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Catalysis Today 66 (2001) 335–344

CATALYSIS TODAY

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On the interfacial mass transfer and the location of the chemical reaction in a fluid/fluid reacting system at elevated temperatures and pressures

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Abstract

In a two-phase (supercritical fluid–fluid) system, the rate of conversion of a bimolecular reaction $A + B \rightarrow AB$ reacting in the layer adjacent to the interface and in the bulk phase was determined. The mass transfer associated with the chemical reaction was measured in a stirred and thermostatically controlled cell varying reaction temperature, pressure and stirring speed. As model system, the Diels–Alder reaction between 9-hydroxymethylanthracene and maleic acid was chosen in the solvent pair supercritical propane/water. The cell was developed for high pressures and temperatures. The reaction was monitored in both phases with on line UV-spectroscopy. The experimental results are compared to simulated data obtained by using a film model. An improved theoretical model describing the changes in concentration of the reactants in the two phases is presented.

Keywords: Mass transfer with chemical reaction; Stirred cell for high pressure; Supercritical fluid

1. Introduction

Heterogeneous two-phase systems with chemical reaction are of increasing importance in industrial processes [1–3], e.g., in solvent extraction and phase-transfer catalysis with key applications in (petro)chemistry, biotechnology and environmental areas. Although the kinetics of the mass transfer between two phases and simultaneous chemical reaction have been actively studied [3], a systematic investigation on the influence of temperature, pressure and flow conditions on the portion of conversion of a chemical reaction, which occurs in the interfacial region, has not been reported so far and is the aim of this work.

The overall process of mass transfer with simultaneous chemical reaction $A + B \rightarrow AB$ can be described by four elementary steps [4]:

1. Diffusion of reactant A from the bulk of phase I to the interface between the two phases.
2. Diffusion of reactant A from the interface to the bulk of phase II (in the specific case B does not enter phase I).
3. Chemical reaction in the layer adjacent to the interface and within phase II.
4. Diffusion of reactants initially present within phase II.

If step 1 is rate determining, the overall rate is not influenced by the chemical reaction. The analysis of mass transfer with chemical reaction is of interest when the overall phenomenon resulting from steps 2–4 is rate-controlling. An increase in the total area of the

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PII: S0920-5861(00)00620-9

interface or in the solubility of compound A in phase II will lead to an increased reaction rate, if step 2 is rate determining. The hydrogenation of fats and oils is a well-known example, where the rate is increased dramatically in comparison with traditional hydrogenation techniques (approximately by a factor of 1000) by adding supercritical propane to the reaction mixture [5]. Here, the low solubility of hydrogen in oils and the limited transport through the gas/oil/catalyst interface restricts the maximum possible reaction rates.

Generally, in two-phase fluid/fluid systems the chemical reaction $A + B \rightarrow AB$ may occur at the phase boundary between the fluids containing A and B, or in the main body of the fluid (phase II), or both within the film and the main body of the fluid. The kinetic regime for mass transfer and reaction in two-phase systems depends on the relative rates of reaction and mass transfer [6]. These relative rates varying from one extreme to the other may be expressed with the dimensionless characteristic Hatta number (*Ha*) [3].

$$Ha = \frac{D_{A}\, k_{II}\, c_{B,II}}{\beta_{A,II}} \qquad (1)$$

Here D_A is the molecular diffusivity of A, k_{II} the chemical rate constant in phase II, $c_{B,II}$ the concentration of B in phase II and $\beta_{A,II}$ the mass-transfer coefficient of A (side to phase II). For moderately fast reactions ($0.3 < Ha < 3$), the rate of reaction is of the same magnitude as the mass transfer. Since Hatta reported the first major analysis of this problem in the late 1929 [7], general rate expressions for this regime are nowadays still unavailable.

2. Choice of the two-solvent system and the chemical reaction

Supercritical propane and water were chosen as solvents in the two-solvent system. The large difference in density between supercritical propane and water ensures a stable interface between the two phases. A characteristic feature of solvents in the supercritical region is that their compressibility is large. Small changes in the pressure result in large changes of the density and, hence, of the solubility of various solutes. Whereas density and solvent power of supercritical fluid phases are comparable to those of liquids, diffusion coefficients and viscosities resemble more those of gases. As a consequence, rather large diffusion coefficients and low viscosities are found in the fluid phase [8]. For this study, the Diels–Alder reaction between 9-hydroxymethylanthracene (A) and maleic acid (B) was chosen as a moderately fast reaction. Note that the use of water as solvent in organic chemistry for irreversible second-order Diels–Alder reactions was rediscovered some years ago [9]. The concentration of A can easily be determined by UV-spectroscopy. In contrast to reactant A, which is soluble in both phases (more in supercritical propane than in water), reactant B is exclusively dissolved in water.

