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The capillary-microreactor: a new reactor concept for the intensification of heat and mass transfer in liquid–liquid reactions

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Abstract

The capillary-microreactor was used for studying the nitration of a single ring aromatic in an exothermic liquid–liquid two-phase reaction. In the capillary-microreactor, isothermal behaviour can be assumed due to the high heat transfer rates. In addition, a liquid–liquid two-phase plug-flow with a well-defined flow pattern of alternating plugs of the two phases is formed, giving a constant, uniform specific surface area for mass transfer between the two phases. In the nitration reaction, not only the mononitrated main product is formed, but also various by-products via consecutive and parallel reactions. Mass transfer experiments with different flow velocities, but identical residence times, carried out in the capillary-microreactor, yielded differences in conversions and the amounts of by-products formed. Simulations using a mathematical model describing interphase mass transfer and homogeneous chemical reaction indicate increasing mass transfer coefficients at higher flow velocities, suggesting that the mass transfer between the two phases is enhanced by the flow velocity. The enhancement of the mass transfer can be interpreted in terms of an internal circulation flow within the plugs, a conclusion corroborated by CFD calculations. The capillary-microreactor has thus proved to be a useful instrument for the quantitative elucidation of the mechanisms of exothermic liquid–liquid two-phase reactions.

Keywords: Process intensification; Microreactor; Capillary flow; Liquid–liquid flow; Nitration

1. Introduction

In the chemical industry numerous reactions are carried out on a large scale which are both strongly exothermic and involve two-phase liquid–liquid systems as a result of the immiscibility of the participating fluids. Unambiguously resolving the contributions of the reaction kinetics and the mass transfer between the phases in such systems is something of a challenge, since mass transfer and the homogeneous reaction in one of the liquid phases occur simultaneously and are intimately linked. Nevertheless, a

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precise determination of the individual effects is essential for reliably predicting the performance of the two-phase liquid–liquid reaction system as a whole under a wide range of conditions.

An industrially relevant nitration of a single ring aromatic was selected as an appropriate test case for an exothermic two-phase liquid–liquid reaction, in which the aqueous phase is comprised of nitration acid—a mixture of concentrated sulphuric and nitric acids.

In this work, the nitration reaction chosen was investigated in a capillary-microreactor, similar to a device proposed by Burns and Ramshaw [1,2] for studying the nitration of various organic compounds. Such capillary-microreactors are eminently suitable for research on exothermic two-phase liquid–liquid reactions by virtue of the uniform structured flow and isothermal temperature profile resulting from the narrow capillary diameter.

2. Experimental method

The basic arrangement of the capillary-microreactor, in which the experimental studies on the nitration of the single ring aromatic were carried out, is depicted in Fig. 1.

Both the aromatic component and the premixed nitration acid were introduced by continuously operating high-precision piston pumps into a Y-piece mixing element, with an angle of 120° between the uniform cylindrical inlet channels of 0.5 to 1.0 mm lumen.

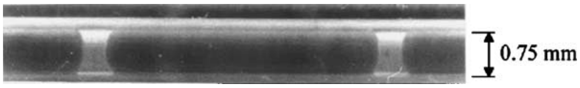

Fig. 2. Liquid–liquid two-phase plug-flow with plugs of nitrating acid (stained) and organic phase (colourless) in a capillary-microreactor of 0.75 mm diameter.

The capillary-microreactor is attached directly downstream of the Y-piece and consists of a PTFE capillary also having a diameter of 0.5 to 1.0 mm surrounded by a thermostatted jacket. This jacket is maintained at a uniform temperature in the range of 60 to 120 °C by a high countercurrent flow of silicone oil. The heat liberated by the strongly exothermic reaction is removed very effectively owing to the excellent heat transfer achieved, which is mainly due to the small diameter of the capillary and the resulting high specific surface area. The nitration of the aromatic can thus be carried out under isothermal conditions in spite of the highly negative value of the reaction enthalpy. This feature is a fundamental prerequisite for unambiguous measurements on the homogeneous reaction kinetics.

