaction goes up substantially with the suggested strategy of using microemulsions, solutions of swollen micelles and surfactant (micellar solutions), respectively.

The extent of enhancement increases with an increase in the hold-up of any of the constituents—surfactant, co-surfactant or oil.

The difference in the specific reaction rate for a true microemulsion formulation and its corresponding swollen micellar (i.e. no chlorobenzene) solution was marginal.

Dissolved isopropanol (co-surfactant) to the extent of 5% did not affect the specific rates of reaction.

While formulating the microemulsions isopropanol was found to be a more efficient co-surfactant, as compared to *n*-propanol, since it was required in lesser quantity for 'solubilizing' the same amount of oil (chlorobenzene). Similarly cyclohexane was a 'better' oil compared to chlorobenzene since it required less of surfactant plus co-surfactant in order to be 'solubilized'.

Before considering a systematic application of theory to the above system it is necessary to focus on some special characteristics of the formulations used here.

Microemulsions and micellar (including swollen ones) solutions are inherently different from microdispersions in that they are thermodynamically stable and usually transparent to light. The dispersed phase consists of small droplets with diameters in the range of 10 to 100 nm (Holt, 1980). However, on account of these dispersed phase 'packets' being of a macromolecular size and dynamic character (i.e. a fraction of their constituents are constantly being exchanged with the surrounding continuous medium) having lifetimes over milliseconds (Armstrong, 1985; Aniansson, 1985; this means that complete redistribution of micellar material can occur in a millisecond time scale: the average residence time of a monomer in the micelle on the other hand, is of the order of nano- to microseconds) they are more appropriately referred to as a pseudophase (Romsted, 1984).

In spite of the above mentioned thermodynamic and structural pecularities the concepts of a distribution coefficient, m_A (for a solute A), between the continuous and dispersed phases as well as that of micellar rate constants have been used along with the pseudophase approximation with considerable success (Mittal and Lindman, 1984). However, no worthwhile methods for predicting the solubilizing power of given formulation exist in the literature.

The situation is complicated by the structural changes that occur in the system as a function of concentrations of any of the constituents. This is reflected in the change in m_A upon increasing the microphase hold-up. Experimental measurements of m_A were made by determining the total amount of ester solubilized by a media, prepared by using an aqueous solution of KCl (the ionic strength being equivalent to that of KOH) as the continuous phase and then using eq. (1) for computing m_A. The total ester amount

Table 8. Enhancement factors for the alkaline hydrolysis of 2,4-dichlorophenyl benzoate in microemulsions and micellar media

l_0 (v/v)	Surfactant (v/v %)	Co-surf. / surf. ratio (volumetric)	Oil (v/v %)	R_A (kmol/m^2 s) $\times 10^9$	$\phi_{A,\mathrm{exp}}$	$m_{A,\mathrm{exp}}$	$k_{1\mathrm{org,calc}}$ (s^{-1})
0.025	2.5	—	—	4.80	6.9	7590	0.02
0.050	5.0	—	—	9.03	13.0	6335	0.24
0.100	10.0	—	—	15.10	21.75	4015	0.71
0.090	3.3	1.50	0.75	9.83	14.15	2270	0.56
0.083	3.3	1.50	—	9.20	13.25	2285	0.53
0.1125	4.5	1.50	—	11.88	17.10	1970	0.81
0.150	6.0	1.50	—	15.70	22.60	1625	1.37
0.1580	4.3	2.32	1.5	20.43	29.4	1585	2.36
0.0997	4.3	2.32	—	12.37	17.8	1905	1.07
0.1430	4.3	2.32	—	17.93	25.8	1615	1.94
0.1825	5.5	2.32	—	20.10	28.9	1445	2.15
0.150	4.0	2.50†	1.0	19.10	27.5	—	—
0.140	4.0	2.50	—	18.07	26.0	—	—
0.162	4.2	2.14	3.0‡	18.34	26.4	—	—
0.132	4.2	2.14	—	17.03	24.5	—	—

†*n*-Propanol.

‡Cyclohexane.

Speed of stirring = 20 rps, $T = 301$ K, surfactant = lauryl alcohol (7 moles ethylene oxide per mole of alcohol), co-surfactant = isopropanol, oil = chlorobenzene, Other physico-chemical data as in Table 1.

solubilized was determined spectrophotometrically as well as by the loss of weight method. Whatever isopropanol (co-surfactant) may have partitioned into the continuous phase did not effect any physicochemical parameter (e.g. solubility), as is borne out by the lack of a significant effect on the specific rate (base case) due to just dissolved alcohol. Also, for ethoxylated C_{12} alcohols the CMC values are so small (9.0×10^{-5} M at 25°C; Fendler and Fendler, 1975) so as to be negligible compared to the total concentration of the surfactant used. Therefore the amount of surfactant existing in monomer dissolved form may always be neglected and all of it presumed to exist in micellar form. It is likely that the excess uptake of A is due to the solubilization capacity of the micellar aggregates.

