Chemical Engineering Journal 162 (2010) 350–354

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Kinetic study of ionic liquid synthesis in a microchannel reactor

Shaozheng Hu[a,b], Anjie Wang[a,b,*], Holger Löwe[b,c], Xiang Li[a,b], Yao Wang[b], Changhong Li[b], Dong Yang[b]

[a] Department of Catalysis, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China
[b] CMPT-R&D Center and Liaoning Key Laboratory of Petrochemical Technology and Equipments, Dalian 116012, China
[c] Johannes Gutenberg University Mainz, Institute of Organic Chemistry Duisbergweg 10-14, 55128 Mainz, Germany

ARTICLE INFO

Article history:
Received 9 October 2009
Received in revised form 25 March 2010
Accepted 7 April 2010

Keywords:
Ionic liquid
Synthesis
Kinetics
Microreactor
[BMIM]Br

ABSTRACT

A microchannel reaction system, mainly consisting of a micromixer and a tubular reactor, was used to investigate the kinetics of butylation of 1-methyl-imidazole [MIM] for the synthesis of the ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM]Br). The low variance ($\sigma_\theta{}^2 = 0.019$) of the residence time distribution, measured by a step stimuli–response tracer method, implies that this reaction system could be regarded as a plug flow reactor. As a fast and reliable method, the titration of bromide was established to determine the yield of [BMIM]Br. The reaction kinetics was studied by varying the molar ratio of 1-bromobutane [BrBu] to [MIM] (1.04–1.49) and temperature (75–90 °C). A second-order kinetics with respect to [MIM] and [BrBu] and an activation energy of 78.4 kJ/mol were found.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

There have been increasing research interests in the applications of ionic liquids as environmentally benign solvents [1–4], reaction media [5–7], catalysts [8], electrolytes [9], lubricants, and others. This is due to the unique properties of ionic liquids, such as negligible vapor pressure, relatively high conductivity, high thermal and chemical stability, non-flammability, and reduced friction. However, no large scale commercial application of ionic liquids has been reported, probably due to the high costs and the unavailability of ionic liquids in large volume.

Currently, ionic liquids are mainly produced in batch reactors. The synthesis of ionic liquids, such as 1-butyl-3-methylimidazolium bromide, is highly exothermic in the alkylation, and the alkylation kinetics is often dramatically fast [10]. It is reported that high temperature had a detrimental effect on the quality of the obtained ionic liquids [11]. Therefore, an efficient removal of released reaction heat is crucial in order to improve the purity of ionic liquids. Since heat generation rate is the product of reaction rate and intrinsic reaction heat, one way to control the temperature in a highly exothermic reaction is to slow it down. The decrease of reaction rate can be achieved by diluting the reactants with solvents and/or slowly adding one of the reactants. For the production of ionic liquids in a batch reactor, large quantity of organic solvents, such as 1,1,1-trichloromethane, ethanol, and THF, are often used to dilute the reactants. Moreover, it is often necessary to add the reactants slowly to avoid hot-spot formation and to ensure a narrow operational temperature window. The use of large solvent volumes gives a rise of costs and possibly pollution, and a slow addition of reactants lead to very long processing times (hours or even days). Therefore, a solvent-free synthesis system with enhanced heat transfer is highly desirable.

Recently, several groups [10,12,13] reported the syntheses of ionic liquids in microchannel mixing and reaction systems. In such a microchannel reaction system, the investigated reaction became controllable even without adding an additional solvent due to the dramatically enhanced heat and mass transfer by shortening the diffusion distances, precisely structuring the fluids, and significantly increasing specific surface area (10,000–50,000 m^2/m^3) [10,14]. Moreover, the quality of the ionic liquids was greatly improved, and the reaction time was significantly reduced down to minutes [10]. Microchannel reactors show great potential in continuous flow processing with high heat release in general, and especially for the synthesis ionic liquids.

