Synthesis of Ionic Liquids in Microstructured Reactors – a Brief Introduction

H. Loewe*

Johannes Gutenberg University Mainz, Institute of Organic Chemistry, Chemical Micro Process Technology, Duesbergweg 10-14, 55128 Mainz, Germany

IMM Institut fuer Mikrotechnik Mainz GmbH, Carl-Zeiss-Str. 18-20, 55129 Mainz, Germany

* email: loewe@uni-mainz.de

The synthesis of Ionic Liquids (ILs) looks simple on a first sight. Mostly an amine reacts with an alkylating agent to a quaternary ammonium salt and the pathway of this reaction indicates that remarkable formation of unwanted side products is not expected, and purification by recrystallization from a suitable solvent is possible if necessary. In the case of ILs however, contrary to simple ammonium salts, cannot easily purified neither by recrystallization nor by distillation due to their physical properties. Nonetheless, the synthesized ILs have to be on highest grade quality even as raw product.

Remarks on the conventional way of ILs syntheses

The synthesis of ILs, especially from 1-alkyl-imidazole, suffers from the extreme heat release of this typically very fast reaction. By using standard batch procedure this reaction is hard to control. Normally, an alkylating agent is added drop wise to the bulky amine in the vessel to avoid hot-spots and to ensure a constant reaction temperature. How fast the temperature rise can be is given in Fig.1. To a stirred small glass vessel containing 0.065 mol 1-methyl-imidazole (room temperature) an equimolar amount of a) diethyl sulfate or b) trifluoromethyl-sulfonic acid methyl ester (triflate) was added and the temperature was measured by thermocouples. By using diethyl sulfate an induction period can be observed followed by a steep temperature rise. In the case of methyl-triflate as alkylating agent, the reaction takes place immediately, and it can be assumed that the measured temperature value is lower than the real hot-spot. Too high temperatures and too long reaction times are common reasons for low product quality, discoloration and possible polymerization.

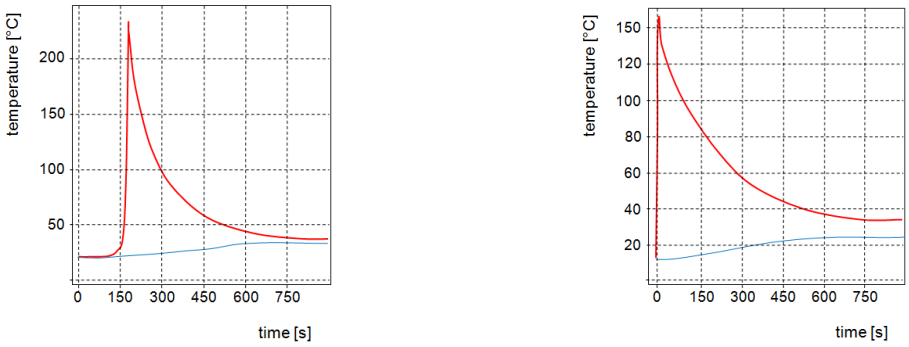


Fig.1: Temperature rise for equimolar (0.065 mol) reaction of 1-methyl-imidazole with diethyl sulfate (left) and methyl- triflate (right). The blue line indicates the temperature change of the heat transfer liquid in the thermostat. The temperature sampling rate is 1 per second.

If the temperature is set too low by intense cooling, the reaction slows down and it can take hours or days until completion. Also, due to a phase separation, the reaction can shift from a single to a two phase system[1] and vigorous stirring is necessary to form large enough interfacial area.

To summarize, the ILs synthesis may have drawbacks caused by heat and mass transfer problems as well as by phase changes and different solubility of the reactants within the formed phases.

Why microstructured reactors for IL syntheses?

The final aim of using microstructured reactors is not to perform chemical reactions in micro space or microchannels as end in itself but it is to intensify chemical processes. The ideal situation will be processing close to the kinetic limit together with a high throughput and space time yield.

Microstructured reactors, sometimes described as microreactors, have proven as useful tools for chemical research for widespread applications and in a vast number of laboratories as well as in some cases used for industrial applications. Microreactors are most commonly understood as flow-through systems containing three-dimensional structures with extremely small inner dimensions between ten to several hundred micrometers. This results in significantly larger specific surface-to-volume ratios and, consequently in superior heat exchange properties compared to conventional technology, permitting very fast heating and cooling of reaction mixtures[2].

