Ionic Liquids

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Direct Observation of Self-Organized Water-Containing Structures in the Liquid Phase and Their Influence on 5-(Hydroxymethyl)furfural Formation in Ionic Liquids

*Alexey S. Kashin, Konstantin I. Galkin, Elena A. Khokhlova, and Valentine P. Ananikov**

Abstract: *Water-containing organic solutions are widespread reaction media in organic synthesis and catalysis. This type of multicomponent liquid system has a number of unique properties because of the tendency for water to self-organize in mixtures with other liquids. The characterization of these water domains is a challenging task because of their soft and dynamic nature. In the present study, the morphology and dynamics of micrometer- and nanometer-scale water-containing compartments in ionic liquids were directly observed by electron microscopy. A variety of morphologies, including isolated droplets, dense structures, aggregates, and 2D meshworks, have been experimentally detected and studied. Using the developed method, the impact of water on the acid-catalyzed biomass conversion reaction was studied at the microscopic level. The process that produced nanostructured domains in solution led to better yields and higher selectivities compared with reactions involving the bulk system.*

Water-containing systems play crucial roles in chemical and biochemical processes. The effect of water is of paramount importance in the synthesis of organic compounds, key molecular building blocks, nanostructured materials, and complex supramolecular assemblies.[1] Enzymatic processes in living cells are exclusively governed by the presence of water.[2] Several industrial processes in the chemical and biotechnological sectors are based on aqueous systems. Chemical or enzymatic hydrolysis in water-based systems is an important step of crude biomass conversion.[3]

Organic solutions containing water have a number of unique properties. These systems are in high demand in synthesis and catalysis because they increase reaction rates and selectivities, as well as allowing chemical transformations that are difficult to achieve under standard conditions to be carried out.[4] Heterogeneous "on-water" reactions also show high efficiency in the preparation of various organic compounds.[5] Aqueous–organic systems can be distinguished at the macroscopic level and may involve uniform mixing with the formation of a homogeneous solution (Figure 1a) or the separation of immiscible phases (Figure 1b).

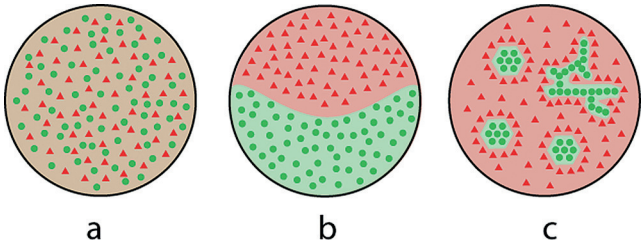

Figure 1. Aqueous–organic systems: a) systems with uniform mixing of components, b) with separation of phases, and c) with the formation of structured water (● water, ▲ organic molecule).

However, a number of processes that occur after the addition of water to organic systems cannot be described by simple models. The most unique and interesting effects exceed the limitations of these common assumptions. There is an increasing body of evidence that suggests the formation of nanostructured and microstructured water compartments (Figure 1c). Thus, chemical and biochemical transformations may occur in these self-organized soft/dynamic liquid-phase microcapsules. Such microcapsules contain structured water and possess unique water/organic interfaces. The properties of the structured micro- and nanosized water compartments substantially differ compared with regular bulk water. The reactivity patterns governed by nanostructured media (Figure 1c) cannot be reproduced in pure water or organic solvents or in regular water/organic mixtures (Figure 1a,b).