The second characteristic of the capillary-microreactor that makes it especially suitable for investigating two-phase liquid–liquid reactions is the formation of a stable two-phase plug-flow pattern for the immiscible liquids, previously described by Irandoust et al. [3], as illustrated in Fig. 2. This flow pattern ensures a uniform specific interfacial area, thus fulfilling a basic requirement for reliably determining mass transfer behaviour. The extensive investigations on the

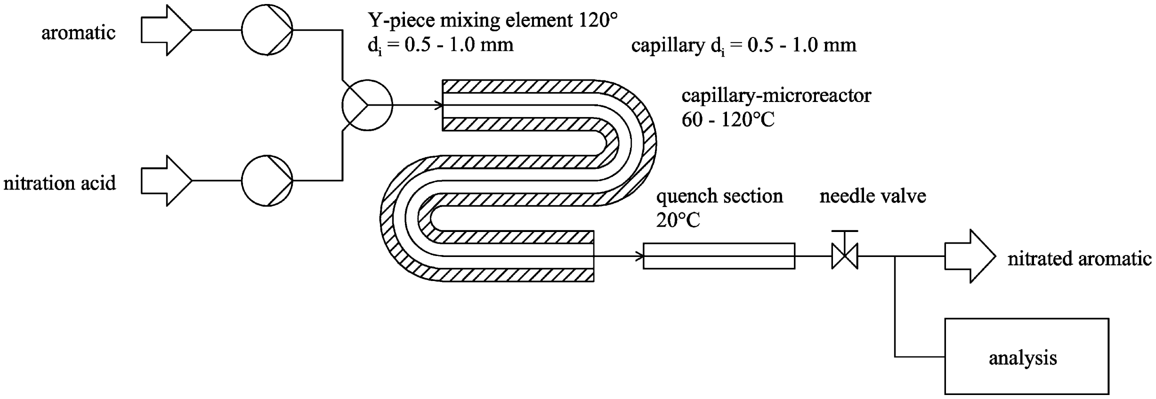

Fig. 1. Experimental set-up of the capillary-microreactor system.

two-phase flow in the capillary-microreactor are described in Section 3.

Following the thermostatted section of the capillary-microreactor with a length of between 1 and 8 m, there is a short quench section, in which the reacting liquid–liquid mixture is rapidly cooled to 20 °C to stop the reaction. A needle valve after the quench section serves to release the pressure from the slight excess of around 4 bar, at which the reactor is operated to avoid formation of gas and vapour bubbles, down to ambient pressure for analytical sampling.

Sampling takes place directly after the needle valve. The addition of cooled water brings the reaction to a complete stop by both cooling and dilution of the nitration acid. The composition of the organic phase is determined by gas chromatography following appropriate preparation. The levels of the reactant, the main product and the major by-products down to trace concentrations are analysed. Standards are added to the samples to facilitate the evaluation of the GC results.

3. Results and discussion

3.1. Two-phase liquid–liquid plug-flow

As described in the preceding experimental section, a two-phase plug-flow of the immiscible nitration reactants arises in the capillary-microreactor. Fig. 2 shows a photograph of this two-phase plug-flow in a capillary of 0.75 mm diameter taken under the microscope. To better visualise the two phases, the aqueous phase has been stained to appear darker than the colourless organic phase.

The individual alternating plugs of the aqueous and organic phase flowing down the capillary-microreactor are clearly identifiable. The photographic evidence shows that the two-phase flow is comprised of a uniform sequence of plugs of uniform size. The difference in volumes between the plugs of the two phases corresponds to the ratio of the phases in the industrial process and only depends on the ratio of the volumetric flows from the two connected feed pumps.

Further studies of the two-phase plug-flow indicate that for constant volumetric flow rate the volume of the individual plugs formed in the Y-piece mixing element are dictated only by the diameter of the Y-piece channels. Reducing the channel diameter diminishes the volume of the plugs and thus increases the specific interfacial area for mass transfer. The capillary downstream of the mixing element simply stabilises the plugs formed and determines the length of the plugs by imposing a given diameter. For narrower capillaries, the diameter of the plugs necessarily becomes lower and the plugs are elongated as a consequence, their volume remaining constant while the specific interfacial area is reduced.

The statistics of plug size distribution were an important feature of the capillary-microreactor that needed to be clarified in advance for the reaction system being investigated. Using numerous photographs taken under the microscope, the dimensions of individual plugs were measured and the corresponding volumes calculated. Fig. 3 shows the distribution of the plug size of the organic phase and indicates that the plug volumes only deviate by around ±5% from the mean value and the two-phase flow consists of uniform alternating plugs. Due to the constant size of the plugs, the flow in the capillary-microreactor exhibits an interfacial area between the immiscible liquid which is also constant and, furthermore, well defined.

3.2. By-product formation

In the nitration of single ring aromatics with nitration acid several side reactions occur in addition to the main reaction as illustrated in Fig. 4. The nitration of the single ring aromatic (A) primarily yields the desired mononitrated product (B). Additionally dinitrated by-products (C) and phenolic by-products (D) are also formed. The dinitrated by-products (C) represent consecutive reaction products of the mononitrated component (B) due to further nitration.

