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COMMUNICATION

Micellar catalysis in aqueous–ionic liquid systems†‡

Katharina Bica,*[a] Peter Gärtner,[a] Philipp J. Gritsch,§[a] Anna K. Ressmann,[a] Christian Schröder[b] and Ronald Zirbs[c]

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We present the application of ionic liquid–aqueous micellar solutions as reaction media for Diels–Alder reaction and found that reaction rates could be significantly increased compared to the reaction in water.

Ionic liquids have been thoroughly investigated as reaction media in most types of catalytic reactions, and a number of critical aspects make them interesting media for synthesis and catalysis with distinct chemistry of their own compared to traditional molecular solvents.[1,2]

Recently, there has been a tremendous increase of interest in the behaviour of ionic liquids in the presence of water, and it has been shown that certain ionic liquids can form aggregates in aqueous solution.[3] In the case of 1-alkyl-3-methylimidazolium chloride salts [$C_n$mim]Cl, a polarizable molecular dynamics simulation of a 50 mM [C_{12}mim]Cl solution showed that the polar head groups of the imidazolium cation are completely covered by water (Fig. 1).

The water cage of apolar imidazolium side chains is fragmented by contacts with other cations, and hence micelles are formed.[4] The strength of the network of these cation–cation contacts determines the size and shape of the micelles, and alkyl chain length, counter ion as well as temperature were found to have a vital effect on the critical micelle concentration (CMC) values.[5]

A variety of experimental techniques, including surface tension and conductivity measurements, potentiometry, fluorescence probes, NMR spectroscopy, mass spectrometry, light scattering and small-angle X-ray and neutron scattering (SAXS and SANS), has been applied to understand the aggregation behaviour of ionic liquids, showing that micelles are formed with alkyl chains of greater than eight carbon atoms ($n \geq 8$) at a concentration higher than their CMC.[6] Most of the studies of ionic liquid behaviour in aqueous solution deal with 1-alkyl-3-methylimidazolium salts [$C_n$mim]X, where the anion X is typically Cl^-, Br^-, BF_4^- or PF_6^-, and a linear relationship between the logarithm of CMC and the number of carbon atoms n was found (Fig. 1).[7]

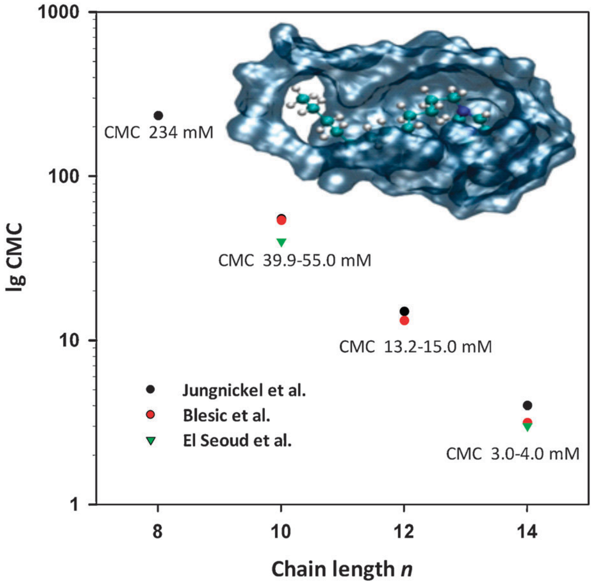

Fig. 1 Structure of [C_{12}mim]Cl in H_2O and CMC values of surface-active ILs used in this study.

Although progress in the studies of ionic liquid self-aggregation in aqueous solution has been made by a number of authors, these investigations are entirely restricted to physico-chemical studies while the potential for synthesis and catalysis remains unexplored. An amphiphilic aggregate in aqueous media will provide a reaction environment different from bulk water, leading to a kinetic influence on a reaction and hence will be able to catalyze or inhibit organic reactions.[8] Considering the highly polar character of ionic liquids and their influence on organic reactions, novel reactivities and selectivities of ionic liquid–water micellar systems can be expected.