3. Experimental

3.1. The two-phase stirred cell for high pressure application

Fig. 1 shows the experimental setup. The central part is the stirred cell suitable for operation under high pressures and temperatures (Fig. 2) with the online-analytical equipment for UV-spectroscopy [10]. The stirred cell employed for the investigation is a further development of a cell built by Nitsch and Kähni [11] modified for high pressures and temperatures. A few noteworthy points about the stirred cell (Fig. 2) are mentioned here (see also [12]):

1. The stirrers (1) are coupled magnetically to the motor. The rotating speed can be adjusted in both phases separately by magnetic coupling (7).
2. The interface renewal is affected by the axial flow properties. Fitting of draft tubes (2) in both phases together with the selected angle of the stirrer blades (5) produces a central suction along the interface regions from both sides and flow in the annular space.
3. The hydrodynamic performance of the stirrer blades (5) has been optimized with the aim to achieve maximum circulation at minimum stirring speed, in order to protect the sealing surfaces between the shafts and their guide tubes (2).
4. Conveyor threads (6) support the flow in the region of the magnetic coupling (1) in order to eliminate dead volumes.
5. Two pairs of axial moveable spectroscopy probes (4) for high pressures and temperatures are installed in the cell for on line analysis in both phases.

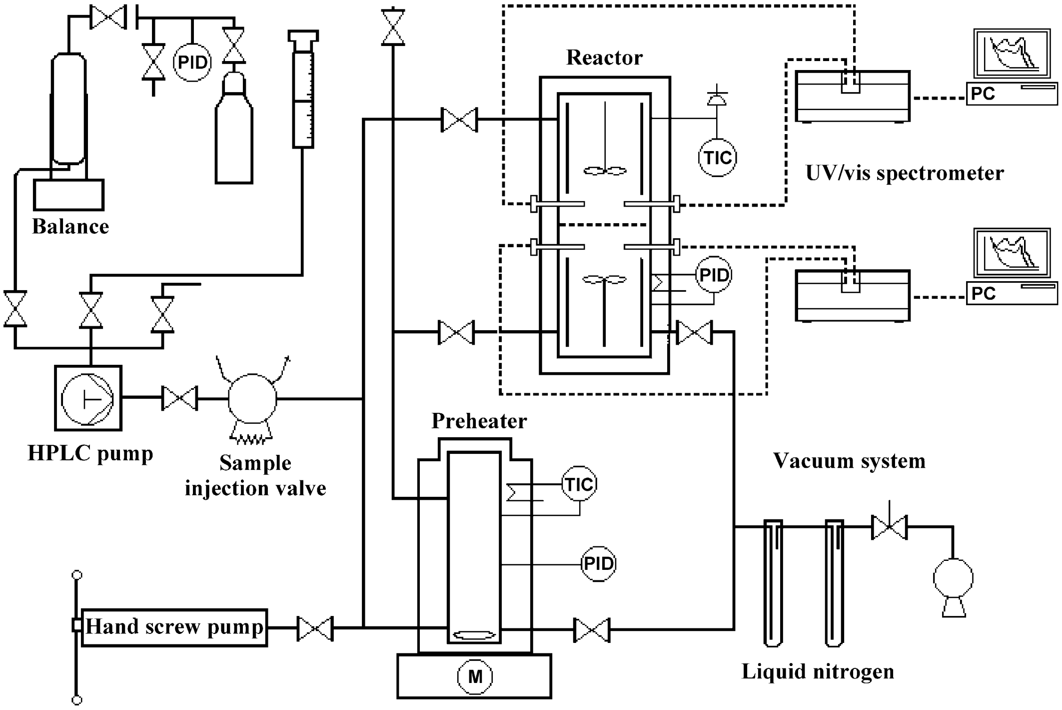

Fig. 1. Schematic diagram of the experimental apparatus.

6. Two windows (3) made from sapphire enable the direct observation of the interface.
7. Internal electric heating (heating wires in the wall of reactor) and external heating (by running water at the desired temperature in a canal-system in the wall of the reactor) are possible. For both cases the temperature fluctuation in the bulk phase is ±0.1 K.

To test the apparatus the mass-transfer coefficients of toluene in the system toluene/water at 25°C were determined by varying the stirring speed in the complementary phases. The results (Fig. 3) show a linear relationship between the mass-transfer coefficients of toluene ($\beta_{\mathrm{T,W}}$) and stirring speed (n) in agreement with Nitsch and Kähni [11].

3.2. Experimental procedure

All kinetic measurements of mass transfer with chemical reaction were performed according to the following procedure: The heavier water phase (known volume and a defined amount of B) was introduced at the bottom of the cell. The level of the interface was in the region of the monitoring window. The lighter supercritical propane (a known volume containing a defined concentration in A) was introduced in the thermostatically controlled preheater under high pressure. The temperatures in the cell were identical with those in the preheater. The process was started by introducing the lighter phase from the preheater into the main reactor. The concentration of A in both phases was measured by UV-spectroscopy in the range from 420 to 320 nm. After the reaction, the apparatus was emptied, rinsed several times with solvents and finally dried by evacuation.