The observed large heat release at the beginning of the quarterisation reactions shown in Fig. 1 indicates extremely fast kinetics. It can be assumed that these reactions are faster than conventional mixing takes place[3]. Calculated mixing times range from below one second down to several milliseconds. Such timescale can be achieved by a pre-structurization of liquid (or even gas) fluid streams down to micrometer-scale and subsequent contacting in a confined space. Several principles of such fluid-structured mixing are shown exemplarily in Fig. 2.

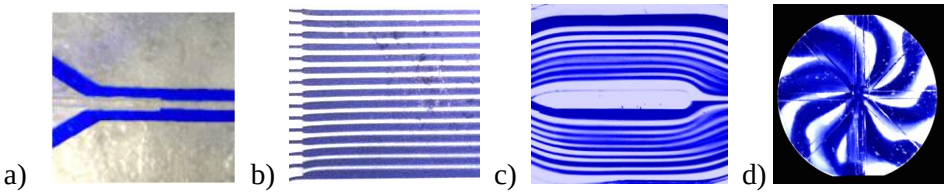


Fig.2: Fluid pattern for different micro-mixing principles. Fluids are colorized and pure water a) Y-mixer, b) multi-lamination[4] , c)split-and-recombine[4] , d) cyclone[5]

A review on microstructured equipment, e.g. mixer, heat exchangers and plant set-ups are given elsewhere[6].

The basic function of so-called microstructured devices can then be defined as providing a kind of fluid flow pattern to ensure increased mass and heat transfer, minimized back-mixing and better temperature- and residence time control.

Mixing and heat exchange in the micro scale can be achieved by comparably simple mixer-tube-reactor set-ups. If the mixer and tube, with a hydraulic diameter similar to the internal mixer dimensions, are immersed into a thermostated bath the reaction takes place nearly under isothermal conditions. To ensure necessary residence time the flow rate of the reactants must be adjusted properly (Fig. 3).

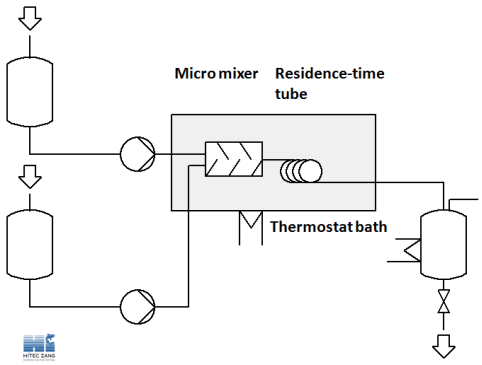


Fig.3: Scheme of a micro-mixer - tube reactor set-up. Mixer and tube are immersed in a thermostat bath. The tubes at the entrance of the micro-mixer are long enough to heat up the reactants prior entering the mixer.

From Fig. 3 can be derived that an increased throughput might be possible by repeating the mixer – tube reactor set-up. Indeed, such so-called "numbering-up" is possible but the experimental effort is too high for industrial application and not economically practical. Much more efficient is the stacking of mixer and tube to form compact multi-channel arrays as chemical reactor (Fig. 4). Microstructured reactors are not limited in outer size, i.e. they range from sizes similar to a SIM-card to two-storey house[7].

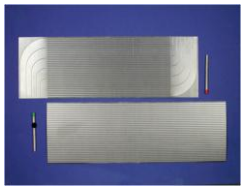
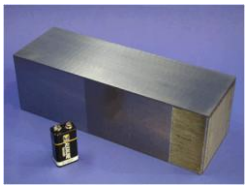
a)  b)  c) 

Fig.4: Examples for a) plates with channel arrays, b) stack of such plates, c) ready-to use multichannel reactor. (by courtesy of IMM)

Focusing on the microstructured internals only does not fully cope with the philosophy behind chemical microprocessing. Also small plugs divided by a non-miscible medium flowing inside a channel or tube can be perceive as single microreactor. Single droplets, often used in Lab-on-a-Chip analytical devices, providing very small reaction volumes which can be temperature controlled easily under plug-flow conditions. To increase the throughput, multi-droplet flow can be formed by special multi-lamination mixers and laminar flow conditions in a wide flat tube (Fig. 5).