Nanostructured organization was introduced in the task-specific optimization of solvent properties of ionic liquids (also called "designer solvents").[6–9] The strong impact of aqueous additives on the physicochemical properties of ionic liquids is illustrated by several examples.[10,11] For instance, it was demonstrated that mixtures of ionic liquids with water, known as hydrated ionic liquids, showed excellent biocompatibility and high performance as solvents and stabilizers for peptides and DNA.[12,13] The critical roles of water in biomass conversion and cellulose processing were also demonstrated.[14,15] The properties of an organic medium are changed between solvent and "antisolvent" behavior when going from the pure medium to an approximately 5 wt% water content in solution.[15]

In spite of the key importance of the topic, an experimental characterization of soft and dynamic water microcapsules in a liquid phase is a challenging task. In principle, electron microscopy techniques would allow the direct observation of the water structure. However, electron mi-

[*] Dr. A. S. Kashin, Dr. K. I. Galkin, Dr. E. A. Khokhlova, Prof. V. P. Ananikov
Zelinsky Institute of Organic Chemistry
Russian Academy of Sciences
Leninsky Prospect, 47, Moscow 119991 (Russia)
E-mail: val@ioc.ac.ru

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croscopy requires vacuum conditions that may lead to an evaporation (modification) of aqueous–organic systems.

In the present work, we used important features of ionic liquids, that is, high stability under vacuum conditions and compatibility with microscopic observations,[16] to overcome this difficulty and perform direct studies of the water-containing ionic liquid systems. The formation of self-organized microstructures and nanostructures of various sizes and shapes were experimentally observed, and the dynamic behavior was captured by electron microscopy videos. The influence of added water on the selectivity of biomass conversion was studied at the microscopic level.

The ionic liquid [BMIM][BF_4], which is miscible with water at all ratios,[17] was employed as the medium for microscopy. A standard copper transmission electron microscopy (TEM) grid was used as a support for the studied samples to ensure good electrical and thermal conductivity. A series of experiments were conducted with varying amounts of water added to the ionic liquid.

Field-emission scanning electron microscopy (FE-SEM) showed that freshly dried ionic liquid possessed uniform surface without observable microstructures (Figure 2a). However, the presence of only trace amounts of water absorbed from air during storage dramatically changes the surface morphology (Figure 2b). The formation of small droplets with nearly round shapes and diameters of approximately 2–4 μm was detected in the ionic liquid/water system. Surprisingly, the addition of extra water (5 vol%) did not lead to droplet growth, as was expected, but induced their distortion and the formation of bright nuclei within the droplets (Figure 2c).

When the amount of added water was increased to 10 vol%, the nuclei transformed into nonuniform structures (particle-like) with 0.3–1.5 μm diameters packed in dense aggregates surrounded by uniform liquid areas (Figure 2d). The further growth and incorporation of aggregates resulted in the formation of a 2D meshwork where the diameters of channels varied from hundreds of nanometers to 5–10 μm (Figures 2e,f). Thus, in the studied system, neither homogeneous mixing (Figure 1a) nor phase separation (Figure 1b) were observed. The presence of water induced the self-organization of the microscale compartments with varying morphologies (Figure S2).

To investigate the dynamic properties of the studied systems, the effects of electron-beam irradiation were investigated. The resulting dynamic processes were monitored in real time by using the fast scanning mode. Because the routine microscope hardware was not able to record a representative set of images that reflect the fast processes in sensitive samples, a direct video capture with a home-made assembly was used (see the Supporting Information for details). Snapshots taken from the recorded videos are shown in Figure 3 (the complete videos are available in the Supporting Information).

Figures 3a,b clearly show the differences in the behaviors of small and large droplets under electron-beam irradiation. Small droplets moved to the edges of the irradiated area and maintained their round shape (Figure 3a). At an accelerating voltage of 2 kV and a $45 \times 30\ \mu m^2$ observation area, an approximate particle movement speed of $1\ \mu m\,s^{-1}$ was observed. Cavity formation and growth were observed for the large droplets. For droplets approximately 20 μm in diameter, 18 cavities were formed within 2 seconds, and the size of the cavities increased to approximately 2–3 μm within 4 seconds (Figure 3b).

Under the same conditions, the meshwork reorganized under the influence of an electron beam, which made it straighter and in some cases, induced the cleavage of the meshwork (Figure 3c). At higher magnifications, it was possible to monitor the process for a single structural element.