Reliable kinetic data are essential for the design and operation of a reactor. However, the kinetic data are not easy to obtain for the synthesis of ionic liquids due to the high reaction heat rate at low conversion and to the high viscosity of the reaction mixture at high conversion. Böwing and Jess studied the kinetics of the synthesis of 1-butyl-3-methylimidazolium chloride in a stirred

---

[*] Corresponding author at: School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, China. Tel.: +86 411 39893693; fax: +86 411 39893693.
E-mail addresses: anjwang@chem.dlut.edu.cn, ajwang@dlut.edu.cn (A. Wang).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.04.063

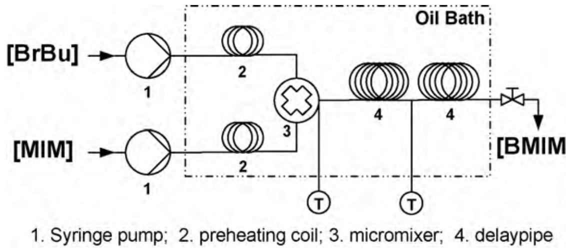


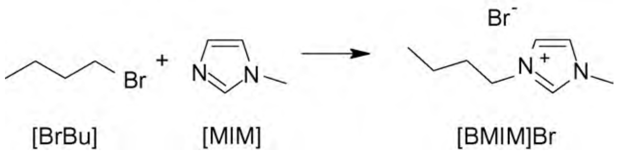
Fig. 1. Schematic diagram of the microchannel reaction system.

lab-scale glass reactor [11]. To achieve an isothermal conditions, the reaction was conducted at 66–70 °C for >1 d. They concluded that the synthesis of 1-butyl-3-methylimidazolium chloride followed an overall second-order kinetics, *i.e.* first order with respect to both reactants. Later they used a flow type tubular reactor to investigate the synthesis kinetics of ethylmethylimidazole ethylsulfate, and used a one-dimensional pseudo-homogeneous reactor model to simulate the reactor [15]. Similarly, they found that the reaction follows an overall second-order kinetics. The simulation results show that an adiabatic loop reactor gives a better controllable performance compared to a tubular reactor or the multi-tubular reactor. Renken et al. set up a reaction system, including a micromixer, and a microreactor conntected serially to two tubular reactors, to study the feasibility of the flow type reactor system for the synthesis of ethylmethylimidazole ehylsulfate [10]. Their kinetic study indicated the second-order kinetics of the reaction. Waterkamp et al. used a similar set up to study the kinetics of the synthesis of 1-butyl-3-methylimidazolium bromide, and simulated the reactor, assuming a plug flow reactor model [16]. They concluded that the reaction followed a second order kinetics, and the modeling of the reactor and the experimental observation indicated that hot spot did not occur at temperatures below 100 °C.

In the present paper, we report the investigation of the residence time distribution (RTD) in a flow type microchannel reaction system, and the kinetics of the synthesis of 1-butyl-3-methylimidazolium bromide ([BMIM]Br).

2. Material and methods

As a representative reaction in the synthesis of ionic liquids, the butylation of methylimidazole [MIM] with 1-bromobutane [BrBu] to yield [BMIM]Br was chosen as an instructive example for the kinetic study. The reaction equation is as follows:



[MIM] and [BrBu] are of AR grade, and used without further purification. As reference substance, [BMIM]Br was obtained from Shanghai Meisibei Co., China.

The setup of the microchannel reactor is shown in Fig. 1. It consists of two pumps, two preheating tube coils, one SIMM-V2 micro-mixer (IMM Mainz, Germany) with a standard mixing channel of 45 μm × 200 μm and a total inner volume of 8 μL (Fig. 2) [17], and a loop tubular reactor (1.80 mm in inner diameter and 1.13 m in length). The preheating tube coils, the mixer and the reactor were emerged in a circulating oil bath (volume: 40 L). The temperature of the oil bath was kept constant during the reaction. The advantage of our set-up lies in the fact that the reactants are preheated separately and thus the reaction is triggered at the desired temperature when they meet in the micro-mixer. Because the retention time in the mixer is in the milliseconds range, the reaction proceeds mainly in the tubular reactor. We measured the temperatures at the outlet of the micro-mixer and in the middle of the tubular reactor. The measurement at nearly complete conversion indicated that the temperature difference was only 0.8 °C. It is therefore assumed that the reaction takes place at nearly isothermal conditions, which is in accordance with the prediction of the modeling from Waterkamp et al. [16].