Herein, we report for the first time the application of aqueous–ionic liquid micellar systems in catalysis and provide insight into the influence of structural features of surface active ionic liquids on the Diels–Alder reaction of 1,3-cyclohexadiene **1** with *N*-benzylmaleimide **2** (Fig. 2).¶ The chosen reaction works reasonably well in water and takes place within 60 minutes, but is substantially

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[a] *Institute of Applied Synthetic Chemistry,*
Vienna University of Technology, Getreidemarkt 9/163,
1060 Vienna, Austria. E-mail: kbica@ioc.tuwien.ac.at;
Fax: +43 1 58801 16360; Tel: +43 1 58801 163601
[b] *Institute of Computational Biological Chemistry,*
University of Vienna, Währingerstr. 17, 1090 Vienna, Austria
[c] *Group for Biologically Inspired Materials, Institute of*
Nanobiotechnology (DNBT), University of Natural Resources and
Life Sciences, Muthgasse 11, 1190 Vienna, Austria

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§ Current address: Institute of Organic Chemistry, Leibniz University of Hannover, Schneiderberg 1, 30167 Hannover, Germany.

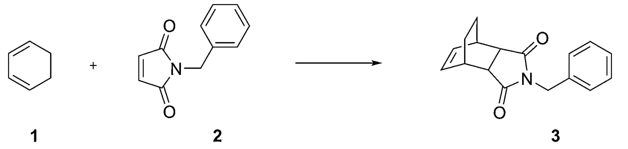

Fig. 2 Diels–Alder reaction of *N*-benzylmaleimide with 1,3-cyclohexadiene in ionic liquid–water micellar solutions.

slower with reaction times of >48 h in organic solvents, *e.g.* Et_2O or DCM.[9,10] Ionic liquids have considerable potential for Diels–Alder reactions, especially when hydrogen-bond donating cations are used in combination with non-polar and weakly coordinating anions.[11] Since the first example was reported by Jäger and Tucker in 1989,[12] intensive studies on solvent effects of different ionic liquids were published.[13] Yet, despite the variety of cation–anion combinations available in ionic liquids, higher reaction rates have been reported when the reaction was performed in water.[14]

In order to obtain reliable and reproducible results for micellar catalysis, solutions of 1-alkyl-3-methylimidazolium ionic liquids ($[C_n\text{mim}]Cl$, n = 8–14) were prepared and shaken for 24 h at 360 min^{-1}. Solutions of diene and dienophile were independently prepared, combined, and immediately transferred to a UV-vis spectrometer to follow the disappearance of the dienophile at 298 nm (ESI‡, Fig. S1). A ratio of dienophile–diene 1 : 60 was chosen to calculate pseudo-first-order rate constants.

Initially, we determined the aqueous rate constant for the reaction run with 0.0002 mmol dienophile and 0.012 mmol diene in 1 ml H_2O and found a reaction rate of k = 0.0091 ± 0.0007.‖ Subsequently, we performed the reaction in aqueous solutions of amphiphilic 1-alkyl-3-methylimidazolium chloride ILs ($[C_n\text{mim}]Cl$, n = 8–14) and compared the rate constants with the values obtained for pure water.[10]

We did not only observe enhanced reaction rates (up to $k_{IL}/k_w \approx 4.1$) for ionic liquid–aqueous micellar systems compared to the reaction in pure water, but also found that the maximum of the reaction rate occurred above the CMC of the respective amphiphilic ionic liquid (Fig. 3). For example, the observed rate constants for $[C_{10}\text{mim}]Cl$ reach a maximum at concentrations of ~60 mM, which is above the CMC and then decrease again with a further increase in the concentration of $[C_{10}\text{mim}]Cl$. A similar effect was reported by Rispens and Engbert for related Diels–Alder reactions in SDS- or CTAB-aqueous solutions.[10] For this, the dilution of both reactants over increasingly more micelles has been held responsible for the decreasing reaction rate at higher concentrations.

Comparable results were observed for the ionic liquids $[C_{12}\text{mim}]Cl$ and $[C_{14}\text{mim}]Cl$, and the monitored reaction rates reach a maximum at concentration just above the CMC. The maxima of the relative rate constants k_{IL}/k_W were dependent on the chain length of the ionic liquids, and we found the highest k_{IL}/k_W values for $[C_{14}\text{mim}]Cl$. In contrast to 1-alkyl-3-methylimidazolium ionic liquids $[C_n\text{mim}]Cl$ with n = 10–14, we were unable to repeat the series with $[C_8\text{mim}]Cl$ since the reaction mixture became turbid and rate constants were unreproducible when approaching the CMC. However, we could determine a relative rate constant of k_{IL}/k_W 0.91 in a 50 mM solution, and again the order of relative rate constants k_{IL}/k_W $C_8 < C_{10} < C_{12} < C_{14}$ was confirmed.