4. Results

4.1. Equilibrium solubility

The solubility coefficient K_{A} of A is defined as the ratio of the concentrations $c^*_{\mathrm{A,I}}$ and $c^*_{\mathrm{A,II}}$ at thermodynamic equilibrium; i.e.

$$K_{\mathrm{A}} = \frac{c^*_{\mathrm{A,I}}}{c^*_{\mathrm{A,II}}} \tag{2}$$

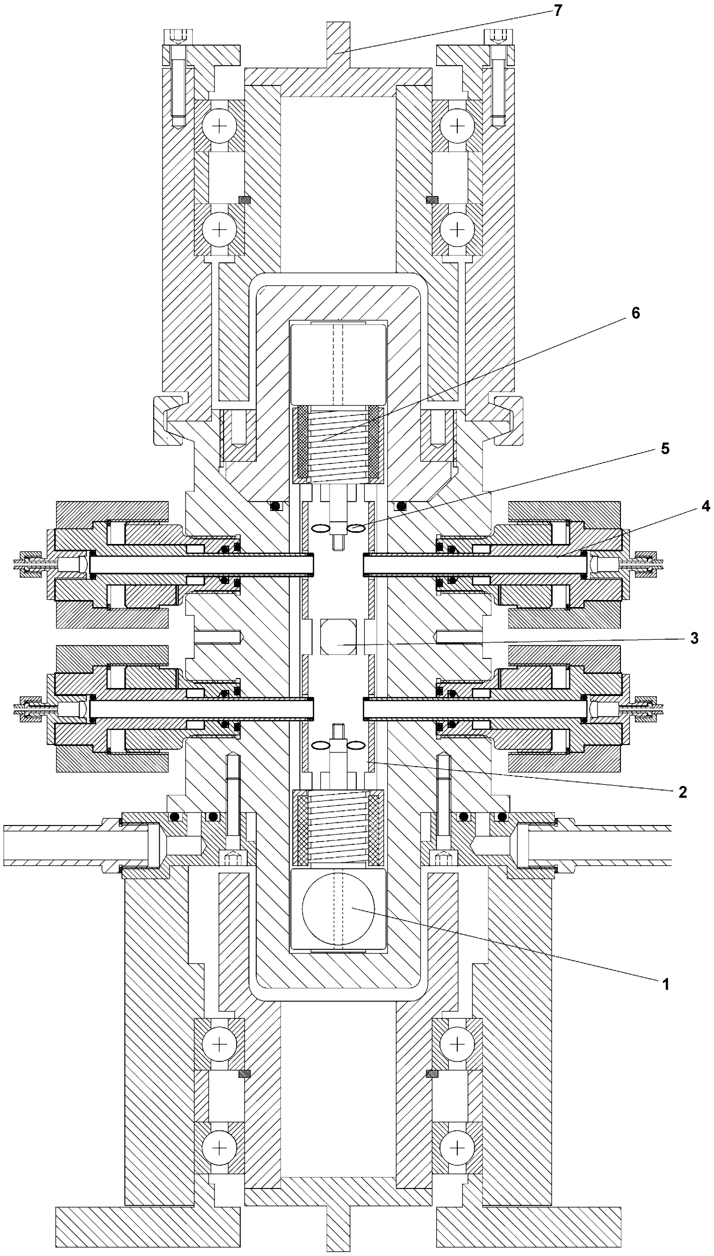

Fig. 2. The two-phase stirred cell for high pressure applications.

Due to the chemical reaction, which occurs in phase II, it is not possible to obtain K_A directly and, therefore, it must be estimated from corresponding data of similar nonreacting substances [13]. In our case, succinic acid (SA) was used as the analogon to maleic acid. The solubility data for 9-hydroxymethylanthracene in supercritical propane/water and in supercritical propane/aqueous solution of 0.5 M succinic acid

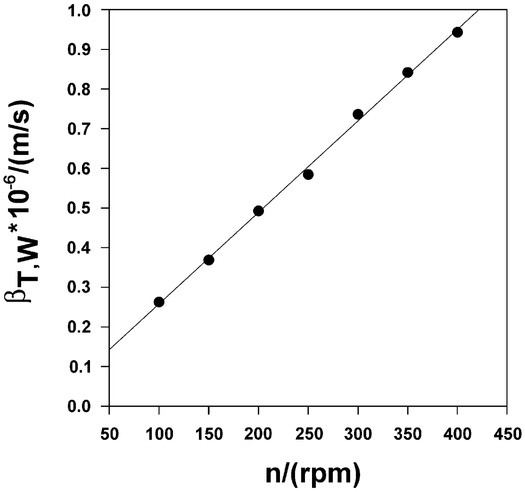

Fig. 3. The water-side mass-transfer coefficients of toluene in toluene/water system at 25°C.

are given in Fig. 4a. The solubility coefficient K_A for 9-hydroxymethylanthracene in the supercritical propane/0.5 M succinic acid in water are described by correlation (3),

$$K_\mathrm{A} = \varepsilon + \omega p + \chi \frac{p}{T} \tag{3}$$

where T is the temperature in K and p the pressure in bar (Fig. 4b), $\varepsilon = 0.1605$, $\omega = -0.4030$, $\chi = 169.2$.

4.2. Conversion in the bulk and in the layer adjacent to the interface

The portion of chemical conversion occurring in the layer adjacent to the interface J_IP is defined as the difference between the total molar flux and loss of component A by chemical reaction in the bulk (Eqs. (4) and (5)).

$$J_\mathrm{IP} = J_\mathrm{Total} - J_\mathrm{Bulk} \tag{4}$$

$$J_\mathrm{IP} = \left(-\frac{\mathrm{d}c_\mathrm{A,I}}{\mathrm{d}t} V_\mathrm{I} - \frac{\mathrm{d}c_\mathrm{A,II}}{\mathrm{d}t} V_\mathrm{II}\right) - (k_\mathrm{I}\, c_\mathrm{A,I}\, c_\mathrm{B,I}\, V_\mathrm{I} + k_\mathrm{II}\, c_\mathrm{A,II}\, c_\mathrm{B,II}\, V_\mathrm{II}) \tag{5}$$

Here $c_\mathrm{A,I}$ and $c_\mathrm{A,II}$ are the concentrations of A in phase I and II; V_I and V_II the volumes of phase I and II; k_I and k_II the rate constant of the reaction in phase I and II, which can be determined from experimental data in homogeneous phase. Because of the very low content of maleic acid in the propane phase, the term $\{k_\mathrm{I}\, c_\mathrm{A,I}\, c_\mathrm{B,I}\, V_\mathrm{I}\}$ can be neglected. The concentration of maleic acid is large enough ($c_\mathrm{B,II} > 1000\, c_\mathrm{A,II}$) to be assumed constant during the reaction.