Based on the reaction mechanism postulated by Titov and Bennett, described by Hanson et al. [4], it can be assumed that the phenolic by-products (D) are not formed via a consecutive reaction of the mononitrated component (B), but arise rather through reaction of the single ring aromatic (A) in a pathway parallel to the main nitration route (1).

Our own studies on the nitration of various substrates confirm the mechanism proposed. Analysing the by-products formed during the nitration of the aromatic reactant (A) showed that, even after a relatively short residence time of 4.42 min at 120 °C, considerable amounts of dinitrated phenolic by-products (C)

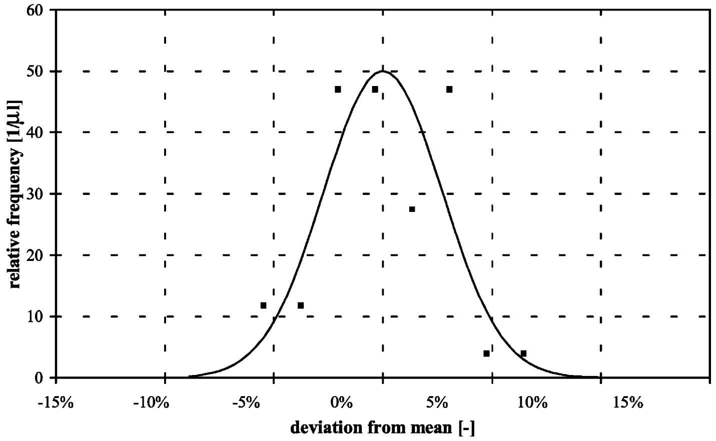

Fig. 3. Plug size distribution for organic phase.

are present, as can been seen in the chromatogram depicted in Fig. 5a. For the nitration of the mononitrated component (B), i.e. the primary product of the original main reaction, as starting material, no phenolic by-products could be detected even after 20 min at the same temperature of 120 °C as shown in the chromatogram illustrated in Fig. 5b. Higher amounts of dinitrated by-products (C) and even the trinitrated by-product were formed at such high reaction times.

The variation of the organic substrate thus proved that that the di- and trinitrated by-products are produced in a consecutive reaction of the main product (B), while the phenolic by-products are formed in a parallel reaction to this primary product.

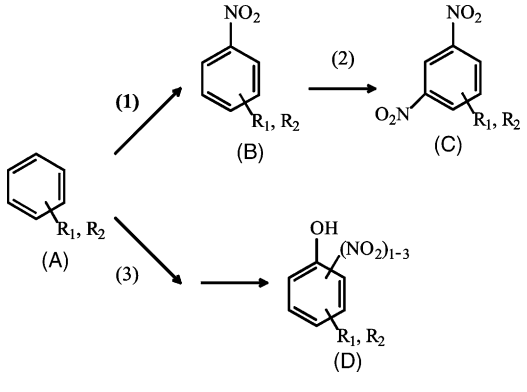

Fig. 4. Reaction scheme of the nitration of a single ring aromatic (A) to the mononitro compound (B), dinitrated by-products (C) and phenolic by-products (D).

3.3. Temperature dependence

The temperature dependence of the main and side reactions were studied in initial experiments on the nitration of the aromatic component. In Fig. 6, the results from two experiments carried out at different temperatures and residence times are compared with respect to conversion and dinitrated/phenolic by-product yields.

The first experiment was carried out in a 4 m long capillary with 0.75 mm diameter at 60 °C and the second in a 1 m capillary also of 0.75 mm diameter at 120 °C. The conversion of around 50% achieved in both experiments is roughly similar, if slightly higher in the 60 °C experiment. The by-product levels differ dramatically however: the experiment at the lower temperature yielding considerably less by-product. One can thus draw the conclusion, that the activation energies of the side reactions ((2), (3)) must be higher than that of the main reaction (1) to the mononitrated product (B).

3.4. Interphase mass transfer

The influence of the linear flow velocity, as opposed to the volumetric flow, of the two-phase plug-flow on conversion and by-product levels was of particular interest in the investigations of single ring aromatic nitration. To this end, a 0.75 mm capillary of several lengths was operated at 120 °C and with different volumetric throughputs to give a constant residence time of 2.95 min, but at differing linear flow velocities and