The m_A value is indeed found to decrease with an increase in the microphase hold up, implying possibly that structural changes occurring due to higher concentrations of microphase (Nilsson *et al.*, 1984) may be responsible for the lower solubilizing power at higher hold-ups.

Preliminary calculations, assuming that no reaction occurs within the microphase, indicate that the solubilizing power of these formulations is unable to account for the observed enhancements in the specific hydrolysis rates. This probably implies that the micellar phase allows within itself the reaction of the ester with the hydroxyl group as has been reported by other investigators (Janakiraman, 1984; Bhagwat and Sharma, 1986) for the system 2,4-DCPB/OH^- with sodium lauryl sulfate (SLS) micelles. Bhagwat and Sharma (1988) have suggested a unique structure for micellar solubilization/reaction, wherein the $> C{=}O$ bond in the ester, on account of being polar in nature projects out of the micellar structure, the residual ester molecule residing in the relatively non-polar core of the micelle. Sviridov *et al.* (1985) have also made this assumption in their studies on ester hydrolysis. The projected $> C{=}O$ bond thus becomes available for attack by the OH^- ions situated in the aqueous phase.

This argument can be extended to the non-ionic, lauryl alcohol ethoxylate (LAE/7EO) used for the hydrolysis studies. The structure of the non-ionic micelle (including swollen ones) can be taken to consist of a hydrophobic interior (core) comprising the non-polar lauryl alcohol groups with the polar ethoxylate chains constituting a 'loose' exterior (Sorensen, 1984). It is likely that water penetration (along with some amount of the other ionic species present) into the exterior part of the micelle will be significant whereas there will be none into the micelle interior (Nilsson *et al.*, 1984). On account of the polarity of the $> C{=}O$ bond in the ester it is likely to project itself into the ethoxylated chain exterior of the micelle where it is prone to attack by the hydroxyl ion, whereas the bulk of the ester molecule is expected to reside in the hydrophobic micelle interior (Warr *et al.*, 1984). The orientation of $> C = O$ bond at the interior–exterior micelle 'boundary' has an interesting implication. The intrinsic value of the micellar rate constant may be remarkably higher than that in the aqueous phase, on account of the larger number of successful collisions between the reactive molecules, due to the projecting nature of the $> C{=}O$ bond. The overall micellar rate constant will be a function of the OH^- concentrations in the micellar exterior (m_B), the total ester solubilized per unit amount of microphase (m_A) and the micellar surface area per unit amount of microphase (a_m). Therefore, we can write:

$$k_{ov} = f(k_{2,\mathrm{int}}, m_B, m_A, a_m). \qquad (6)$$

As a first approximation, using a pseudo first order assumption for the micellar rate constant, we may write, as per form given in eq. (I.2a)

$$k_{ov} = m_A k_{1\mathrm{org}} = m_A k_{2,\mathrm{int}}(a_m)(m_B \cdot [B_0]). \qquad (6)$$

The micellar rate constant value cannot be determined *a priori*. However, it is possible to calculate a value for $k_{1\mathrm{org}}$ from the rate data. Assuming a microdroplet size of 100 nm, K_0 [eq. (I.10)] is calculated as $7.0 \times 10^5\ s^{-1}$. D_p is of the order of $1.0 \times 10^{-12}\ m^2/s$ and condition (I.19) can be shown to hold simply due to the large value of K_0. Also K_0/m_A is likely to be much greater than the calculated values of $k_{1\mathrm{org}}$ (condition I.22) and can be checked later. Therefore, eq. (I.29) [or (I.29a)] may be used for the calculation of $k_{1\mathrm{org}}$ from the experimentally observed enhancements. Table 8 shows that $k_{1\mathrm{org}}$ values increase with an increase in the microphase hold-up for both micellar and as well as swollen micellar formulations. It may also be seen that addition of co-surfactant leads to a reduction in the m_A value but increase in the value of $k_{1\mathrm{org}}$.

The effect of the co-surfactant in reducing the m_A value may partly be due to the fact that isopropanol is a poorer solvent for 2,4-DCPB compared to bulk (liquid) surfactant. The m_A value of 2,4-DCPB isopropanol/water is only 1085 whereas it is 7615 between LAE7EO/water (ratio of respective solubilities). The increase in $k_{1\mathrm{org}}$ upon addition of isopropanol, may similarly be due to the increased accessibility of the hydroxyl group for the micelle exterior on account of isopropanol being reasonably polar. However, structural aspects may also be very significant in producing the observed effects, as has been discussed below.