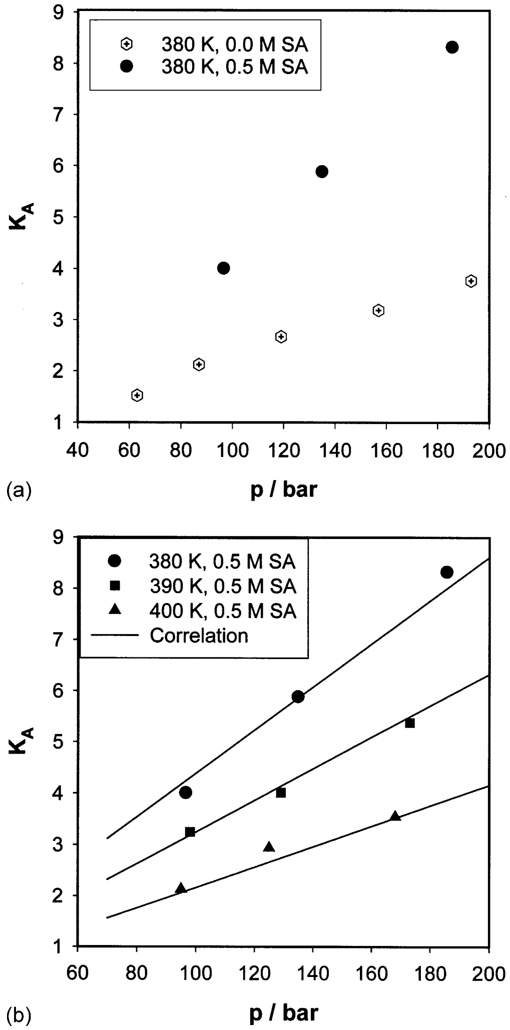

Fig. 4. (a) Solubility coefficient K_A of 9-hydroxymethylanthracene between phase I (supercritical propane) and phase II (water or 0.5 M succinic acid (SA) in water) at 380 K and different pressures. (b) Solubility coefficient K_A of 9-hydroxymethylanthracene between phase I (supercritical propane) and phase II (0.5 M succinic acid (SA) in water) at different temperatures and pressures.

From experimental data in the homogeneous aqueous phase k_II can be obtained (Table 1). The temperature dependence of the reaction is described by the

Table 1
The rate constant k_{II} of the Diels–Alder reaction between 9-hydroxymethylanthracene and maleic acid at 380, 390, 400 K in water

T (K)	k_{II} (l/mol/s)
380	2.14×10^{-3}
390	3.81×10^{-3}
400	6.80×10^{-3}

Arrhenius equation and an apparent activation energy (E_A) 106 kJ/mol is calculated. A pressure dependence of k_{II} in the homogenous aqueous phase was not observed.

Fig. 5a and b shows typical changes in the concentration of reactant A in the organic and aqueous phase. The difference in concentration between the reacting and nonreacting system at the same time is a measure for the reaction extent. The changes in concentration of the reactants in the two phases can be described by Eqs. (6) and (7):

$$c_{\mathrm{A,I}} = c_{\mathrm{A,I,0}} \exp(-\gamma t) \tag{6}$$

$$c_{\mathrm{A,II}} = (1 - \exp(-\alpha t))\phi \exp(-\lambda t) \tag{7}$$

The physical meaning of the parameters is explained in Appendix A. The parameter ϕ is directly proportional to the initial concentration of A ($c_{\mathrm{A,I,0}}$) and $1/K_A$. The parameter α is specific for interfacial mass transport with chemical reaction and depends mainly on the temperature. In an ideal case both parameters γ and λ have the same value. The results compiled in Table 2 shows that the parameters γ and λ are very similar.

The overall rate of conversion J_{Total} increased with increasing temperature and decreasing pressure (see Fig. 6a and b). We attribute this to the fact that the rate of chemical reaction increases with increasing temperature. Thus, the difference between the equilibrium concentration of A in the interface ($c^*_{\mathrm{A,II}}$) and the actual concentration of A in the bulk ($c_{\mathrm{A,II}}$) increases with increasing temperature. The interfacial mass transfer is enhanced by chemical reaction. Both processes (mass transfer and chemical reaction) raise the overall rate with increasing temperature. With increasing pressure, on the other hand, the solubility coefficient K_A increases, i.e. $c^*_{\mathrm{A,II}}$ and $c_{\mathrm{A,II}}$ decreases. As the rate of chemical reaction is independent of the pressure, the overall rate decreases.