Because the butylation reaction continues slowly at room temperature, a sample treatment and a fast analysis is essential to ensure valid kinetic data. Since [MIM] and [BrBu] are non-ionic whereas [BMIM]Br is ionic, we developed a fast method of determining the conversion. The procedure is based on the determination of Br^- concentration in the reaction mixture, which is associated with the conversion of [BrBu], by the Volhard titration method [18]. A series of "standard" solutions at given [MIM] conversions ($x_{[MIM]}$) were prepared by mixing [MIM], [BrBu], and [BMIM]Br. Fig. 3 shows the correlation of the calculated [MIM] conversion with that measured by the titration method. It is apparent that an excellent linearity could be found, indicating that the titration method is satisfactory for determining $x_{[MIM]}$.

In the kinetic study, the product containing [BMIM]Br was collected at the outlet of the tubular reactor. 1 ml of the product was immediately dissolved in 1 ml ethanol, and then Br^- concentration in the solution was determined as follows: 0.1 ml of the solution,

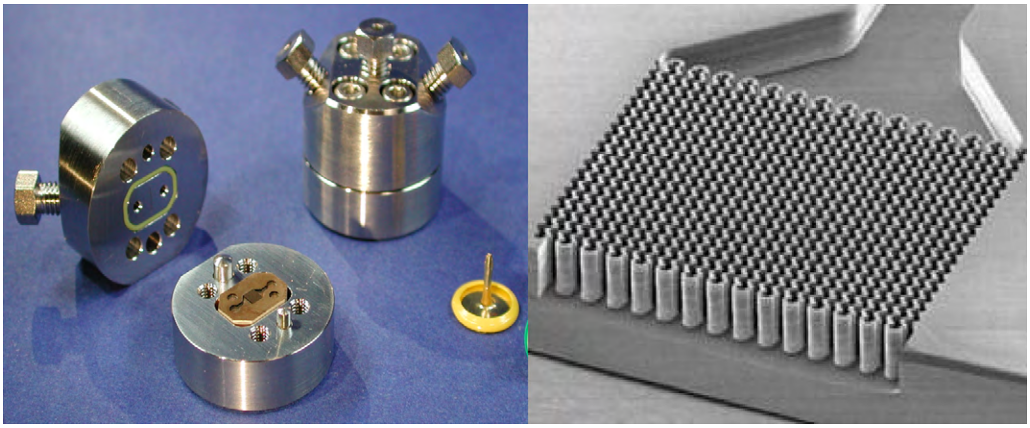


Fig. 2. Photo (left) and inner structure (right) of SIMM-V2 micro-mixer.

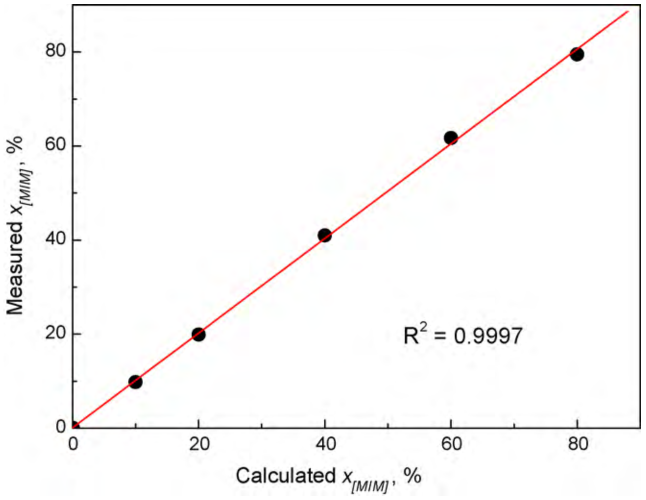


Fig. 3. Correlation between the measured [MIM] conversion and the calculated one.