The definition of ‘microreactor’ should be also extended to free falling or flowing droplets surrounded by another liquid or gas, and the size of the droplets can be adjusted by suitable flow conditions ranging from millimeter down to micrometer scale. These droplets do not touch any solid wall.

With this definition in mind allows one to focus on the essential, performing a chemical reaction close to the kinetic limits. Such kind of free (non-encased) flow is already realized, e.g. as impinging jets with narrow jet diameter[8,9], levitated droplets[10], spinning disk reactors[11,12], or spray.

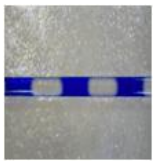
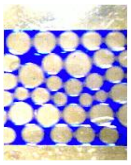
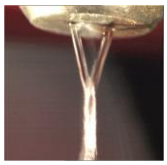
a)  b)  c)  d) 

Fig. 5: Examples for a) droplet plug-flow in a microchannel, b) multi-droplet flow, generated by special micromixers, in a wide channel, c) free flow of an impinging jet, d)spray of micro-droplets.

In all cases microstructured reactors work as continuous flow-through systems. While transferring the protocols used for performing chemical reactions in a commonly given equipment means to fill “old wine into new tubes”, processing in microstructured reactors allow possibly to overcome conventional drawbacks, e.g. adding of solvents, heating restricted by the boiling point or slow or irregular mixing by stirring. The chemical protocol now can be changed to apply unusual process regimes, e.g. high temperature or pressure[13,14].

IL syntheses performed in microstructured reactors – a brief overview

Possibilities for IL synthesis in microstructured reactors are, in general:

- The reactants are preheated and subsequently mixed in a micromixer and the reaction takes place in a thermostated tube to control reaction temperature and residence time by adjusting the flow rate.
- Pre-structurization of preheated educts into micro parts or droplets and subsequent interaction at reaction temperature. Extremely fast mixing and superior heat exchange by a guided fluid flow through the walls of microchannels.
- Chemical reaction in droplets formed by jet-collision, levitated droplets, spinning disk reactors etc.

Waterkamp et al[15] describe a continuous synthesis of 1-butyl-3-methylimidazolium bromide [C_4MIM]Br from butyl bromide and 1-methylimidazole by using a micro reactor system. In a vortex-type micromixer both reactants are rapidly mixed and the mixture subsequently flows though a stainless steel tube system which consists of a series of three tubes with increasing inner diameter ranging from 2 to 6 mm. Each part tube has a length of 6 m and the total volume is 306 ml. The temperature is set to 65 – 85°C, i.e. the reaction is performed under

nearly isothermal conditions, and the pressure ranges from ambient up to 2 bar. With residence time up to 48 min a conversion of 97% and a purity of 99% could be achieved.

Renken and Hessel et al[16,17] describing a reactor system composed of a microstructured reactor in combination with tubular reactors with diameters in the range of several millimeters. Compared to capillary reactors operating at two different temperature levels the space-time yield is reduced from 4 h down to 4.6 min. With this non-isothermal system the performance of the reaction could be increased by a factor of 50. The throughput of the reactor system can be possibly increased by simply numbering up of the system.

Minrath et al[18] introduced a microwave assisted microreactor processing (μ^2) for the synthesis of 1-methyl-3-hexyl-imidazolium bromide. A micromixer-tubular ($d<500\mu m$) reactor was used to perform the reaction with microwave heating. The residence time could be decreased from 10 min for 50 W down to 2 min for 200 W MW-power.

Thoeming et al[19] used cyclone-micromixer and single- and multistep tubular microreactor set-ups to investigate the influence of different molar rations of reactants on the final quality of the formed ILs. For example, colorless 1-methyl-3-butylimidazolium bromide could achieve at low temperatures in a multi-step synthesis. The conversion of 1-methylimidazole was found to 99%.

Wilms et al[20,21] developed a continuous flow process for the synthesis of ionic liquids, bearing additional aromatic and nitro-aromatic units, in a microstructured reactor. Also vinyl-group containing imidazolium salts were synthesized in a micromixer-tubular reactor set-up.

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