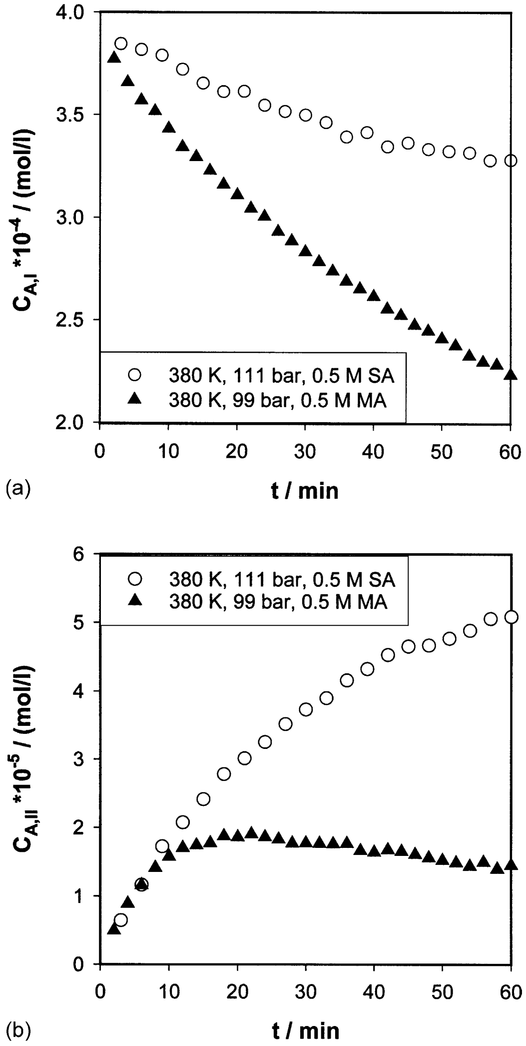

Fig. 5. (a) Change in concentration of 9-hydroxymethylanthracene at $c_{\mathrm{A,I,0}} = 0.38 \times 10^{-3}$ mol/l and 100 rpm in the organic phase for nonreacting system (0.5 M succinic acid) and reacting system (0.5 M maleic acid). (b) Change in concentration of 9-hydroxymethylanthracene at $c_{\mathrm{A,I,0}} = 0.38 \times 10^{-3}$ mol/l and 100 rpm in the aqueous phase for nonreacting system (0.5 M succinic acid) and reacting system (0.5 M maleic acid).

The relative ratio between the conversion in the layer adjacent to the interface (J_{IP}) and the overall conversion (J_{Total}) can be seen in Fig. 7a–c. While the temperature dependence is large, the pressure dependence is small. Between 100 and 200 rpm the dependence

Table 2
Parameter fitted for describing the change in concentration of 9-hydroxymethylanthracene with time in the organic (I) and aqueous phase (II) ($c_{A,I,0} = 0.38 \times 10^{-3}$ mol/l, $V_{II}/F = 5.5$ cm)

T (K)	p (bar)	Speed (rpm)	Phase II $\alpha \times 10^{-2}$	$\phi \times 10^{-4}$	$\lambda \times 10^{-3}$	Phase I ($\gamma \times 10^{-3}$)
380	99	100	0.2297	0.2327	0.1364	0.1368
	106	200	0.2224	0.3078	0.1632	0.1484
	120	300	0.2204	0.3401	0.1805	0.1557
	196	100	0.2320	0.1285	0.0654	0.0632
	167	200	0.2293	0.2153	0.0964	0.0944
	176	300	0.2264	0.2285	0.1214	0.1112
390	88	100	0.3967	0.2656	0.2225	0.2235
	93	200	0.3836	0.3733	0.2866	0.2880
	84	300	0.3479	0.5319	0.4060	0.3911
	177	100	0.3954	0.0949	0.1077	0.1103
	165	200	0.4001	0.1459	0.1348	0.1228
	187	300	0.3477	0.1774	0.1744	0.1294
400	94	200	0.6070	0.4431	0.4359	0.4415
	88	300	0.5935	0.4520	0.6694	0.5554
	170	100	0.7076	0.7744	0.1246	0.1284
	169	200	0.6804	0.1224	0.1515	0.1453

on stirring speed is large, whereas between 200 and 300 rpm it is smaller.

4.3. Description with two film — Hatta model

As predictions based on the simple film model, especially when a chemical reaction occurs, are usually similar to those based on more sophisticated models [3], we have applied the two film — Hatta model. Following the film-theory model and Hatta model [1,7], the molar flux of component A in the layer adjacent to the interface $J_{A,IP}$ is the difference between the molar flux of A from phase I into the layer adjacent to the interface $J_{A,in}$ and the molar flux of A from the layer adjacent to the surface in phase II $J_{A,out}$

$$J_{A,IP} = J_{A,in} - J_{A,out} \tag{8}$$

This is expressed by

$$J_{A,IP} = F\beta_{A,II}(c_{A,II} + c^{*}_{A,II})\ ((Ha(\cosh(Ha) - 1)/(\sinh(Ha))) \tag{9}$$

This molar flux $J_{A,IP}$ is the rate of conversion in the layer adjacent to the surface. Here F is the area of interphase between two fluids, $\beta_{A,II}$ the physical mass-transfer coefficient and can be determined from the change in concentration of A (without chemical reaction) by

$$\beta_{A,II} = \frac{V_{II}}{F}\frac{\partial c_{A,II}}{\partial t}\frac{1}{(c_{A,I}/K_A) - c_{A,II}} \tag{10}$$