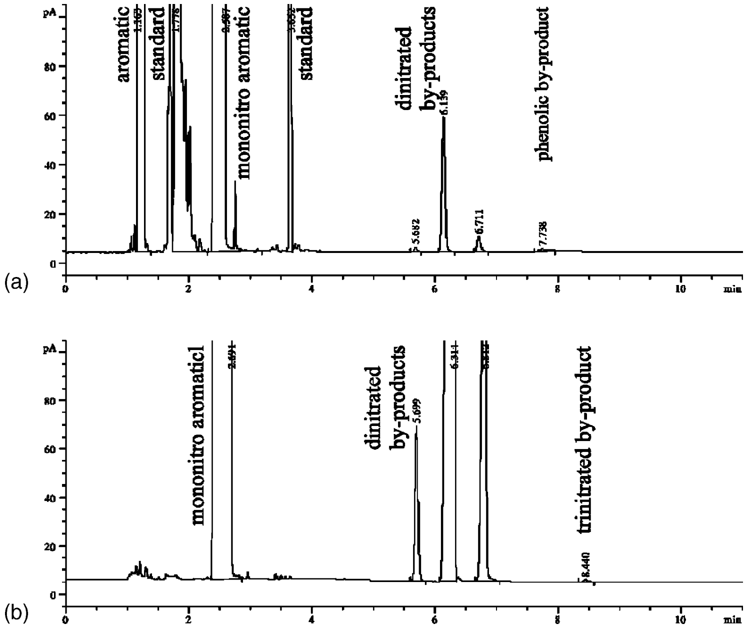

Fig. 5. (a) By-products of single ring aromatic (A) nitrations; (b) by-products of mononitro component (B) nitration.

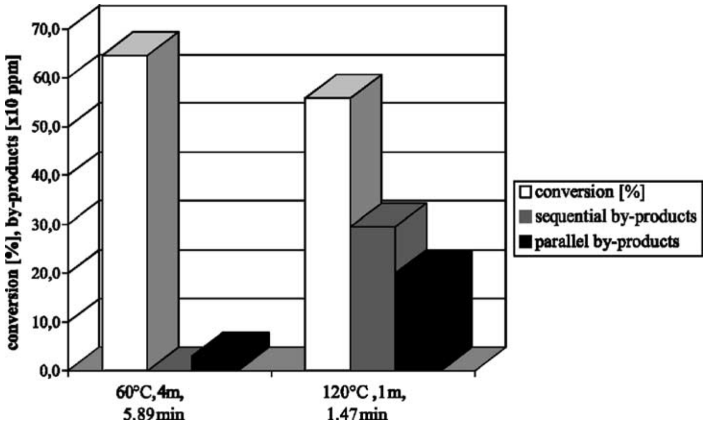

Fig. 6. Conversion and by-product levels at different reaction temperatures.

the conversion achieved together with the concentrations of dinitrated and phenolic by-products were monitored. The values of the volumetric throughputs and capillary lengths employed are listed in Table 1.

Fig. 7 shows the results of these experiments at various linear flow velocities. The results clearly demonstrate that the linear flow velocity in the capillary-microreactor exerts a direct influence on both conversion and the level of by-products formed.

Table 1
Volumetric throughput, capillary length and resultant residence time in mass transfer experiments

Volumetric flow (ml/h)	Capillary length (m)	Residence time (min)
9.0	1.0	2.95
18.0	2.0	2.95
27.0	3.0	2.95
36.0	4.0	2.95

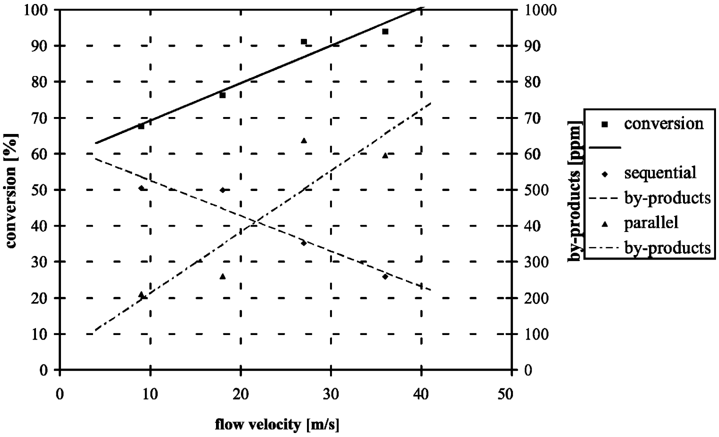

Fig. 7. Dependence of conversion and the amounts of dinitrated (C) and phenolic by-products (D) on flow velocity ($T = 120\,^{\circ}\mathrm{C}$, $t = 2.95\,\mathrm{min}$).

The conversion increases with increasing velocity, which can be explained by an enhancement of the mass transfer, thus indicating that the reaction rate observed is limited by mass transfer.