10 ml $AgNO_3$ aqueous solution (0.053 M), 10 ml $NH_4Fe(SO_4)_2$ aqueous solution (0.2 M), and 10 ml HNO_3 aqueous solution (3.2 M) were added to 70 ml de-ionized water, giving a white suspension. 0.0353 M NH_4SCN was used to titrate the above suspension until the $Fe(SCN)_3$ precipitate (red color) was formed. Our preliminary investigation showed that no byproduct was detected, suggeting that one mole of Br^- is formed when one mole of [MIM] is converted in the synthesis. Thus, $x_{[MIM]}$ can be determined from the titration volume (V):

$$x_{[MIM]} = \frac{(0.053 \times 10 - 0.0353V) \times M_{[MIM]} \times 10^{-3}}{\rho_{[MIM]} \times 0.1\upsilon_{[MIM]}/[2(\upsilon_{[MIM]} + \upsilon_{[BrBu]})]} \quad (1)$$

where $\upsilon_{[MIM]}$ and $\upsilon_{[BrBr]}$ are the volumetric flow rates of [MIM] and [BrBu], respectively; $M_{[MIM]}$ is the molar mass of [MIM] (82.1), and $\rho_{[MIM]}$ is the density of [MIM]. Consequently, the concentration of [MIM] ($C_{[MIM]}$) can be obtained:

$$C_{[MIM]} = C_{[MIM],0}(1 - x_{[MIM]}) \quad (2)$$

3. Results and discussion

3.1. Determination of residence time distribution

The residence time distribution (RTD) is generally used to check if the flow type reactor is ideal plug flow reactor (PFR). We measured the RTD in our reaction system by means of the stimuli–response tracer method. The tracer was the reactive briliant blue dye KN-R (CAS No. 2580-78-1), and its concentration was determined by an UV–vis spectrophotometer at a wavelength of 600 nm.

A step input was used in finding the F curve of RTD in the microchannel reaction system. Water and KN-R aqueous solution were fed into the reaction system by two separate syringe pumps. When the concentration of KN-R became constant, the KN-R solution pump was stopped. After the concentration of KN-R in the effluent had become zero, the KN-R solution pump was restarted. Meanwhile, liquid samples were collected at an interval of 1 min at the outlet of the reaction system. The F curve (Fig. 4) was obtained by dividing the concentration of KN-R in the effluent by that in the feed at various times. According to the experimental data in Fig. 4, the mean residence time was estimated to be 7.3 min, and the variance ($\sigma_\theta{}^2$) was 0.019. In a dispersion model, when $D/uL < 0.01$, the maximum error is less than 5% if the reactor is treated as a PFR [19]. If the deviation from PFR is small, D/uL equals to $\sigma_\theta{}^2/2$. Consequently, D/uL for the present reaction system was 0.0095, smaller than 0.01. It is therefore suggested that the microchannel reaction system could be regarded as a PFR.

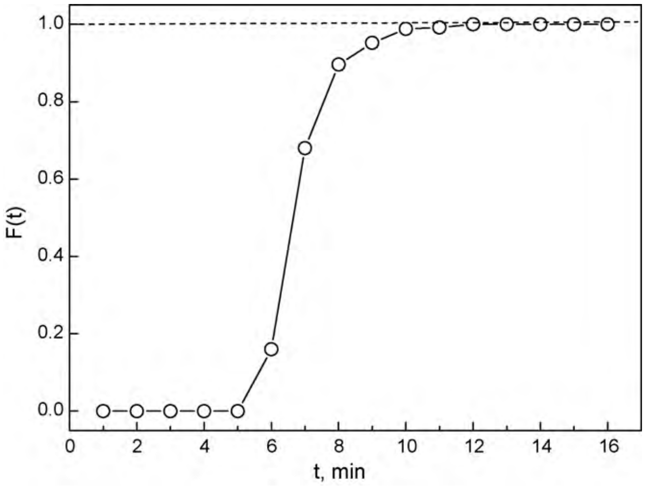


Fig. 4. *F* curve of RTD measured by a step stimuli–response tracer method.