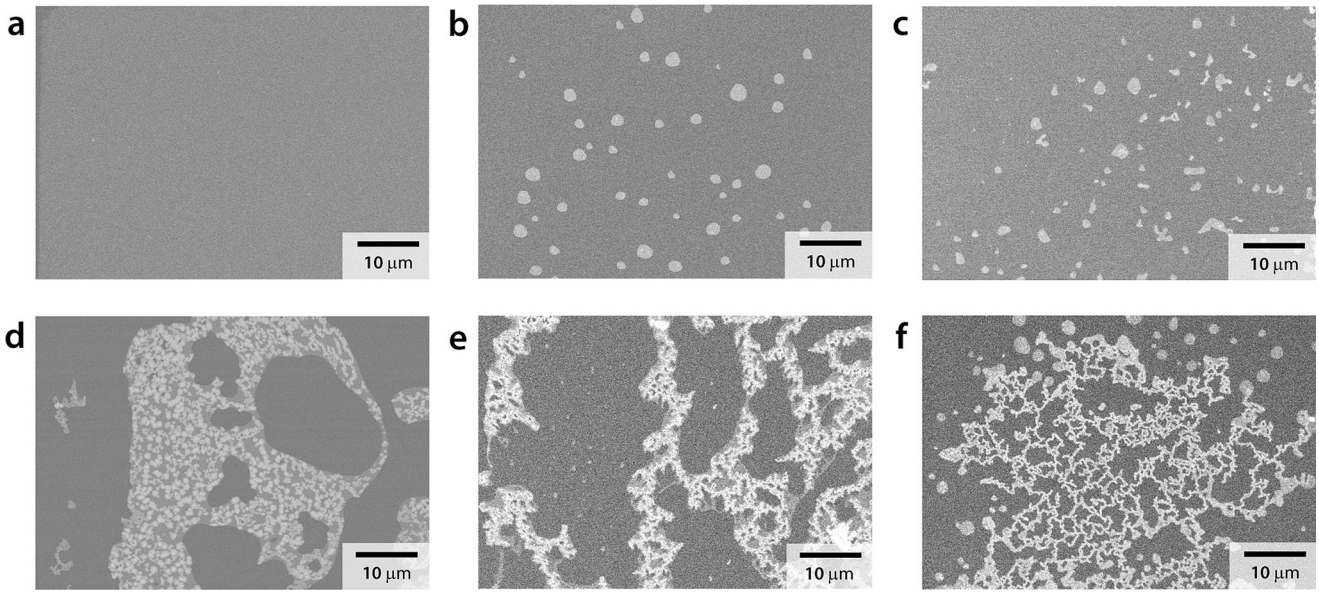


Figure 2. FE-SEM images of [BMIM][BF_4] after addition of varying amounts of water: a) freshly dried ionic liquid; b) ionic liquid with traces of water; c–f) mixtures of ionic liquid with 5 (c), 10 (d), and 20 (e,f) vol% added water.