Nilsson *et al.* (1984) have shown that the aggregation number (size) of these ethoxylated non-ionic micelles can vary in either direction with a change in the surfactant concentration. Bhagwat and Sharma (1988) have also demonstrated that the aggregation number for SLS micelles upon the addition of *n*-butanol (co-surfactant), decreases the aggregation number. It can be shown by an approximate geometric calculation that the reduction in m_A values and increase in $k_{1\mathrm{org}}$ is consistent with the assumption of a reduction in the aggregation number with increase in the hold-up for a micellar system. Consider the hydrophobic lauryl alcohol heads to be represented by small spheres (diameter d) which lie on a hypothetical spherical surface the diameter of which is equal to the micelle interior diameter (D). If the projected area of the small spheres completely covers the larger spherical surface, i.e. $d/D \ll 1$, then the void volume inside the micelle interior per unit amount of surfactant (or equivalently per monomer molecule) is given by,

$$\frac{V_{\text{void}}}{n} = \frac{\pi d^3}{6}\left(\frac{n^{1/2}}{8} - \frac{1}{2}\right) \tag{7}$$

where n is aggregation number (number of monomers per micelle). A decrease in the aggregation number, n decreases the V_{void}/n which is one of the measures of the solubilization power of the micelle, i.e. m_A. It also implies a smaller micelle size and hence larger area (a_m) per unit amount of surfactant. This argument may be easily extended to the case of swollen micelle, at least qualitatively, since the isopropanol residing in the micellar phase is expected to lie largely in the micelle exterior and hence will influence the interior–exterior micelle boundary only to a limited extent (the basis for reporting m_A values for swollen micellar and microemulsion formulations is per unit volume of microphase, i.e. total of the constituent volumes. Therefore even though on a volumetric basis different m_A values can be compared, they are not reducible to a per monomer basis as was possible for (non-swollen) micellar systems).

Apparently the effect of the oil phase on the rates, m_A values and the micellar rate constant, $k_{1\text{org}}$ is somewhat similar to that of co-surfactant, but on account of being not as polar as isopropanol, these effects are likely to be only due to size/structural changes in the microphase.

Condition (I.22) can now be checked:

$$K_0/m_A \gg k_{1\text{org}}$$

for all entries in Table 8. Therefore eqs (I.29) or (I.29a) hold. The product,

$$k_1'' t_c = 0.16\text{–}18.3 \quad [\text{condition (I.30)}]$$

which implies that for some cases, solubilization as well as micellar reaction are contributing to the enhancement in the specific rate of reaction.

In order to calculate the theoretical value of the specific rate of absorption using, say, eq. (I.29) the exact distribution of B between the continuous and microphase need not be known since,

$$l_0 m_A \gg (1 - l_0) \quad \text{and}$$

$$l_0 m_A k_{1\text{org}} \gg (1 - l_0) k_1.$$

Therefore,

$$k_1'' = \frac{(1 - l_0)k_1 + l_0 k_{1\text{org}} m_A}{(1 - l_0) + l_0 m_A} \approx k_{1\text{org}}$$

which may be conveniently calculated from the experimental rate data and eq. (I.29).

The significance of the theory, developed in Part I of this study, lies in the fact that none of the previously existing models in the literature could provide for accumulation as well as microphase reaction contributing simultaneously to the rate enhancement [see validity of condition (I.22)].

It has been shown that just as in the case of anionic micelles (Janakiraman, 1984; Bhagwat and Sharma, 1986), non-ionic micelles (including swollen ones) can also promote micellar reaction as well as solubilize considerable amounts of the rate limiting solute.

The possible effects of structural changes in the microphase, on the solubilization capacity (m_A) and micellar rate constant ($k_{1\text{org}}$), have also been elucidated.

(II) *Absorption of but-1-ene, propylene and isobutylene, respectively, in microemulsion/micellar media.* The formulations used in these studies were very similar to the ones discussed above except that a larger variety of formulations including some of the higher alcohols as co-surfactant were used, as has been described in the experimental section.

Some typical results are given in Table 9 along with the relevant experimental conditions.

It can be seen clearly that substantial enhancements in the specific rates of absorption are obtained when microemulsions/micellar solutions are used in place of plain sulfuric acid.

The extent of enhancement rises with an increase in the hold up of any of the dispersed constituents surfactant, co-surfactant or oil. Changes in enhancement due to addition of the oil phase into a swollen micellar solution, are in some instances, quite sharp.

For microemulsions containing identical volumetric hold ups of the (total) microphase but constituted by different co-surfactant alcohols, the enhancement factors show the following trend: 2-ethyl hexanol > n-hexanol > n-pentanol > n-butanol under the constraint that the volumetric co-surfactant/surfactant ratio is identical for all the alcohols.

