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Benzene nitration: validation of heterogeneous reaction models

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Abstract

The film and the Danckwerts penetration models were used to model the heterogeneous liquid–liquid reaction of benzene nitration. Analytical solutions were developed for both models considering a pseudo-first order reaction. Models were confronted with experimental results showing good predictions in the intermediate reaction regime ($0.3 < Ha < 2$). Profiles of both models were evaluated confirming similarities and identical approximate behaviours. Therefore, both models seem adequate to model industrial systems operating mostly in this intermediate reaction regime, although the film model allows a simpler mathematical treatment.

Keywords: Reaction engineering; Multiphase reactions; Mass transfer; Kinetics; Model reduction; Benzene nitration

1. Introduction

Fluid phase heterogeneous reactions play an important role in the chemical industry. In these systems the chemical compounds are located in distinct phases and mass transfer occurs between them by diffusion and/or convection, simultaneous to chemical reaction.

Different mechanistic models have been developed to describe this process of mass transfer with chemical reaction, either in gas–liquid or liquid–liquid systems. The most common approach uses the film model, which considers a stagnant layer of thickness δ between the interface and the bulk of the reacting phase, where the mass transfer occurs, according to a stationary process (Whitman, 1923). More complex descriptions have been developed by Higbie (1935) and later by Danckwerts (1951) assuming that, at the interface, small stagnant elements of liquid are constantly replaced leading to a non-stationary diffusional mass transfer process. After a contact time, these elements are withdrawn from the interface to be mixed with the liquid bulk, and are replaced by fresh ones. While Higbie considers an equal renewal rate for each element, Danckwerts suggests an equal probability s for each element to be replaced at any instant of time, independent of its age. Each of these three models has only one fundamental parameter.

The reaction regime is defined by the Hatta number (*Ha*), and the best model approach can depend on this regime. Despite originating different mathematical solutions, all these models predict the same asymptotic solutions for fast ($Ha > 2$) and slow reactions ($Ha < 0.3$); their main differences are located in the intermediate regime where $0.3 < Ha < 2$ (Westerterp et al., 1990). In the available literature few studies cover the intermediate regime (Doraiswamy and Sharma, 1984; van-Elk et al., 2000), and the use of experimental data to confront the model predictions is even more rare. In a recent work Benbelkacem and Debellefontaine (2003) used a fumaric acid ozonation in a semi-batch reactor to validate the film model predictions in the intermediate reaction regime.

The benzene nitration with nitric acid, using sulphuric acid as catalyst, is an excellent example of a heterogeneous catalysed liquid–liquid reaction that can range from the slow to the fast reaction regimes by changing the sulphuric acid strength, as in the toluene nitration (Cox and Strachan, 1972). In industry, the benzene nitration is usually

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carried out adiabatically, with a set of operating conditions that corresponds to the intermediate regime (Quadros et al., 2004b). In this work, analytical mathematical solutions for the film and the Danckwerts penetration models are developed and validated with experimental data collected in a pilot plant built for benzene nitration, described in Quadros et al. (2004a).

2. Benzene nitration

The benzene nitration with nitric acid is a liquid–liquid reaction where benzene (B) is transferred from the organic to the aqueous phase to react with the nitronium ion (NO_2^+) according to a second order reaction (Deno and Stein, 1956; Coombes et al., 1968). The nitronium ion is produced by the dissociation of nitric acid in the presence of sulphuric acid that acts as a catalyst (Olah et al., 1989). The reaction is considered to occur only in the aqueous phase, producing mononitrobenzene (MNB) that transfers into the organic phase. Due to the low solubility of the benzene in the aqueous phase (Schiefferle et al., 1976), this nitration can be assumed as a pseudo-first order reaction, since the nitric acid concentration in the aqueous phase is much higher than the benzene concentration. This process is carried out adiabatically in a continuous stirred reactor using operating conditions similar to industrial practice, as described in Quadros et al. (2004a).

3. The film model

The film model considers a stagnant film near the interface between the two phases, where the resistance is concentrated, and assumes a steady state mass transfer process (Westerterp et al., 1990). A mass balance to the film leads to an ordinary differential equation (space dependent) that, once solved with the appropriated boundary conditions, produces an algebraic equation to quantify the simultaneous reaction and mass transfer across the film. The benzene nitration CSTR is represented in Fig. 1 according to the film model. Distinction is made between the organic and the aqueous phases; this latter is divided into film and bulk. It is assumed that the aqueous bulk and the organic phases are perfectly mixed, and that all resistances to benzene mass transfer are confined to a film phase of thickness $\delta = D/k_L$, according to Westerterp et al. (1990).