When comparing reaction rates for ionic liquid–aqueous micellar solutions with those obtained for conventional surfactants, we found that the surface-active ionic liquid $[C_{14}\text{mim}]Cl$ ($k_{IL}/k_W \approx 4.10$ in a 50 mM solution) can be more efficient in this particular Diels–Alder reaction than the cationic surfactant CTAB ($k_S/k_W \approx 3.68$ in a 50 mM solution), the anionic surfactant sodium dodecylsulfate SDS ($k_S/k_w \approx 3.82$ in a 50 mM solution) or the zwitterionic surfactant Empigen® ($k_S/k_w \approx 3.72$ in a 50 mM solution).

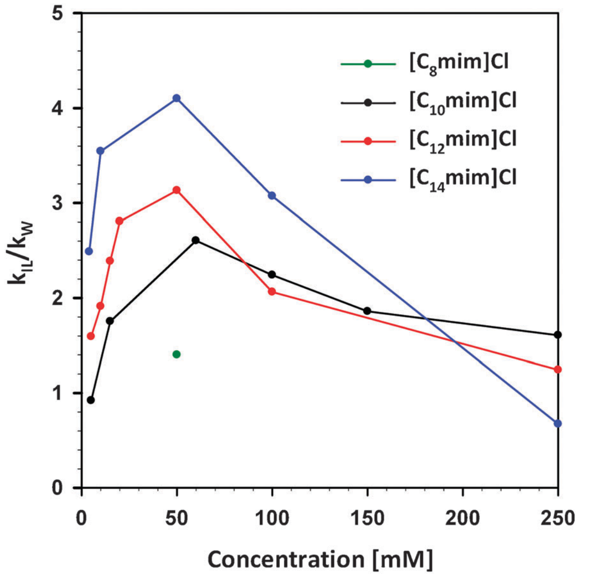

Fig. 3 Relative reaction rate k_{IL}/k_W of a Diels–Alder reaction in aqueous solutions of the amphiphilic ionic liquids $[C_n\text{mim}]Cl$, n = 8–14.

The reaction rates could be further increased *via* addition of a Lewis-acid that is able to coordinate with 1-alkyl-3-methylimidazolium chlorides to form Lewis acidic ionic liquids of the type $[C_n\text{mim}]Me_xX_y$. Although chloroaluminate(III) ionic liquids have been the most prominent examples, they suffer from limited stability and fast hydrolysis. Recently, more benign and stable metal-containing ionic liquids, *e.g.* In(III) and Fe(III)-based ionic liquids, have been successfully used for catalysis.[15,16] For example, Earle *et al.* could recover and successfully reuse the ionic liquid $[C_4\text{mim}]Cl–InCl_3$ (χ = 0.6) from aqueous solution, thus indicating a substantial water stability. Furthermore, indium(III) halide has been shown to be an effective Lewis acid for various reactions in aqueous medium, and thus we further investigated the Diels–Alder reaction with surface active chloroindate ionic liquids.[17] We found that the addition of indium(III) chloride resulted in a further increase in the reaction rate, and best results were obtained when 0.1 eq. of $InCl_3$ (corresponding to $[C_{12}\text{mim}]Cl–InCl_3$ χ = 0.09) were added (Table 1, entry 4). Unfortunately, we could not further increase the mole fractions of $InCl_3$ since the solution became turbid.