It may be seen that for a fixed value of the volume ratio of the co-surfactant/surfactant the corresponding molar ratio declines with increasing number of carbon atoms on the co-surfactant alcohol. If molar ratios are conserved (i.e. volumetric ratios for the heavier alcohols made higher) and the total volumetric hold up kept constant, the enhancement factors increase even more. The highest enhancement factor was obtained for the case of the swollen micellar solution wherein 2-ethylhexanol was used as the co-surfactant.

The enhancement factors in the specific absorption rates are higher for but-1-ene than for propylene in identical formulations.

The specific rates of reaction were negligibly different whether the acid concentration was conserved on the total liquid phase or just on an aqueous phase basis.

The effect of the speed of stirring in the range 1–1.5 rps on the specific rate of absorption was found to be small (maximum 30% over the range).

For the case of n-butanol (as co-surfactant) the specific rate, in the presence of the alcohol alone, was affected only marginally. Other alcohols were relatively insoluble in the aqueous acid.

It was also noticed that at higher acid concentrations the microemulsions were easier to obtain than at lower acid strengths indicating the importance of the presence of sulfuric acid for favourable thermodynamics.

Table 9. Enhancement factors for the absorption of but-1-ene, propylene and isobutylene, respectively in microemulsions and allied micellar media

l_0 (v/v) 1	Surfactant (v/v, %) 2	Co-surfactant/ surfactant ratio (m^3/m^3) [name: co-surfactant] 3	Oil (v/v, %) 4	$R_A \times 10^7$ kmol/m^2 s 5	$\phi_{A,\mathrm{exp}}$ 6	$m_{A,\mathrm{calc}}$ 7	m_{A0} 8
Gas: but-1-ene	$k_1 = 0.1\ s^{-1}$†		$[B_0] = 10.1$ kmol/m^3				
0.035	3.5	—	—	4.313	2.63	175	$m_{A0,\mathrm{exp}} = 95$ $m_{A0,\mathrm{calc}} = 85$
0.07	7.0	—	—	7.544	4.60	280	
0.1	10.0	—	—	9.938	6.06	370	
0.03	1.5	1.0 [*n*-butanol]	—	5.773	3.52	380	$m_{A0,\mathrm{exp}} = 350$ $m_{A0,\mathrm{calc}} = 300$
0.07	3.5	1.0 "	—	10.512	6.41	560	
0.1	5.0	1.0 "	—	15.203	9.27	830	
0.08	3.5	1.0 "	1.0	14.596	8.90	980	
0.07	3.5	1.0 [2-ethyl hexanol]	—	17.876	10.90	1650	
0.1	5.0	1.0 "	—	25.584	15.60	2300	
0.08	3.5	1.0 "	1.0	22.796	13.90	2300	
0.03	1.1	1.73 ["]‡	—	12.726	7.76	1400	$m_{A0,\mathrm{exp}} = 650$ $m_{A0,\mathrm{calc}} = 750$
0.07	2.56	1.73 "	—	25.698	15.67	3390	
0.1	3.66	1.73 "	—	41.656	25.4	6350	
0.08	3.5	1.0 [*n*-pentanol]	1.0	15.252	9.3	1050	
0.08	3.5	1.0 [*n*-hexanol]	1.0	22.796	13.9	2300	
0.08	3.5	1.0 [2-ethyl hexanol]	1.0	22.796	13.9	2300	
Gas: propylene	$k_1 = 0.05\ s^{-1}$†		$[B_0] = 10.1$ kmol/m^3				
0.035	3.5	—	—	4.57	3.01	160	$m_{A0,\mathrm{exp}} = 92$ $m_{A0\cdot\mathrm{calc}} = 80$
0.07	7.0	—	—	7.068	4.65	210	
0.1	10.0	—	—	9.774	6.43	300	
0.07	3.5	1.0 [*n*-butanol]	—	9.728	6.4	400	
0.1	5.0	1.0 "	—	12.023	7.91	425	
0.08	3.5	1.0 "	1.0	12.068	7.94	580	
0.07	2.56	1.73 [2-ethyl hexanol]	—	15.276	10.05	1000	
0.1	3.66	1.73 "	—	19.532	12.85	1200	
Gas: isobutylene	$k_1 = 0.321\ s^{-1}$		$[B_0] = 5.28$ kmol/m^3				
0.1	10.0	—	—	14.010	3.77	280	
0.1	5.0	1.0 [2-ethyl hexanol]	—	27.302	7.30	1150	
0.08	3.5	1.0 [*n*-butanol]	—	12.716	3.4	300	

$R_{A\mathrm{base}}$ (butene-1) $= 1.64 \times 10^{-8}$ kmol/m^2 s
$R_{A\mathrm{base}}$ (propylene) $= 1.52 \times 10^{-8}$ kmol/m^2 s
$R_{A\mathrm{base}}$ (isobutylene) $= 3.74 \times 10^{-8}$ kmol/m^2 s
†Approximate values.
‡Equal to that of *n*-butanol on a mole basis.
$T = 300$ K, $P = 1.0132 \times 10^5$ Pa, speed of stirring = 1 rps, $a = 59.8 \times 10^{-4}\ m^2$, $V = 1 \times 10^{-4}\ m^3$, typical $k_L = 1.2 \times 10^{-5}$ m/s.