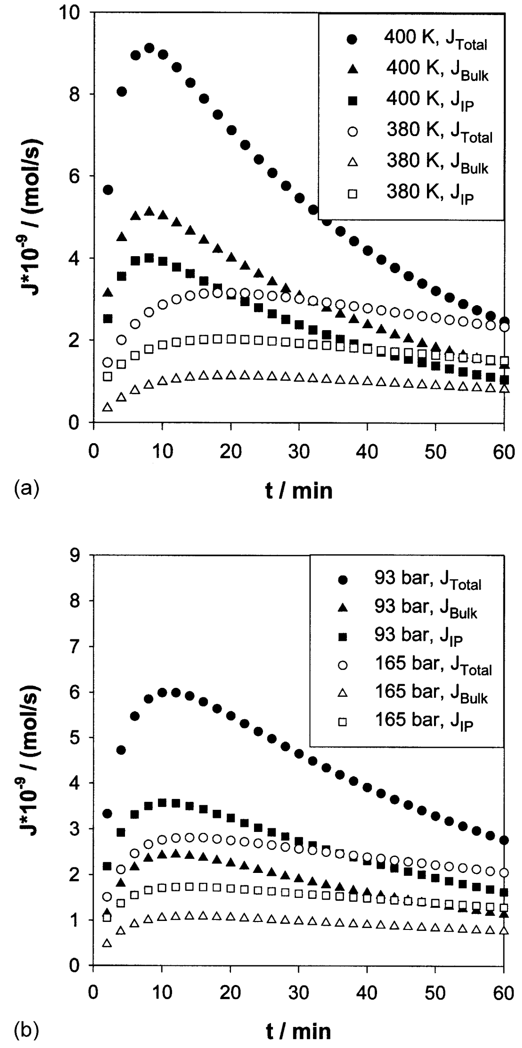

Fig. 6. (a) Comparison of the total molar flux (J_{Total}), the portion of chemical conversion occurring in bulk (J_{Bulk}) and in the layer adjacent to the interface (J_{IP}) at two different temperatures (p = 94 bar, 200 rpm, $c_{A,I,0} = 0.38 \times 10^{-3}$ mol/l, $V_{II}/F = 5.5$ cm). (b) Comparison of J_{Total}, J_{Bulk} and J_{IP} at two different pressures (T = 390 K, 200 rpm, $c_{A,I,0} = 0.38 \times 10^{-3}$ mol/l, $V_{II}/F = 5.5$ cm).