3.2. Kinetic study

It has been reported that the butylation reaction follows a second-order kinetics, with respect to [BrBu] and [MIM] [16].

$$r = kC_{[BrBu]}C_{[MIM]} \quad (3)$$

In the feed, excess [BrBu] was usually used in the continuous synthesis of [BMIM]Br in order to achieve complete conversion of [MIM]. In the present study, the effect of the molar ratio of $C_{[BrBu]}$ to $C_{[MIM]}$ (a) on the reaction rate was also investigated. Thus,

$$C_{[BrBu]} = (a-1)C_{[MIM],0} + C_{[MIM]} \quad (4)$$

and

$$r = k[(a-1)C_{[MIM],0} + C_{[MIM]}]C_{[MIM]} \quad (5)$$

From the performance equation of an ideal PFR, we get

$$t = -\int_{C_{[MIM],0}}^{C_{[MIM],f}} \frac{1}{k[(a-1)C_{[MIM],0} + C_{[MIM]}]C_{[MIM]}}\, dC_{[MIM]} \quad (6)$$

Rearranging and integrating then gives

$$\ln\left[\frac{(a-1)C_{[MIM],0} + C_{[MIM]}}{C_{[MIM]}}\right] = (a-1)C_{[MIM],0}kt + \ln a \quad (7)$$

If plots of $\ln[((a-1)C_{[MIM],0} + C_{[MIM]})/C_{[MIM]}]$ against t give straight lines through (0, $\ln a$) at different a, the rate expression is proven to be suitable for the butylation reaction.

Fig. 5 shows the plots of $\ln[((a-1)C_{[MIM],0} + C_{[MIM]})/C_{[MIM]}]$ against t at various a, when the reaction took place at 75 °C. The experimental data fit well a straight line for each a. Moreover, the rate constants obtained from the slopes of different lines were the same [0.0076 L/(mol min)]. Similar results were obtained for the butylation reaction at 80, 85, and 90 °C. It is therefore concluded that Eq. (3) can well express the butylation rate in the synthesis of [BMIM]Br. In other words, the synthesis of [BMIM]Br follows a second-order kinetics, first-order with respect to [MIM] and [BrBu], respectively. With these results the fast heat release and the reaction speed at early stage can be explained.

The rate constants of butylation at different temperatures are summarized in Table 1. Accordingly, the Arrhenius plot is shown in Fig. 6. It is indicated that a straight line was obtained. From the slope and intercept of the line, the frequency factor (k_0) and