For example, to get a swollen micellar solution in water instead of sulfuric acid was not possible in cases where higher alcohols were used as co-surfactants or when an oil phase (chlorobenzene) was to be 'solubilized'.

Determination of m_A, *a priori*, for the various formulations, was not possible on account of the solubilizate being a gas, the liquid phase containing components like the surfactant and the electrolytic behaviour of sulfuric acid being extremely difficult to simulate experimentally. However, the solubility of the various gases in bulk surfactant (LAE/7EO is a liquid at room temperature) and mixtures of surfactant plus co-surfactant with and without oil, respectively, was estimated by dead end absorption. From this a relative solubility value, m_{A0}, can be calculated, the solubility of the relevant gas in aqueous acid being known.

Furthermore, reaction is unlikely to occur in the microphase since the site of solubilization of these gases is expected to lie within the non-polar hydrophobic interior of the micelle where the H^+ ion has no access to it. Even assuming that some H^+ ions could get into the micelle interior, especially for the case of swollen micelles, the intrinsic rate constant value is expected to be extremely low since the rate constant varies exponentially with the acidity (Gehlawat and Sharma, 1968; Sankholkar, 1974; Deckwer, 1977). The changes in enhancement factor upon changing to a higher alcohol co-surfactant were quite marked and this was also the case when chlorobenzene was used. This indicates the dominating influence of the solubilization capacity of the microphase constituents. The absence of micellar reaction may also be supported by the fact that different conservation strategies for acid strength did not affect the absorption rate significantly, in the presence of the microphase, since even small changes in acid concentration should have produced large changes in the value of even the micellar rate constant (exponential variation).

Thus under the assumption of $k_{1\mathrm{org}} = 0$ condition (I.34) becomes,

$$t_c K_0 / m_A \gg 1$$

and eqs (I.29) and (I.29a) are valid. For the higher hold-ups of the microphase when the converse of condition (I.30) is always likely to be satisfied eq. (I.32) can be used. The rate is dependent upon the mass transfer coefficient and this is experimentally supported. Also under such conditions, changes in k_1 occurring due to changes in acid strength (because of different conservation strategies) will not affect the specific rate as eq. (I.32) indicates.

Using the general eqs (I.29) or (I.29a) (since for all cases eq. (I.32) does not apply) the m_A values may be back calculated from the rate data since they cannot be determined *a priori*. A plot of m_A vs hold up, l_0, when extrapolated to zero hold up gives m_A values which match closely with the m_{A0} values determined by the dead end absorption technique. Table 9 displays this information. The variation of m_A values with the hold up of the microphase is probably on account of structural reasons generally discussed in the section on hydrolysis studies. An increase in the aggregation number with increasing hold up can explain the increase in m_A value (note that this trend is reverse of what was expected in the alkaline medium of the hydrolysis studies).

The greater solubilizing power of the formulations where higher alcohols were used is on account of their greater lipophilicity and thus larger affinities for the solubilizate A, as compared to those containing lower alcohols. The differences in the enhancement factors for but-1-ene and propylene are also to be expected since these gases will display different affinities for the microphase, as has been shown in the section on macroemulsions also.

The solubilizing power of these thermodynamically stable formulations is larger than that of macroemulsions, as is reflected in the respective m_A values.

The validity and implications of the simplest form of the rate expression [eq. (I.32)] when only solubilization by the microphase is significant, have been brought out in a more comprehensive way, than the previously existing studies, including the effect of the continuous phase rate constant on the rate enhancement.

CONCLUSIONS

The specific rates of mass transfer accompanied by slow or fast reactions, in gas–liquid and solid–liquid systems, can increase markedly in the presence of 'emulsified' droplets of a second liquid phase which shows a relatively high solubility for the sparingly soluble solute. This is also true of microemulsions and allied micellar media, where, in addition, reaction may also occur within the microphase. Enhancements ranging from 2–25 have been realised for the systems studied herein.

The theory developed in Part I of this study, when applied to the typical gas–liquid and solid–liquid systems (with additional emulsified liquid phase) studied here, predicted values for the rate enhancement, which agreed well with the experimental values.

The enhancement in specific rates in microemulsions and allied micellar media can be successfully correlated using the pseudo heterogeneous approximation along with the theory developed in Part I of this study.

For the cases analysed here, the film theory should not be applied as accumulation in the microphase is a significant phenomena. This is clearly brought out during the course of analysis of the experimental data. The film theory of mass transfer is applicable under restrictive conditions as outlined in the first part of this study. Danckwerts' surface renewal theory offers computational advantages over Higbie's penetration theory, as can be seen from the respective rate expressions presented in Part I and those presented here.