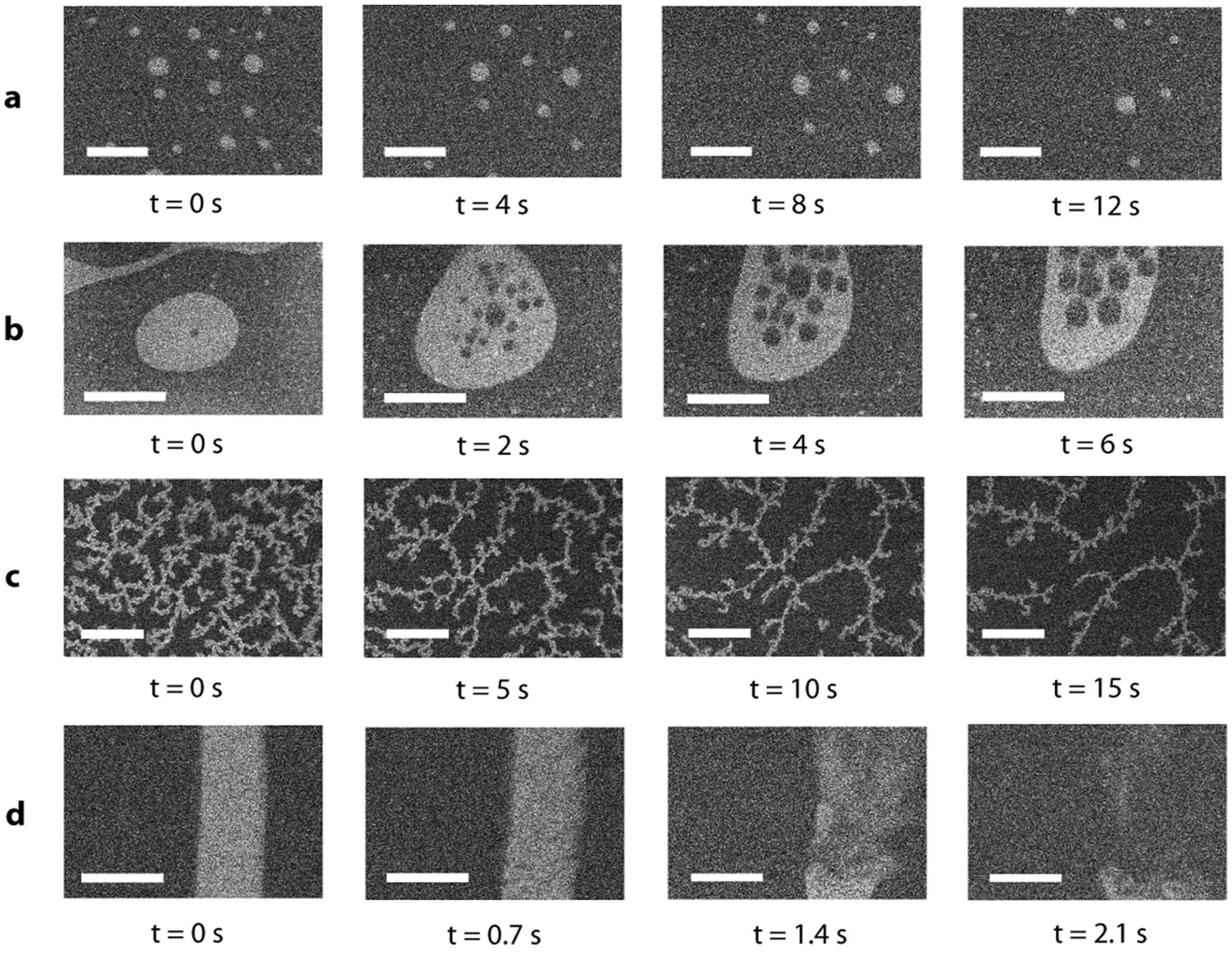


Figure 3. Snapshots taken from the videos reflecting the dynamic processes in the [BMIM][BF_4]/H_2O system under electron-beam irradiation: a) movement of droplets, b) formation of cavities within the droplet, c) movement and cleavage of the meshwork, d) rupture of the channel. Scale bars correspond to 10 (a, c), 20 for $t = 0$ s and 15 for $t = 2$–6 s (b), and 5 μm (d).

The 4-μm-thick channel underwent explosive cleavage within approximately 2 seconds of irradiation, probably because the applied stress exceeded a critical value (Figure 3 d).

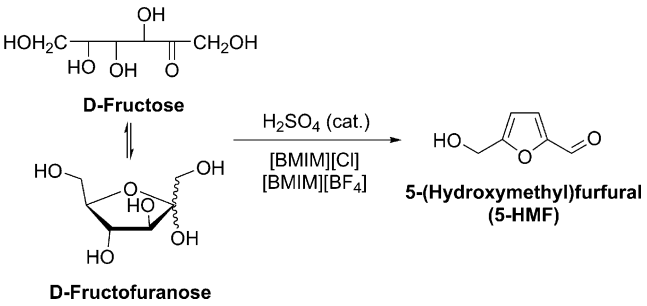
The dynamic behavior of the studied soft structures under the influence of electron beam can be described by the charging of the water-containing structures with the subsequent appearance of repulsion forces, which caused movement of the droplets and channels or distortion of their structure. Local sample heating from the irradiation may also contribute to the overall dynamics. Real time FE-SEM monitoring confirmed the dynamic nature of the studied system. The influence of the electron beam irradiation is not limited to the observation of self-organized microstructures and provides a useful tool for manipulating these soft systems and to change their morphology.