A mass balance to the benzene in the organic phase and in the bulk of aqueous phase leads to the following set of algebraic equations:

$$0 = Q_1 C_{1B} - Q_3 C_{3B} - J_B|_{x=0} aV, \tag{1}$$

$$0 = -\frac{\varepsilon_B}{\varepsilon_{aq}} Q_4 C_{B,\text{bulk}} + J_B|_{x=\delta} aV - \varepsilon_B k C_{B,\text{bulk}} V. \tag{2}$$

To predict the outlet benzene concentration in the organic phase (C_{3B}) it is necessary to know the benzene molar flux (J_B) at $x=0$ and $x=\delta$. Assuming that benzene is brought into the film only by diffusion, and that it reacts there according to a pseudo-first order reaction, it is possible to write the benzene mass balance to the aqueous film, Eq. (3):

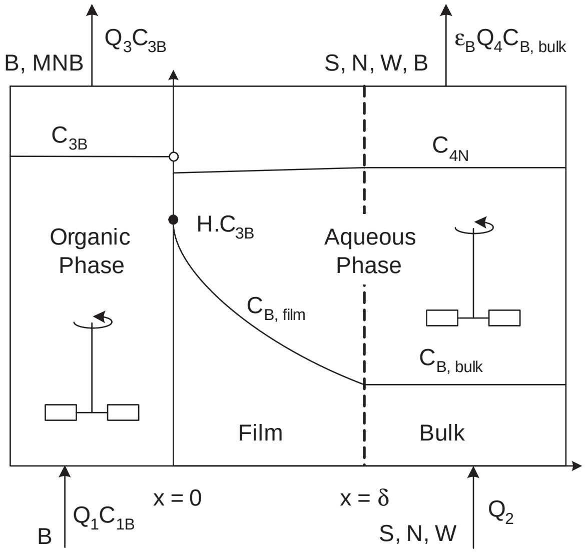

Fig. 1. Film model reactor.

$$D\frac{d^2 C_{B,\text{film}}}{dx^2} - kC_{B,\text{film}} = 0, \tag{3}$$

$$C_{B,\text{film}} = H.C_{3B} \quad \text{for } x = 0,$$

$$C_{B,\text{film}} = C_{B,\text{bulk}} \quad \text{for } x = \delta.$$

The solution of Eq. (3) gives the benzene film concentration between *0* and δ, as function of the space coordinate x:

$$C_{B,\text{film}}(x) = \frac{H.C_{3B}}{\sinh[Ha]}\left\{\sinh\left[Ha - x\sqrt{\frac{k}{D}}\right] + \frac{C_{B,\text{bulk}}}{H.C_{3B}}\sinh\left[x\sqrt{\frac{k}{D}}\right]\right\}. \tag{4}$$

The molar flux at a generic space coordinate x is obtained by differentiating Eq. (4):

$$J_B = -D\frac{dC_{B,\text{film}}}{dx} = k_L\left\{H.C_{3B}\cosh\left[Ha - x\sqrt{\frac{k}{D}}\right] - C_{B,\text{bulk}}\cosh\left[x\sqrt{\frac{k}{D}}\right]\right\}\frac{Ha}{\sinh[Ha]}. \tag{5}$$

Evaluating Eq. (5) at $x = 0$ and δ and replacing these terms in Eqs. (1) and (2), respectively, it is possible to predict the benzene outlet concentration. This requires two other parameters: the effective interfacial area for this system, a (Quadros and Baptista, 2003) and the bulk hold-up fraction defined as function of the Hinterland ratio (Westerterp et al., 1990; Quadros et al., 2004b).

4. The Danckwerts penetration model

The penetration theory for the heterogeneous mass transfer process was first presented by Higbie (1935) and later modified by Danckwerts (1951). Contrarily to the film theory, it considers the mass transfer as a non-stationary process. At the interface, the mass transfer occurs by diffusion through small stagnant fluid elements that are periodically replaced by fresh new elements coming from the well-mixed bulk. Complex mathematical equations arise from these approaches, and a numerical solution is usually necessary to solve these problems (van-Elk et al., 2000). While Higbie considers an equal renewal rate for each element, Danckwerts suggests that each element has an equal probability s to be replaced at any time instant independent of its age. This supports the adoption of Danckwerts model in this work.