NOTATION

A	solute A (gas or solid)
$[A]$	concentration of A in continuous phase, kmol/m^3 cont.
$[A^*]$	solubility of A in continuous phase, kmol/m^3 cont.
$[A_L]$	concentration of A in the microphase on an equivalent continuous phase basis, kmol/m^3 cont.
$[A_b]$	concentration of A in bulk continuous phase, kmol/m^3 cont.
$[A_{bm}]$	concentration of A in bulk continuous phase in presence of emulsified phase, kmol/m^3 cont.
a	gas–liquid interfacial area, m^2
$\underline{a}$	specific gas–liquid interfacial area, m^2/m^3 tot.
a_m	micelle interfacial area, m^2/m^3 micl.
a_{LL}	liquid–microphase interfacial area, m^2/m^3 mic.
$[B]$	concentration of liquid phase reactant B in continuous phase, kmol/m^3 cont.
$[B_0]$	concentration of liquid phase reactant in bulk continuous phase, kmol/m^3 cont.
C	constant defined in eq. (A11), s
D	diameter of a interior–exterior micelle boundary, nm
D_0	constant defined in eq. (A11), dimensionless
D_A	diffusivity of A in continuous phase, m^2/s
D_p	microdroplet/particle diffusivity in continuous phase, m^2/s
d	diameter of non polar head group on surfactant, nm
d_p	microphase droplet/particle size, μm
h_e	height of penetration element, m
I	constant defined in eq. (I.20), s$^{-1/2}$

I'	constant defined in eq. (A6), $s^{-1/2}$
I_1	constant defined in eq. (I.20a), $s^{-1/2}$
I'_1	constant defined in eq. (A7), $s^{-1/2}$
I_s	ionic strength of electrolytes, $kmol/m^3$
k_1	pseudo first order rate constant for reaction $A + zB \rightarrow$ Products, in continuous phase, s^{-1}
k''_1	modified first order rate constant, eq. (I.29), s^{-1}
k_2	second order rate constant, $m^3/kmol\ s$
k_L	mass transfer coefficient (gas–liquid or solid–liquid, liquid–side), m/s
K_0	transport coefficient in continuous phase, s^{-1}
k_{1org}	pseudo first order rate constant for reaction of A in microphase, s^{-1}
k_{ov}	overall first order rate constant, s^{-1}
k_s	salting out parameter for solubility, $m^3/kmol$ (ion)
l_G	volumetric hold-up of gas phase, m^3/m^3 disp.
l_m	volumetric hold-up of micellar phase, m^3/m^3 tot.
l_0	volumetric hold-up of microphase, m^3 mic/m^3 tot.
m_A	distribution coefficient of A between microphase and continuous phase, ($kmol/m^3$ mic.)/$kmol/m^3$ cont.)
m_{A0}	distribution coefficient of A between microphase and continuous phase extrapolated to zero microphase hold-up ($kmol/m^3$ mic.)/($kmol/m^3$ cont.)
m_B	distribution coefficient of B between microphase and continuous phase, (kmol/m^3 mic.)/($kmol/m^3$ cont.)
m_{Am}	distribution coefficient of A between micelles and continuous phase ($kmol/m^3$ micl.)/($kmol/m^3$ cont.)
n	aggregation number for micelle, i.e. monomers per micelle, dimensionless
R_A	specific rate of absorption of A, $kmol/m^2\ s$
S	surface renewal frequency, s^{-1}
$[S]$	surfactant concentration, % (w/w)
T	temperature, K
t	time, s
t_B	batch time, s
t_c	contact time for penetration element; Higbie's model, s
u	dummy variable appearing in eq. (I.20), s
V	total volume of continuous plus microphase, m^3 tot.
V_{void}	void volume inside a micelle, nm^3
w	constant defined in eq. (I.20), s^{-1}
w_1	constant defined in eq. (A10), s
x	distance from gas–liquid interface, m

Greek symbols

α	constant defined in eq. (I.20), s^{-1}
β	constant defined in eq. (I.20), s^{-2}
γ	constant defined in eq. (I.20), s^{-1}
δ	constant defined in eq. (I.20), s^{-1}
ε	constant defined in eq. (A6), s^{-1}
ϕ_A	enhancement factor for increase in specific rate of absorption in the presence of microphase, dimensionless.