Like the conversion, the amount of phenolic by-products (D) also increases at higher flow velocities. This increase can be explained by the fact that the side reactions responsible, as described in the section about the by-product formation, take place in parallel to the main reaction and are thus profit similarly from an intensification of interphase mass transfer.

In contrast to the conversion and phenolic by-products, the level of dinitrated components (C) falls with increasing flow velocity. This decrease also results from the enhanced mass transfer at higher flow velocities, since the intensified interphase transport not only improves the mass transfer of reactant into the reaction phase but also augments the extraction of the products and intermediates back out of this phase.

3.5. Reactor modelling and computational fluid dynamics modelling

In order to better understand the course of the reaction process between the organic and aqueous plugs, a reactor model was developed, considering both the mass transfer of organic components between the two phases and the homogeneous reaction occurring within the aqueous phase, which had also been studied previously by Zaldivar et al. [5,6].

With the help of this model, the results of the experiments at different flow velocities could be reproduced and corresponding values of a mass transfer coefficient based on the plug end interfacial area derived for each of the various flow velocity values employed. The values of this mass transfer coefficient as a function of flow velocity are illustrated in Fig. 8.

As already discussed in the context of the experimental results, the mass transfer coefficient rises with increasing flow velocity. Using an extended kinetic model that contained the kinetics of the homogeneous side reactions, in addition to those of the main reaction derived from the literature, kinetic parameters for the formation of dinitrated (C) and phenolic by-products (D) could also be estimated. This modelling work yielded the much higher values of the activation energies for the side reactions than for the main reaction as had been anticipated from the considerations given earlier in the temperature dependence section.

To further investigate the two-phase flow arising in the capillary-microreactor, computational fluid dynamics simulations were carried out with FEMLAB software. Fig. 9 shows an aqueous plug in the two-phase flow in which an internal circulation pattern is induced by the motion of the plug down the capillary combined with the alternating phase distribution within the capillary. The intensity of this circulation and of mass transfer at the terminal interfacial

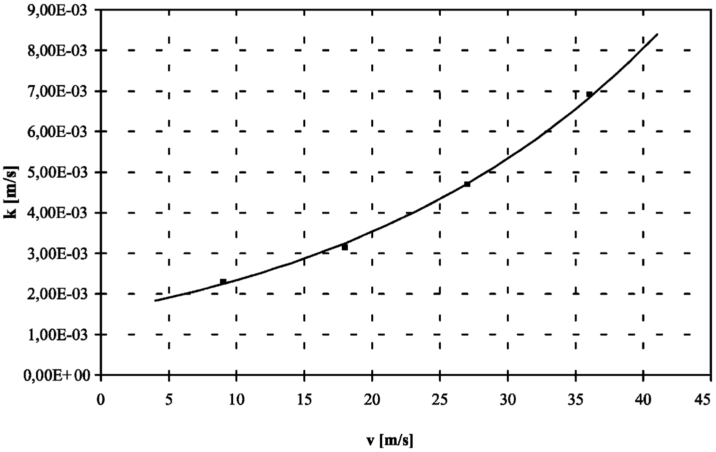

Fig. 8. Interphase mass transfer coefficient obtained from reaction engineering model.

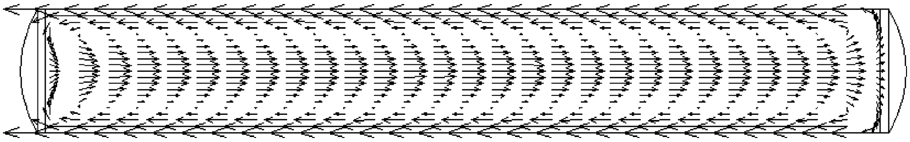

Fig. 9. Internal circulatory flow within an aqueous phase plug.

surfaces is in accordance with the experimentally observed enhancement of mass transfer with increasing flow velocity.

4. Conclusions

The investigation of the nitration of a single ring aromatic has demonstrated, that the capillary-microreactor is an eminently suitable instrument for quantitatively examining exothermic liquid–liquid reaction systems by virtue of the completely isothermal reaction conditions and the well-defined two-phase plug-flow. Closer examination of the two-phase plug-flow arising in the capillary-microreactor revealed that it is comprised of uniformly sized plugs giving a constant specific interfacial area between the two immiscible phases.

An increase in the flow velocity in the capillary-microreactor led to a rise in the conversion of the nitration reaction, clearly indicating the mass transfer limited nature of the reaction process. The simple reactor model used together with computational fluid dynamic simulations suggest that the increased flow velocity enhances mass transfer by inducing a stronger internal circulation within the individual plugs.

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