In Fig. 2 the CSTR is represented accordingly to the Danckwerts penetration model. It is important to stress that the penetration mechanism depends on the distance from the interface and on the microscopic renewal time θ. This non-stationary benzene mass transfer process with chemical reaction through the aqueous phase can be described by

$$\frac{\partial C_B(x,\theta)}{\partial\theta} = D\frac{\partial^2 C_B(x,\theta)}{\partial x^2} - kC_B(x,\theta) \qquad (6)$$

with

$$\begin{array}{ll} C_B(0,\theta) = HC_{3B}, & \theta > 0, \\ C_B(\delta_p \to \infty,\theta) = C_{B,\mathrm{bulk}}\mathrm{e}^{-k\theta}, & \theta > 0, \\ C_B(x,0) = C_{B,\mathrm{bulk}}, & x > 0. \end{array}$$

Applying Laplace transforms to the microscopic time θ in the previous equation leads to the following ordinary differential equation, which is only space dependent:

$$s\tilde{C}_B(x,s) - C_B(x,0) = D\frac{\partial^2 \tilde{C}_B(x,s)}{\partial x^2} - k\tilde{C}_B(x,s) \qquad (7)$$

with

$$\tilde{C}_B(0,s) = \frac{HC_{3B}}{s},$$

$$\tilde{C}_B(\delta \to \infty,s) = \frac{C_{B,\mathrm{bulk}}}{k+s}.$$

Solving Eq. (7), the following benzene concentration profile in the aqueous phase is obtained:

$$\tilde{C}_B(x,s) = \frac{C_{B,\mathrm{bulk}}}{k+s} + \left(\frac{HC_{3B}}{s} - \frac{C_{B,\mathrm{bulk}}}{k+s}\right)\mathrm{e}^{-x\sqrt{(k+s)/D}}. \qquad (8)$$

According to Wang et al. (1997) the average depth of penetration δ_p can be defined by

$$\delta_p = \frac{\varepsilon_{\mathrm{aq}}}{a}. \qquad (9)$$

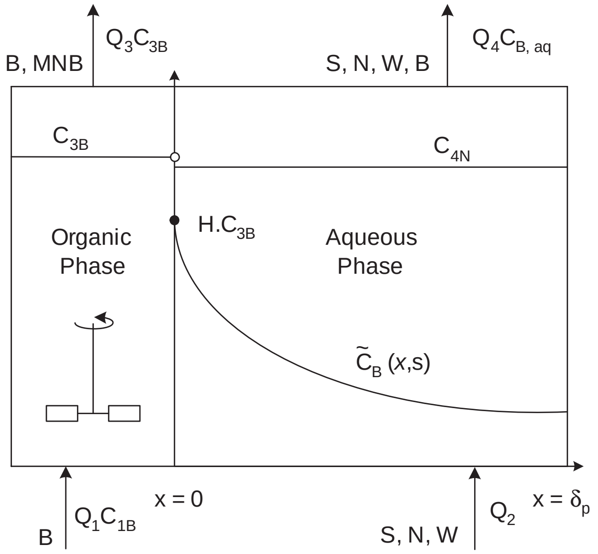

Fig. 2. Danckwerts penetration model reactor.

This models' fundamental parameter, s, according to Westerterp et al. (1990), is defined by

$$s = \frac{k_L^2}{D}. \qquad (10)$$

According to the model Eq. (6), δ_p should mathematically approach infinity; however, having in mind the physical meaning of diffusion penetration depth and the values obtained with Eq. (9), this assumption should remain valid.

The benzene concentration in the outlet stream, C_{3B}, is given by Eq. (1); therefore the molar flux at $x = 0$ has to be calculated. Due to the similarity between the Laplace transform function and the age distribution function (Wang et al., 1997), the Laplace transformation and time average integration can be combined to obtain the time averaged benzene molar flux at the interface ($x = 0$) and the time and space averaged value for the benzene bulk concentration. Therefore, the time averaged molar flux at $x = 0$ can be expressed as

$$\bar{J}_B|_{x=0} = k_L\left(HC_{3B} - \frac{C_{B,\mathrm{bulk}}}{Ha^2+1}\right)\sqrt{Ha^2+1}, \qquad (11)$$

while the time space averaged benzene bulk concentration can be represented by

$$C_{B,\mathrm{bulk}} = \frac{\phi_1 HC_{3B}}{1+\phi_2}, \qquad (12)$$

where

$$\phi_1 = \frac{1}{\delta_p}\sqrt{\frac{D}{k+s}}\left(1 - \mathrm{e}^{-\delta_p\sqrt{(k+s)/D}}\right),$$

$$\phi_2 = \frac{s}{(k+s)\delta_p}\sqrt{\frac{D}{k+s}}\left(1 - \mathrm{e}^{-\delta_p\sqrt{(k+s)/D}}\right) - \frac{s}{k+s}.$$