Subscripts

av	average
calc	calculated
cont	continuous
disp	dispersion
exp	experimental
int	intrinsic
L	limiting
th	theoretical
tot	total (continuous plus microphase)
mic	microphase
micl	micellar phase
w	water

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APPENDIX

The case of finite bulk concentrations of A

The relevant equations and conditions for the base case, i.e. in the absence of the microphase, may be written as:

$$D_A \frac{\partial^2[A]}{\partial x^2} = \frac{\partial[A]}{\partial t} + k_1[A] \tag{A1}$$

with

$$\begin{aligned} t = 0,\ [A] &= [A_b], \quad \text{all } x \\ t > 0,\ [A] &= [A^*] \quad \text{at } x = 0 \\ [A] &= [A_b]\,\mathrm{e}^{-k_1 t} \quad \text{at } x \to \infty \end{aligned} \tag{A2}$$

whence the equation for the specific rate of reaction for Higbie's model, may be deduced to be:

$$R_A = \frac{1}{t_c}\sqrt{\frac{D_A}{k_1}}\left\{\left([A^*](k_1 t_c + \tfrac{1}{2})\,\mathrm{erf}\,(\sqrt{k_1 t_c}) + \frac{k_1 t_c}{\pi}\mathrm{e}^{-k_1 t_c}\right) - [A_b]\,\mathrm{erf}(\sqrt{k_1 t_c})\right\}. \tag{A3}$$

The surface renewal model of Danckwerts (1970) yields from eq. (A1) along with condition (A2), the expression for the specific reaction rate as:

$$R_A = k_L\sqrt{1 + D_A k_1/k_L^2}\,[[A^*] - [A_b]/(1 + D_A k_1/k_L^2)]. \tag{A4}$$

In the presence of the microphase, eqs (I.1a) and (I.2c) hold but the conditions (I.3c) are altered as follows, being more conveniently written in the transformed Laplace (S) domain as:

$$\begin{aligned} t = 0,\ [\bar{A}] &= [A_{bm}]/S, [\bar{A}_L] = [A_{bm}]/S \ \text{ all } x \\ t > 0,\ [\bar{A}] &= [A^*]/S \quad \text{at } x = 0 \\ [\bar{A}] &= \frac{[A_{bm}](S + \varepsilon)}{(S^2 + \alpha S + \beta)} \quad \text{at } x \to \infty. \end{aligned} \tag{A5}$$

Following a procedure similar to the one used for deriving eq. (I.20) the expression for the specific rate of reaction is given by,

$$R_A = \frac{\sqrt{D_A(1 - l_0)}}{t_c}([A^*]I - [A_{bm}]I') \tag{A6}$$

where I is defined as in eq. (I.20) with $k_{1\mathrm{org}} = 0$ and I' is given by,

$$\begin{aligned} I' = &\int_0^{t_c} \frac{\exp(\delta u)}{\sqrt{\pi u}}\exp((\gamma - w)(t_c - u)/2)\,I_0[(w + \gamma) \\ &\times (t_c - u)/2]\,\mathrm{d}u + \int_0^{t_c}\frac{\mathrm{erf}\sqrt{-\delta u}}{\sqrt{-\delta}}\exp((\gamma - w)(t_c - u)/2) \\ &\times I_0[(w + \gamma)(t_c - u)/2]\,\mathrm{d}u \end{aligned}$$

where

$$\varepsilon = \frac{l_0 K_0}{(1 - l_0)} + \frac{K_0}{m_A}$$

and other constants are as in eq. (I.20).

For Danckwerts' surface renewal theory the equation for the specific reaction rate is:

$$R_A = \sqrt{D_A(1 - l_0)}([A^*]I_1 - [A_{bm}]I'_1) \tag{A7}$$

where I_1 is defined in eq. (I.20a) and

$$I'_1 = \frac{S(S + \varepsilon)}{[(S^2 + \alpha S + \beta)(S + K_0/m_A)]^{1/2}}; \quad S = k_L^2/D_A.$$

For estimation of the bulk concentrations of A (with and without the microphase) an integral balance needs to be made on the bulk liquid. According to Higbie's theory, the interfacial area, $\underline{a}$, is renewed once during contact time, t_c. Therefore, in the presence of the microphase,

$$\frac{[A_{bm}]}{[A^*]} = \frac{\sqrt{D_A/k_1}\,\mathrm{erf}(\sqrt{k_1 t_c}) - \sqrt{D_A}\displaystyle\int_0^{t_c}\frac{\mathrm{e}^{-(w_1/t + k_1 t)}}{\sqrt{\pi t}}\mathrm{d}t}{\left(\dfrac{(1 - l_0)k_1 t_c}{\underline{a}\phi_A} + k_L t_c \mathrm{e}^{-k_1 t_c}(1 - \mathrm{e}^{-w_1/t_c}) + h_e\,\mathrm{erfc}(\sqrt{w_1/t_c})\mathrm{e}^{-k_1 t_c} + h_e(1 - \mathrm{e}^{-k_1 t_c}) + \dfrac{l_0 m_A t_c}{t_B \underline{a}\phi_A}\right)}. \tag{A8}$$