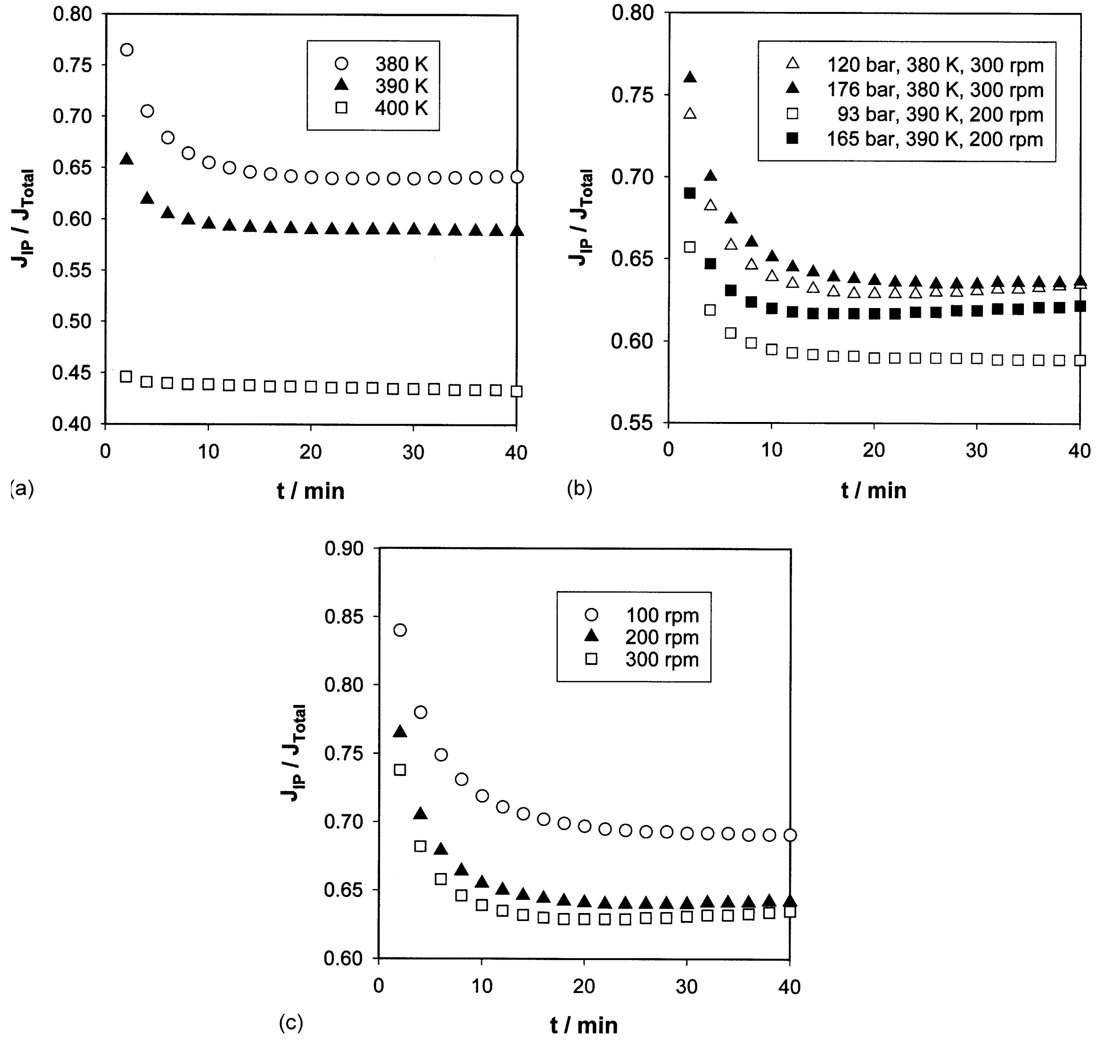

Fig. 7. (a) Change of relative ratio between the portion of chemical conversion occurring in the layer adjacent to the interface (J_{IP}) and the total molar flux (J_{Total}) at different temperatures (200 rpm, $p = 94$ bar, $V_{\mathrm{II}}/F = 5.5$ cm). (b) Change of relative ratio between J_{IP} and J_{Total} at different pressures and at 380 and 390 K ($V_{\mathrm{II}}/F = 5.5$ cm). (c) Change of relative ratio between J_{IP} and J_{Total} at different stirring speeds ($T = 380$ K, $p = 106$ bar, $V_{\mathrm{II}}/F = 5.5$ cm).

Fig. 8 shows the comparison of the portion of conversion in the layer adjacent to the interface (J_{IP}) determined by material balances (Eq. (5)) with the two film — Hatta model (Eq. (9)). The two film — Hatta model could not describe correctly the behavior in the beginning of the batch process. The quasi-stationary assumption of the model is apparently in valid, because some time (t_{s}) to rise the bulk concentration of A ($c_{\mathrm{A,II}}$) from zero to a specified value (the steady-state value) is required [6,14]. After approximately 10 min time on stream the agreement is very good. The values of *Ha* show that the investigated reaction is a moderately fast reaction with respect to the mass transfer. Thus, the reaction is sufficiently slow to allow some A to diffuse through the film into the main body of the fluid. As a consequence, reactant A reacts within the film and in the main body of the fluid.

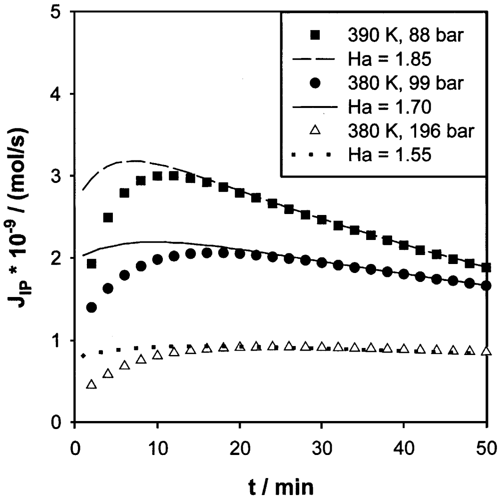

Fig. 8. Comparison of portion of conversion in the layer adjacent to the interface (J_{IP}) determined by material balance (Eq. (5)) and by two film — Hatta model (Eq. (9)) (100 rpm stirring speed, $V_{\mathrm{II}}/F = 5.5\,\mathrm{cm}$).

5. Conclusion

A two-phase stirred cell for high pressures and temperatures was constructed and built with the online-analytical equipment for UV-spectroscopy. It was proven that the setup allows to measure the influence of pressure, temperature and stirring speed on the overall rate of reaction in a two-phase fluid/fluid system. As model system the Diels–Alder reaction between 9-hydroxymethylanthracene and maleic acid was chosen in the solvent pair supercritical propane/water. The overall rate increases with rising temperature, decreasing pressure (because of the equilibrium solubility of the reactants) and increasing stirring speed. However, at low pressures the solubility of A in supercritical propane is very small. Thus, only low initial concentrations of A are possible, resulting in a small capacity of the reactor. From the changes in the concentration of reactants the portions of conversion in the layer adjacent to the interface (J_{IP}) were determined. The relative ratio between J_{IP} and J_{Total} varies much with changing the temperature but only slightly with changing the pressure. Low stirring speeds have a large effect while the ratio is influenced only slightly at higher stirring speeds. Except in the beginning of the batch process the two film — Hatta model could describe well the portions of conversion in the layer adjacent to the interface. The formulation (Eqs. (6) and (7)) for describing the changes in concentration of reactants in the two phases is very general and can be used to describe a large number of fluid/fluid reactions.

Acknowledgements

Financial support of the Deusche Forschungsgemeinschaft is gratefully acknowledged. We especially wish to thank Prof. Dr. Friedrich Kohler (Ruhr-Universittät Bochum), Prof. Dr. Walter Nitsch and Prof. Dr. Erwin Killmann (Technische Universität München) for many helpful discussions.