Solving now Eq. (1) together with Eqs. (11) and (12) it is possible to predict the benzene molar concentration C_{3B} at the reactor outlet.

5. Validation of the heterogeneous models

The pilot plant built to study the adiabatic benzene nitration provided data that will be used to validate the heterogeneous models. A full description of the experimental procedure and analytical techniques used is given in Quadros et al. (2004a). The correlations used in these models are presented and discussed in Quadros et al. (2004b). Due to the operating conditions used, in agreement with industrial practice, every experimental run was conducted in the intermediate regime ($0.3 < Ha < 2$) where chemical reaction and diffusion processes compete.

In Fig. 3 the experimental benzene outlet concentration and the predictions of the film and Danckwerts model for this variable are represented as function of the stirring speed. In this particular run the Hatta number ranged from 0.60 to 1.25, which correspond to the lower and the higher stirring speeds used. The striking feature in Fig. 3 is the good agreement between experimental and models' results. Moreover, the small differences between the film and the penetration model ensure the suitability of these two models to describe this heterogeneous reaction/mass transfer process. Fig. 4 registers that both models predict the concentration of MNB produced within a 15% error, over a wide range. No significant differences were detected between the two models; the maximum difference is 4%, and it was not possible to confirm which model is the most accurate. It should be emphasized that about 60 experimental values have been used to validate models' predictions within this 15% error limit. This very good agreement between the two models' predictions was not expected since, according to Westerterp et al. (1990), in the intermediate regime the differences in the Enhancement factor (*Ea*) for these two models may reach 20%, for $C_{B,\mathrm{bulk}} = \frac{1}{2} HC_{3B}$ and $Ha = 1$. The Enhancement factor is defined in Eq. (13) and represents the ratio between the molar flux at the interface with chemical reaction and the pure mass transfer flux with no reaction:

$$Ea = \frac{\bar{J}_B|_{x=0}}{k_L(HC_{3B} - C_{B,\mathrm{bulk}})}. \tag{13}$$

Fig. 5 confirms a difference between the Enhancement factors for the film and the penetration models. These differences can rise up to 40%, which is even greater than the 20% reported by Westerterp et al. (1990), and the gap increases with the increase in *Ha* and the decrease in $C_{B,\mathrm{bulk}}$. Moreover, *Ea* is always bigger for the Danckwerts model, which is in agreement with the results in the literature where, for the *Ha* and $C_{B,\mathrm{bulk}}$ values referred, the *Ea* for the film model is 1.78 and for Danckwerts 2.12 (Westerterp et al., 1990).

Given these differences in the Enhancement factor, a further look into the concentration profiles is required to understand why both models are able to predict a similar benzene concentration in the exit stream. Figs. 6 and 7 show the benzene concentration profiles in the aqueous phase obtained with the film and the Danckwerts models, for two different sets of experimental conditions, corresponding to Hatta numbers of 0.60 and 1.25. A first reading reveals that in each figure the two models lead to similar profiles, but the profiles in Fig. 6 are clearly different from the ones in Fig. 7, due to the differences in operating conditions. Let us focus first on Fig. 6, which illustrates the profiles for the lowest stirring speed point in Fig. 3 and also for the lowest *Ha*. It is known that a lower effective interfacial area is associated to a lower stirring speed (Quadros and Baptista, 2003), meaning that big drops of the dispersed phase are produced, and, as the volume of organic phase remains approximately constant during a run, fewer drops are present in the reactor for these

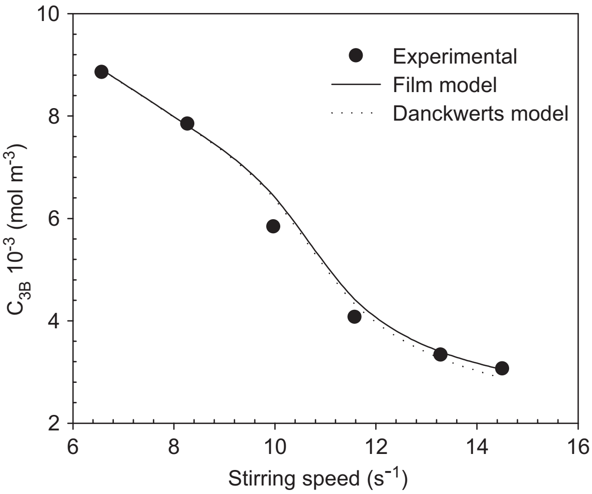

Fig. 3. Experimental and models' results for the benzene outlet concentration as function of the stirring speed for a given run.