For the surface renewal theory, the fractional rate of surface renewal is $S = k_L^2/D_A$. Therefore, the whole surface is rejevunated in a time equal to $1/S$ seconds. Hence,

$$\frac{[A_{bm}]}{[A^*]} = \frac{(1 - \mathrm{e}^{-\sqrt{(S + k_1)/D_A}\,h_e})}{\left(\dfrac{(1 - l_0)k_1}{\underline{a}S\phi_A}\sqrt{\dfrac{S + k_1}{D_A}} + \dfrac{S}{S + k_1}(1 - \mathrm{e}^{-\sqrt{(S + k_1)/D_A}\,h_e}) + \dfrac{h_e k_1}{\sqrt{D_A(S + k_1)}} + \dfrac{l_0 m_A}{t_B \underline{a}S\phi_A}\sqrt{\dfrac{S + k_1}{D_A}}\right)} \tag{A9}$$

h_e may be approximated by the penetration depth, i.e.

$$\left.\begin{aligned} h_e &= 4\sqrt{D_A t_c} \\ w_1 &= h_e^2/D_A \end{aligned}\right\}. \tag{A10}$$

Equation (A8) and (A9) will represent the situation for $[A_b]$ (i.e. without the microphase) when $\phi_A = 1$, $l_0 = 0$ and the last term in the denominator of the right side of both the equations is made to vanish. This term is to account for the solute A accumulated in the microphase in equilibrium with the continuous phase concentration $[A_{bm}]$. Obviously, for large values of batch time, t_B this term becomes negligible. Moreover these balances are approximate and are based on the assumption of negligible reaction in the penetration element near the gas–liquid interface. The rate equations [eqs (A6) and (A7)] in conjunction with the above integral balances may be solved by trial and error to yield values of $[A_{bm}]$ and ϕ_A. Similarly, the experimental values of the base case rates may be used to calculate the values of the rate constant, k_1 and $[A_b]$ with the help of eqs (A3) and (A4) together with modified versions of eqs (A8) and (A9).

A more rigorous transient analysis is possible only for the Danckwerts' model and may be readily developed. The bulk balance on A can be written as,

$$C\frac{\mathrm{d}[A_{\mathrm{bm}}]'}{\mathrm{d}t} = 1 - D_0[A_{\mathrm{bm}}]' \tag{A11}$$

where

$$C = \frac{1}{aS}\left[\frac{(S^2+\alpha S+\beta)(1-l_0)}{(S+K_0/m_A)D_A}\right]^{1/2} \times \frac{\left[(1-l_0)+l_0 m_A\right]}{\left[(1-l_0)+\dfrac{l_0K_0}{(S+K_0/m_A)}\right]}$$

$$D_0 = \frac{S(S+\varepsilon)}{(S^2+\alpha S+\beta)} + \frac{(1-l_0)k_1}{\underline{a}S}\left\{\frac{(S^2+\alpha S+\beta)(1-l_0)}{(S+K_0/m_A)D_A}\right\}^{1/2} \times \frac{1}{\left[(1-l_0)+\dfrac{l_0K_0}{(S+K_0/m_A)}\right]} + \frac{h_e(k_1/D_A)(1-l_0)}{\left\{\dfrac{(S^2+\alpha S+\beta)(1-l_0)}{(S+K_0/m_A)D_A}\right\}^{1/2}}$$

$$[A_{\mathrm{bm}}]' = [A_{\mathrm{bm}}]/[A^*]$$

under the assumption that,

$$\left\{\frac{(S^2+\alpha S+\beta)(1-l_0)}{(S+K_0/m_A)D_A}\right\}^{1/2} h_e \gg 1 \tag{A12}$$

which is likely to be true. Starting with the batch assumption that,

$$t = 0, \quad [A_{\mathrm{bm}}]' = 0 \tag{A13}$$

the bulk concentration as a function of time is given by,

$$\frac{[A_{\mathrm{bm}}](t)}{[A^*]} = \left(1-\exp\left(-\frac{D_0 t}{C}\right)\right)\frac{1}{D_0}. \tag{A14}$$

For large batch times $\dfrac{D_0 t_B}{C} \gg 1$ and therefore,

$$\frac{[A_{\mathrm{bm}}]}{[A^*]} = \frac{1}{D_0}. \tag{A15}$$

The average bulk concentration in time, t_B is given by,

$$\frac{[A_{\mathrm{bm}}]_{\mathrm{av}}}{[A^*]} = \frac{1}{D_0}\left\{1+\frac{C}{D_0 t_B}\left[\exp\left(-\frac{D_0 t_B}{C}\right)-1\right]\right\}. \tag{A16}$$

Equation (A16) along with eq. (A7) will give the value of the average rate measured over a batch time t_B.

Also it may be noted that

$$D_0 \gg 1 \tag{A17}$$

is the rigorous condition for bulk concentration of A to be zero in the presence of a microphase.