Appendix A. Description of the change in concentration of reactants

Our model for aqueous phase (II) is expressed by

$$\mathrm{d}c_{\mathrm{A,II}} = (\beta^{+}_{\mathrm{A,II}}(c^{*}_{\mathrm{A,II}} - c_{\mathrm{A,II}}) - k^{+}_{\mathrm{II}}c_{\mathrm{A,II}})\,\mathrm{d}t \tag{A.1}$$

Here t is the time, $c_{\mathrm{A,II}}$ the concentration of A in aqueous phase, $\beta^{+}_{\mathrm{A,II}} = (F/V_{\mathrm{II}})\beta_{\mathrm{A,II}}$ (where $\beta_{\mathrm{A,II}}$ is the aqueous-side mass-transport coefficient per unit of F/V_{II}), $c^{*}_{\mathrm{A,II}}$ the equilibrium concentration of A, $k^{+}_{\mathrm{II}} = k_{\mathrm{II}}\,c_{\mathrm{B,II}}$ the pseudo-chemical rate constant in aqueous phase. Under boundary conditions (for $t = 0$: $c_{\mathrm{A,II}} = 0$) we obtained the following equation:

$$\begin{aligned} c_{\mathrm{A,II}} &= (1 - \exp(-(\beta^{+}_{\mathrm{A,II}} + k^{+}_{\mathrm{II}})t)) \\ &\quad \times \beta^{+}_{\mathrm{A,II}}c_{\mathrm{A,II}}/(\beta^{+}_{\mathrm{A,II}} + k^{+}_{\mathrm{II}}) \end{aligned} \tag{A.2}$$

The molar flux of 9-hydroxymethylanthracene from the organic phase into the aqueous phase consists of two parts: reaction in the layer adjacent to the interface and the diffusion to the bulk of phase II. The later flux is equivalent to the loss of A by reaction in the aqueous phase. Eq. (A.3) expresses the condition for a pseudo steady-state in means of a slow variation in $c_{\mathrm{A,II}}$ (in Eq. (A.1) $\mathrm{d}c_{\mathrm{A,II}}/\mathrm{d}t$ is small and in Eq. (A.2) t is very large ($t \to \infty$)):

$$\beta^{+}_{\mathrm{A,II}}(c^{*}_{\mathrm{A,II}} - c_{\mathrm{A,II}}) = k^{+}_{\mathrm{II}}c_{\mathrm{A,II}} \tag{A.3}$$

The molar flux $\beta^{+}_{\mathrm{A,II}}(c^{*}_{\mathrm{A,II}} - c_{\mathrm{A,II}})$ can be expressed by

$$\begin{aligned}&\beta^{+}_{\mathrm{A,II}}(c^{*}_{\mathrm{A,II}}-c_{\mathrm{A,II}})\\&\quad=\beta^{+}_{\mathrm{A,II}}c^{*}_{\mathrm{A,II}}(1-(\beta^{+}_{\mathrm{A,II}}/(\beta^{+}_{\mathrm{A,II}}+k_{\mathrm{II}})))\\&\quad=k^{+}_{\mathrm{II}}c^{*}_{\mathrm{A,II}}=k^{+}_{\mathrm{II}}c^{*}_{\mathrm{A,I}}/K_{\mathrm{A}}\end{aligned}\tag{A.4}$$

Here K_{A} is the phase equilibrium coefficient of A between phases I and II. Then the rate of concentration A in phase I is

$$\mathrm{d}c_{\mathrm{A,I}}=\left(-k_{\mathrm{I}}\,c_{\mathrm{A,I}}-k^{+}_{\mathrm{II}}\frac{c_{\mathrm{A,I}}}{K_{\mathrm{A}}}\right)\mathrm{d}t$$

Or

$$c_{\mathrm{A,I}}=c_{\mathrm{A,I,0}}\exp(-\gamma t)\tag{A.5}$$

Where

$$\gamma=k_{\mathrm{I}}+(\beta^{+}_{\mathrm{A,II}}k^{+}_{\mathrm{II}}/((\beta^{+}_{\mathrm{A,II}}+k^{+}_{\mathrm{II}})K_{\mathrm{A}}))\tag{A.6}$$

The first term in Eq. (A.6) is the rate constant in the organic phase (here in the layer adjacent to interface) and the second term is the transport into the aqueous phase. Considering slow variations of $c_{\mathrm{A,II}}$ in t we obtain Eq. (A.7) for $c_{\mathrm{A,II}}$ in phase II from Eq. (A.2):

$$c_{\mathrm{A,II}}=(1-\exp(-\alpha t))\phi\exp(-\gamma t)\tag{A.7}$$

where

$$\alpha=\beta^{+}_{\mathrm{A,II}}+k^{+}_{\mathrm{II}}\tag{A.8}$$

$$\phi=\beta^{+}_{\mathrm{A,II}}c_{\mathrm{A,I,0}}/((\beta^{+}_{\mathrm{A,II}}+k^{+}_{\mathrm{II}})K_{\mathrm{A}})\tag{A.9}$$

$$\lambda=k_{\mathrm{I}}+(\beta^{+}_{\mathrm{A,II}}k^{+}_{\mathrm{II}}/((\beta^{+}_{\mathrm{A,II}}+k^{+}_{\mathrm{II}})K_{\mathrm{A}}))\tag{A.10}$$

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