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Interaction of a homogeneous chemical reaction and mass transfer in a single moving droplet

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HIGHLIGHTS

- Experimental investigation of unsteady mass transfer with a chemical reaction.
- Comparison of experimental and simulated mass transfer coefficients.
- CFD describes interactions between mass transfer and chemical reaction accurately.
- Addition rule shows a reasonable approximation of the Sherwood number only for short contact times.

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ABSTRACT

Mass transfer with a superimposed homogeneous chemical reaction was investigated in the system cyclohexanol (continuous phase)/methyl chloroacetate (transferred component)/sodium hydroxide (dispersed phase). The unsteady mass transfer was measured applying a counter current flow cell for single droplets. The obtained experimental data were compared with CFD simulations, which already have been used successfully for a single drop system with a very fast homogeneous chemical reaction. In this paper the investigated system was selected to be in a regime where the rates of mass transfer and chemical reaction are in the same order of magnitude, so none of them can be considered rate-determining. Additionally, numerical simulations were carried out in order to quantify the results of the interactions between mass transfer and chemical reaction for the specific system.

1. Introduction

The unsteady interfacial mass transfer at single droplets in general is an important aspect for the design of extraction columns in industry. Many scientific publications neglect the mass transfer resistance either in the continuous phase (internal problem) or in the dispersed phase (external problem) and only a few consider both the resistances as a conjugate problem (Ruckenstein, 1967; Brauer, 1978a, 1978b; Kleinman and Reed, 1996; Bäumler et al., 2011). Moreover, the mass transport can be superimposed by interfacial phenomena, e.g., Marangoni convection (Wegener et al., 2007, 2009a, 2009b; Wegener and Paschedag, 2011) or by a chemical reaction (Jeon et al., 2011; Juncu, 2002, 2006; Kleinman and Reed, 1996; Pawelski et al., 2005). Most investigations aim to provide an accurate CFD simulation as well as analytical correlations which are able to predict mass transfer rates in different physical systems accurately allowing an easier and less cost-intensive scale-up of extraction processes. The main difficulty in predicting unsteady mass transfer in parallel with a homogeneous chemical reaction inside a droplet is the time dependent change of resistances in both the phases.

Chemical reactions that lead to a significant mass transfer enhancement are in the focus of this study. The resulting mass transport cannot be predicted by simply neglecting the influence of either mass transfer or reaction on the total mass flux. This paper analyses the complex interactions between mass transfer and chemical reaction experimentally as well as numerically. In the chosen system no macroscopic effects of the Marangoni convection occurred due to the high viscosity of the continuous phase. Experiments were carried out with a mass transfer cell for

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single droplets allowing measurements of mean concentrations within the droplet after a well defined contact time. The data obtained with these experiments was then compared directly with numerical results and with an a priori prediction of the mass transfer rate based on the physico-chemical data of the homogeneous reactive system.

Alkaline hydrolysis of a short chain ester was considered as a model reaction system for these complex interactions. The alkaline hydrolysis of these esters is a well known quantitative second order reaction (Nanda and Sharma, 1967). The reactivity of the esters is significantly increased when the alkyl chain is halogenated. Since the common ethyl acetate and butyl acetate show rather slow reaction rates halogenated compounds like methyl chloroacetate (MCA) and methyl tri-chloroacetate were tested (Sharma, 1983; Brunt and Kanel, 2002). In the case of methyl-tri-chloroacetate, a strong side reaction with water was observed complicating the experimental analysis. On the other hand MCA is showing a negligible side reaction with water and the ratio of reaction to diffusion rate indicates that the rates of mass transfer and reaction are almost in the same order of magnitude. Furthermore, the mass transfer process at a single droplet reaches 90% of the equilibrium concentration in about 20–25 s under the chosen initial concentration, which allows experimental analysis in the mass transfer cell with counter current flow.

Numerical studies on conjugate mass transfer with a second order reaction have been carried out by Juncu (2002, 2006) for a small Peclet number $Pe = 100$ in a study varying parameters like e.g., Reynolds number, diffusivity ratio and Hatta modulus. The investigated system in this work shows a higher Peclet number of about $Pe = 94{,}000$, which is in a more typical range for a technical extraction process. However, the simulation of higher Peclet numbers requires a fine resolution of the discretisation grid to prevent numerical diffusion typically resulting in an overestimation of the asymptotic Sherwood number. Usually the validation of numerical results is realised by comparison with theoretical values or well known empirical equations.