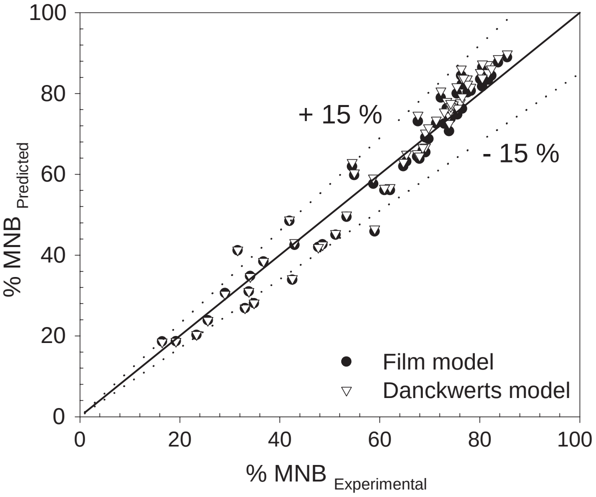

Fig. 4. MNB percentage in the outlet stream—experimental versus predicted values.

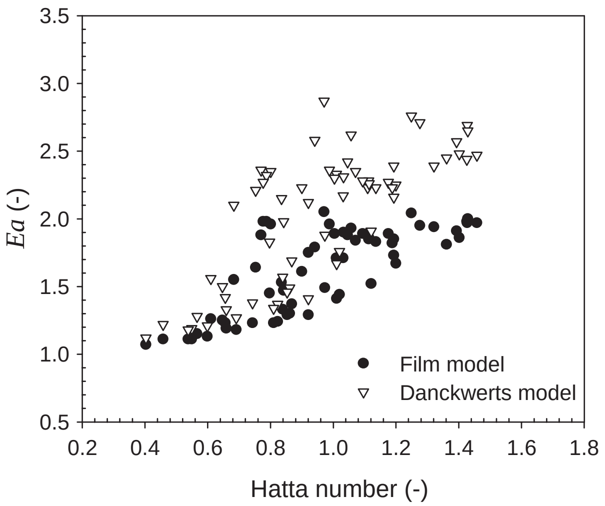

Fig. 5. Enhancement factors for the film and Danckwerts models as a function of the Hatta number for the experimental data points used.

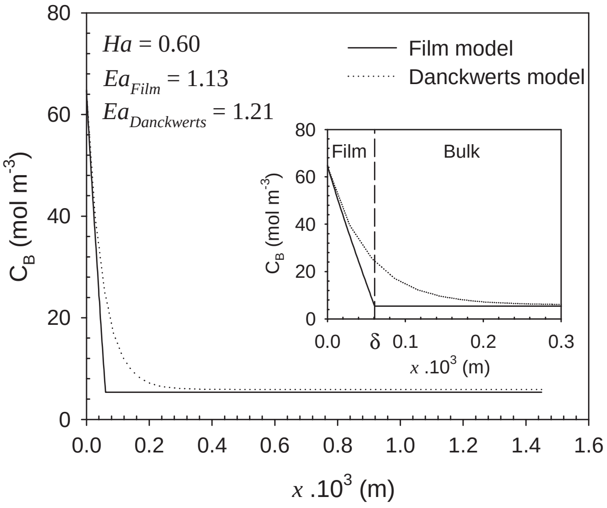

Fig. 6. Benzene concentration profiles predicted by the film and Danckwerts models for a run with $Ha = 0.60$.