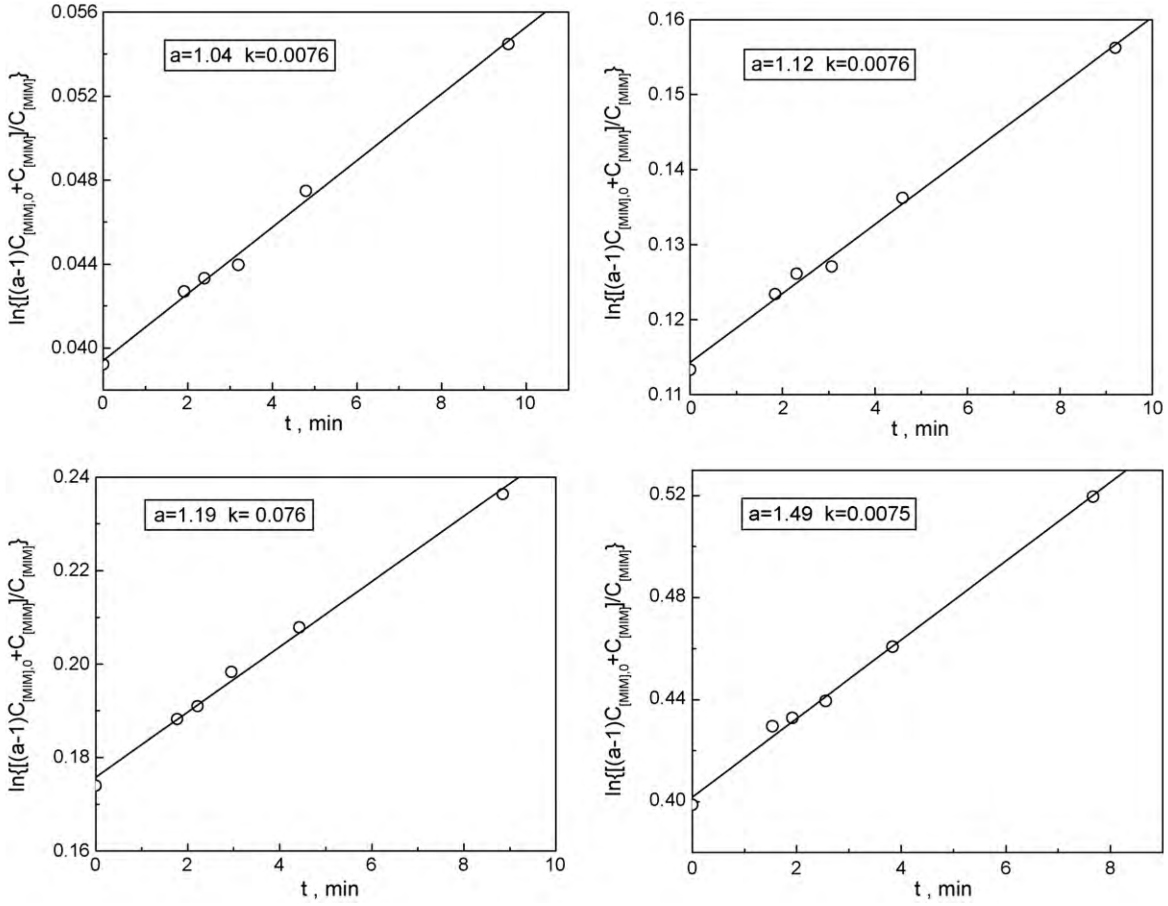


Fig. 5. Plot of $\ln[((a-1)C_{[\mathrm{MIM}],0}+C_{[\mathrm{MIM}]})/C_{[\mathrm{MIM}]}]$ against t in butylation at 75 °C and various a.

Table 1
Rate constants of butylation at different temperatures.

Temperature, °C	k, L/(mol min)
75	0.0076
80	0.012
85	0.017
90	0.024

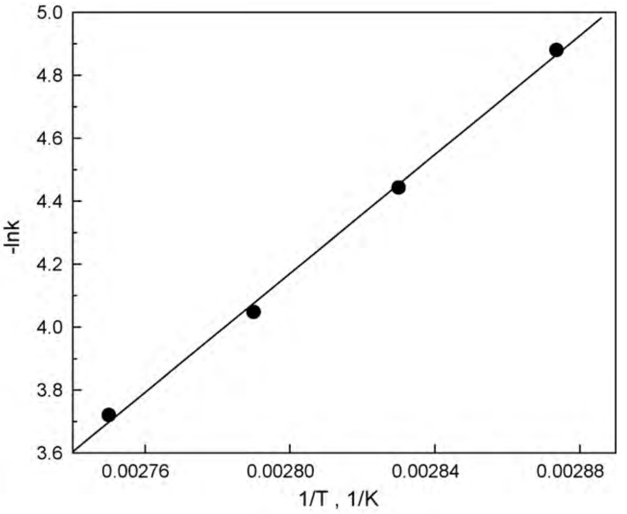


Fig. 6. Arrhenius plot.

activation energy (E_a) were estimated to be 0.027 L/(mol min) and 78.4 kJ/mol, respectively. Therefore the rate constant of butylation in the synthesis of [BMIM]Br could be expressed as:

$$r = 0.027\ \exp\left(\frac{-9.43}{T}\right) C_{[\mathrm{BrBu}]}C_{[\mathrm{MIM}]} \tag{8}$$

4. Conclusions

The measurement of RTD in the microchannel reaction system, composing of a micromixer and a tubular reactor, indicated that the system could be treated as a plug flow reactor. As a case study, the kinetics of butylation in the synthesis of ionic liquid [BMIM]Br, which is characterized by fast reaction, high heat release, and high viscosity, was investigated. The determination of butylation conversion by analyzing the concentration of Br^- in the product is proven to be fast and accurate. The experimental results show that this microchannel reaction system is suitable for the kinetic study of fast reaction with high heat release and/or in a viscous system. The rate of the butylation can be expressed as: $r = 0.027\ \exp(-9.43/T)C_{[\mathrm{BrBu}]}C_{[\mathrm{MIM}]}$.