2. Material and methods

Fig. 1 shows a scheme of the single drop test cell which was used to measure the mass transfer between dispersed and continuous phase. Therefore, the mean concentration in the droplet (aqueous NaOH solution) was determined for various contact times with the continuous phase (cyclohexanol). As depicted in this figure, the dispersed phase was injected through a nozzle by a small scale precision pump 3 forming droplets of highly reproducible size. NaOH concentrations inside the droplets were always set in excess to the amount of transferred MCA. The continuous organic phase was recirculated with pump 1 establishing a counter current flow to the dispersed phase and stopping the settling of the droplet in a glass cone. After a defined contact time the recirculation was switched off and the droplet settled down to the bottom of a glass funnel where it coalesced with the aqueous phase. With a second precision pump 2, a sample from the aqueous phase in the funnel was collected, diluted with cyclohexanol saturated water and analysed by a conductivity probe. A calibration curve was used to determine the concentration of NaOH in the dispersed phase from the measured conductivity. Due to the complete dissociation of the base as well as the high specific conductivity of the hydroxide ion this method is very accurate. 300 droplets were collected to reach a sufficient sample volume for one measuring point. All pumps were fully automated and controlled by a PC.

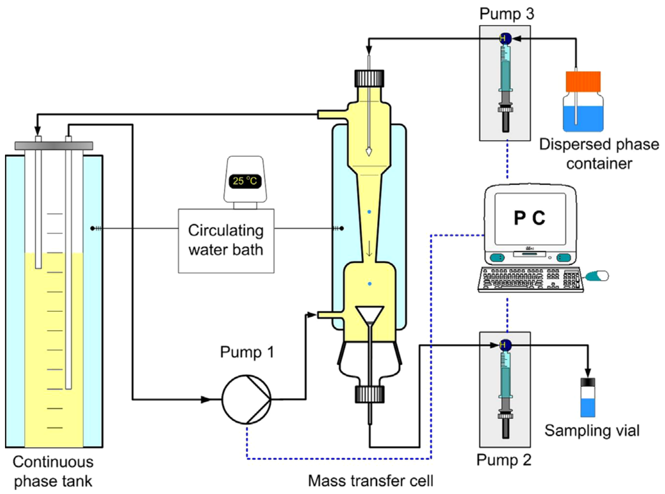

Fig. 1. Schematic flow diagram of the experimental setup of the mass transfer cell.

For contact times longer than the time between drop formation, which was held constant at 6 s for all experiments, two or more drops underwent mass transfer in the counter current flow cell at the same time. For this purpose a continuous counter current flow was set with a decreased flow velocity. Thereby the drops were slowed down but not stopped during their sedimentation in the funnel. The single droplets had a physical distance from each other in the test cell equivalent to 6 s sedimentation time. This operating mode allowed a significant reduction of the time required to collect the necessary sample volumes. By comparison with single drop experiments no effect on the mass transfer was found for more droplets in the system under these specific operating conditions.

2.1. Preparation procedure

Methyl chloroacetate (MCA ≥ 99%) and cyclohexanol (≥ 99%) were purchased (Merck KGaA) and used without further purification. Both the organic and the deionised aqueous phase were saturated with deionised water and cyclohexanol respectively to avoid mass transfer of the pure carrier components, while investigating the sole mass transfer of MCA from the continuous organic phase to the dispersed aqueous phase.

2.2. Distribution coefficient measurement

A defined quantity of MCA was dissolved in 50 mL of water saturated cyclohexanol. The same amount of cyclohexanol saturated water was added and the two phase system was stirred for 3 h at 25 °C. After phase separation 25 mL of the aqueous phase were treated with a defined amount of NaOH solution. The conductivity of the resulting solution was measured and used to determine the MCA concentration of the aqueous sample before undergoing the hydrolysis reaction with NaOH. The MCA concentration of the aqueous phase together with the initial MCA concentration allows the calculation of the equilibrium concentration and the distribution coefficient

$$K = c_{aq}/c_{org}. \tag{1}$$

2.3. Kinetic measurement

The hydrolysis reaction of MCA is described as

$$ClC_2H_2O_2Me + NaOH \rightarrow MeOH + ClC_2H_2O_2Na \tag{2}$$

The reaction rate constant was obtained from a batch reaction experiment. While 220 mL of a NaOH solution were stirred, 30 mL of an aqueous MCA solution with a defined concentration (0.8 eq.)