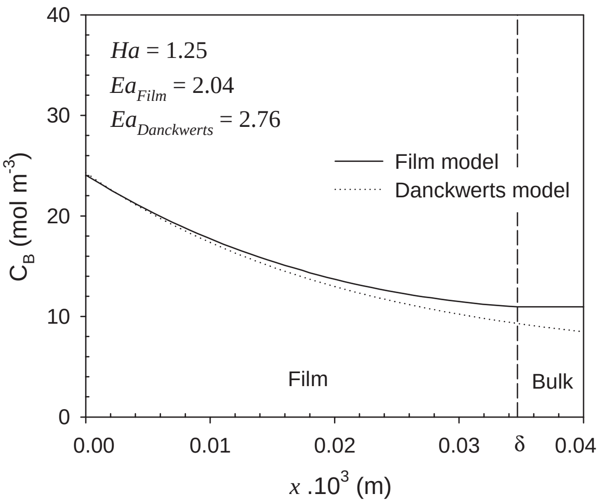

Fig. 7. Benzene concentration profiles predicted by the film and Danckwerts models for a run with $Ha = 1.25$.

operating conditions. Therefore, a large volume of continuous phase will be available to envelop each dispersed drop (higher maximum x). Fig. 6 shows that the concentration of benzene falls down abruptly very near to the interface and reaches a flat profile, for both film and Danckwerts models. A zoom of profiles in Fig. 6 enlightens differences between the two models. While the film model considers a barrier of thickness δ where the mass transfer resistances are confined and a bulk with homogeneous concentration, the Danckwerts model regards a continuous aqueous phase where the benzene concentration falls gradually till it reaches constancy like in the bulk of the film model; at this stage, it can be assumed that the maximum penetration depth was reached. It should be emphasized that both profiles predict similar fluxes at the interface, which is consistent with the similarity of both slopes at $x = 0$. The profiles represented in Fig. 7 correspond to the highest stirring speed in Fig. 3 that result in a larger effective interfacial area and a higher Ha. This means that drops of organic phase with a smaller diameter but in a larger number are formed. Therefore, each drop is wrapped up in a smaller volume of aqueous phase, resulting in a smaller maximum x. Moreover, due to the higher interfacial area produced the ratio of film and bulk thicknesses obtained for the film model is higher than in Fig. 6. Both models lead to similar profiles, differing only far from the interface; therefore, at the interface a similar flux is obtained.

The previous discussion confirms that both models predict similar concentrations and molar fluxes through the interface, but does not explain the differences in Ea in Fig. 5. These are due to the definition of $C_{B,\text{bulk}}$ for each model. In the penetration model this corresponds to the average aqueous phase concentration and this is always greater than $C_{B,\text{bulk}}$ considered by the film model. The understanding of the resemblance of the profiles helps to justify the ability of both models to predict the benzene and MNB concentrations with identical accuracy. Therefore, it is not possible to identify which is the most accurate or suitable heterogeneous model, unless for its theoretical fundamentals or complexity.

6. Conclusions

In this work, two different heterogeneous reaction models were validated with experimental results from the benzene nitration in the intermediate reaction regime. Analytical solutions were developed for the film and the Danckwerts models, and results were tested and confronted. From a physical point of view a physical barrier at a defined distance from the interface to differentiate the film from the bulk, as pictured by the film model, does not seem credible; on the other hand, a non-stationary mass transfer process through a penetration depth seems a much more plausible description. Nevertheless, it is remarkable how these two models, with different assumptions and mathematical expressions, predict almost the same concentration and profile results. This is even more noteworthy considering the relative simplicity of the film model and its capacity to produce good approximate concentration profiles and results. This *cheap* model may be chosen to model existing industrial reactors of this type, given its simplicity and extensive range of application.

Notation

a	effective interfacial area, $m^2\,m^{-3}$
C_B	molar concentration of benzene in the aqueous phase, $mol\,m^{-3}$
C_{ij}	molar concentration of the compound i in the stream j, $mol\,m^{-3}$
D	diffusion coefficient, $m^2\,s^{-1}$
Ea	Enhancement factor
H	partition coefficient
Ha	Hatta number
J_B	molar flux of benzene, $mol\,m^{-2}\,s^{-1}$
k_L	mass transfer coefficient, $m\,s^{-1}$
k	pseudo-first order reaction rate constant, s^{-1}
s	fraction of elements of any age that is replaced per unit of time, s^{-1}
V	reactor volume, m^3
x	space coordinate; Distance from the interface, m

Greek letters

δ	thickness of the stagnant layer of the film, m
δ_p	depth of penetration, m
ε_{aq}	hold-up fraction of the aqueous phase
ε_B	hold-up fraction of the bulk of aqueous phase
θ	microscopic time, s

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