Acknowledgements

This work was financially supported by NSFC (20503003, 20773020, 20973030), NCET, the “863” Project (2008AA030803), and the “111” Project.

References

[1] O.A. El Seoud, A. Koschella, L.C. Fidale, S. Dorn, T. Heinze, Applications of ionic liquids in carbohydrate chemistry: a window of opportunities, Biomacromolecules 8 (2007) 2629–2647.

[2] F. Endres, Ionic liquids: solvents for the electrodeposition of metals and semiconductors, ChemPhysChem 3 (2002) 144–154.

[3] H. Zhao, S.Q. Xia, P.S. Ma, Use of ionic liquids as 'green' solvents for extractions, J. Chem. Technol. Biotechnol. 80 (2005) 1089–1096.

[4] A. Berthod, M.J. Ruiz-Ángel, S. Carda-Broch, Ionic liquids in separation techniques, J. Chromatogr. A 1184 (2008) 6–18.

[5] P. Wasserscheid, W. Keim, Ionic liquids-new "solutions" for transition metal catalysis, Angew. Chem. Int. Ed. 39 (2000) 3772–3789.

[6] C. Chiappe, D. Pieraccini, Ionic liquids: solvent properties and organic reactivity, J. Phys. Org. Chem. 18 (2005) 275–297.

[7] W.S. Miao, T.H. Chan, Ionic-liquid-supported synthesis: a novel liquid-phase strategy for organic synthesis, Acc. Chem. Res. 39 (2006) 897–908.

[8] T. Welton, Ionic liquids in catalysis, Coord. Chem. Rev. 248 (2004) 2459–2477.

[9] M. Galiński, A. Lewandowski, I. Stępniak, Ionic liquids as electrolytes, Electrochim. Acta 51 (2006) 5567–5580.

[10] A. Renken, V. Hessel, P. Löb, R. Miszczuk, M. Uerdingen, L. Kiwi-Minsker, Ionic liquid synthesis in a microstructured reactor for process intensification, Chem. Eng. Process. 46 (2007) 840–845.

[11] A.G. Böwing, A. Jess, Kinetics of single- and two-phase synthesis of the ionic liquid 1-butyl-3-methylimidazolium chloride, Green Chem. 7 (2005) 230–235.

[12] F. Benaskar, V. Hessel, U. Krtschil, P. Löb, A. Stark, Intensification of the capillary-based Kolbe–Schmitt synthesis from resorcinol by reactive ionic liquids, microwave heating, or a combination thereof, Org. Proc. Res. Dev. 13 (2009) 970–982.

[13] D. Wilms, J. Klos, A.F.M. Kilbinger, H. Löwe, H. Frey, Ionic liquids on demand in continuous flow, Org. Proc. Res. Dev. 13 (2009) 961–964.

[14] V. Hessel, P. Löb, H. Löwe, Development of microstructured reactors to enable organic synthesis rather than subduing chemistry, Curr. Org. Chem. 9 (2005) 765–787.

[15] A.G. Böwing, A. Jess, Kinetics and reactor design aspects of the synthesis of ionic liquids—experimental and theoretical studies for ethylmethylimidazole ethylsulfate, Chem. Eng. Sci. 62 (2007) 1760–1769.

[16] D.A. Waterkamp, M. Heiland, M. Schlüter, J.C. Sauvageau, T. Beyersdorff, J. Thöming, Synthesis of ionic liquids in micro-reactors—a process in tensification study, Green Chem. 9 (2007) 1084–1090.

[17] S. Hardt, F. Schönfeld, Laminar mixing in different interdigital micromixers—Part 2: Numerical simulations, AIChE J. 49 (3) (2003) 578–584.

[18] I.M. Kolthoff, V.A. Stenger, Volumetric Analysis, vol. II, second ed., Interscience Publishers Inc., New York, 1947.

[19] O. Levenspiel, Chemical Reaction Engineering, third ed., John Wiley & Sons, New York, 1999.