In parallel to the assessment of reactivity, we performed dynamic light scattering (DLS) experiments to get further insight into the nature of self-organization of ionic liquids in water and their influence on catalysis. We found that a 100 mM solution of $[C_{10}\text{mim}]Cl$ was composed of micelles with an average diameter of 80 nm but also to a large extent of single molecules. Interestingly, the addition of the dienophile *N*-benzylmaleimide **2** resulted in a substantial shift towards micelle formation, and the solution was almost completely

Table 1 Rate constants of the Diels–Alder reaction in a 50 mM solution of chloroindate ionic liquids

Entry[a]	Surfactant	Rate constant		k_{IL}/k_W
1	—	0.0091	0.0007	1.0
2	—[b]	0.0096	0.001	1.06
3	[C$_{12}$mim]Cl	0.0284	0.002	3.13
4	[C$_{12}$mim]Cl–InCl$_3$ χ = 0.09	0.0381	0.002	4.20

[a] Reactions were carried out with 0.0002 mmol dienophile and 0.012 mmol diene (ratio 1 : 60) in 1 ml of solvent at 25 °C. [b] Addition of 0.05 mmol InCl$_3$.

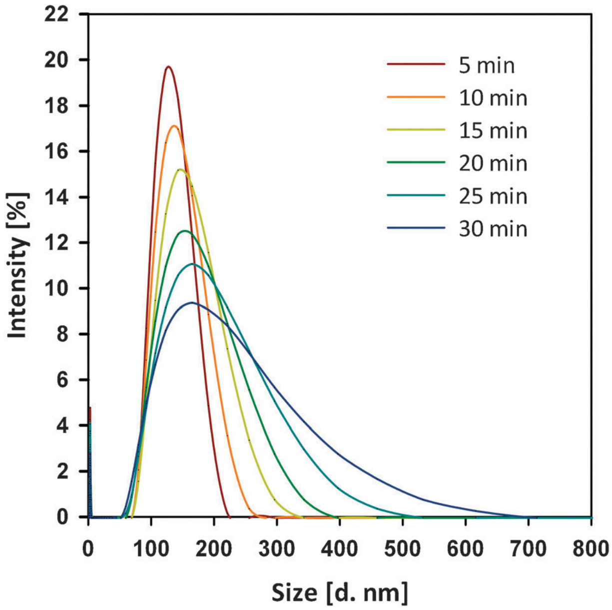

Fig. 4 Size distribution by intensity in the course of the Diels–Alder reaction in 100 mM [C$_{10}$mim]Cl solution.

composed of micelles. Once 1,3-cyclohexadiene was added, the size distribution became significantly broader and was shifted to larger aggregates within the reaction time, until after about 30 min the size and shape did not significantly change anymore (Fig. 4). A similar pattern was observed for Diels–Alder reactions run in aqueous solutions of [C$_{12}$mim]Cl and [C$_{14}$mim]Cl (ESI‡, Fig. S2 and S3).

Our results indicate that ionic liquid–water micellar systems are not only suitable reaction media that can overcome issues of water or ionic liquids as sole solvents. We found that the reaction rate of Diels–Alder reaction in micellar solutions can be enhanced compared to that of the reaction in water. Combining the amphiphilic ionic liquids with a Lewis acid, *e.g.* InCl$_3$, to form surface active chloroindate ionic liquids could further increase the reaction rate. We thus expect that ionic liquid–water micellar systems lead to a new and probably improved reactivity that cannot be obtained with traditional solvents or surfactants, and more investigations towards reactant positioning in the micelles are currently ongoing in our group.

Notes and references

¶ Reaction procedure for the Diels–Alder reaction in ionic liquid–micellar solution on a preparative scale: *N*-benzylmaleimide **2** (18.9 mg, 0.1 mmol) was dissolved in 10 ml of a 100 mM [C$_{10}$mim]Cl solution. Freshly distilled cyclohexadiene (0.5 mmol) was added and the reaction mixture was left stirring for 60 min at 25 °C. After complete reaction the product crystallized from the solution at 0 °C and was collected *via* filtration. Yield: 24.0 mg (92%) colourless crystals. ^{1}H-NMR (CDCl$_3$, 200 MHz): δ (ppm) = 7.28 (m, 5H), 6.06 (dd, J_1 = 4.60 Hz, J_2 = 3.04 Hz, 2H), 4.55 (s, 2H), 3.14 (m, 2H), 2.84 (m, 2H), 1.58 (m, 2H), 1.36 (m, 2H).

‖ All experiments were repeated at least 5 times and reaction rates are reported as mean ± SD; $n \geq 5$.

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