In the next step, we examined a number of two-component systems containing various ionic liquids, water, and alcohols. The results of the observations are summarized in Table 1. Water and hydrophobic ionic liquids quickly formed separate phases after stirring, as observed by the naked eye. Electron microscopy did not show the presence of structured water in the ionic liquid phase (Table 1, entries 1 and 2). These systems appear to involve phase-separation conditions. Other tested ionic liquids were completely miscible with water and formed homogeneous transparent solutions. At the microscopic scale, the behavior of the studied systems was more complicated. In some cases, the formation of microstructures, similar to those previously described (entry 3), was detected by FE-SEM (entries 4 and 5), but in other samples, the solutions appear completely uniform (entries 6 and 7). In addition to water, a number of alcohols with normal carbon chains of different lengths, and benzyl alcohol were employed as solutes. Methanol, ethanol, and benzyl alcohol formed structured microphases (entries 8, 9, and 12), whereas *n*-butanol entirely dissolved in [BMIM]-[BF_4]. The homogeneous nature of the solution was confirmed by FE-SEM (entry 10). Dodecyl alcohol, which exhibits surfactant properties, formed a stable emulsion with the ionic liquid (entry 11). It is important to mention that in the case of volatile alcohols the formation of minor amounts of microdroplets may be caused by traces of water. Thus, the occurrence of microphase formation is determined by the

Table 1: FE-SEM study of the self-organization induced by water and alcohols in various ionic liquids.

Entry	System[a,b]	Morphology observed by SEM	Type of system
1	Water + [BMIM][PF_6]	uniform surface[c]	heterogeneous (Figure 1 b)
2	Water + [BMIM][NTf_2]	uniform surface[c]	heterogeneous (Figure 1 b)
3	Water + [BMIM][BF_4]	droplets, particle-like structures and meshwork	microstructured (Figure 1 c)
4	Water + [1-BuPy][BF_4]	droplets, particle-like structures and meshwork	microstructured (Figure 1 c)
5	Water + [EMIM][OTf]	droplets, particle-like structures	microstructured (Figure 1 c)
6	Water + [BMIM][OTf]	uniform surface	homogeneous (Figure 1 a)
7	Water + [BMIM][HSO_4]	uniform surface	homogeneous (Figure 1 a)
8	MeOH + [BMIM][BF_4]	minor amount of droplets[d]	microstructured (Figure 1 c)
9	EtOH + [BMIM][BF_4]	minor amount of droplets[d]	microstructured (Figure 1 c)
10	*n*BuOH + [BMIM][BF_4]	uniform surface[d]	homogeneous (Figure 1 a)
11	*n*-$C_{12}H_{25}OH$ + [BMIM][BF_4]	large droplets up to 60 μm in diameter	microstructured (Figure 1 c)
12	$PhCH_2OH$ + [BMIM][BF_4]	droplets, particle-like structures and meshwork	microstructured (Figure 1 c)

[a] The structures of the ionic liquids are shown in the supporting information. [b] Ionic liquid/additive = 10:1 (vol/vol). [c] Phase separation was observed with the naked eye; samples for FE-SEM measurements were taken from the ionic liquid phase. [d] Low-molecular-weight alcohols are likely to evaporate under the studied conditions.



Scheme 1. Acid-catalyzed transformation of fructose to 5-HMF. Pyranose form of D-fructose are not shown as it is less important from the mechanistic point of view (see the Supporting Information for details).[19]

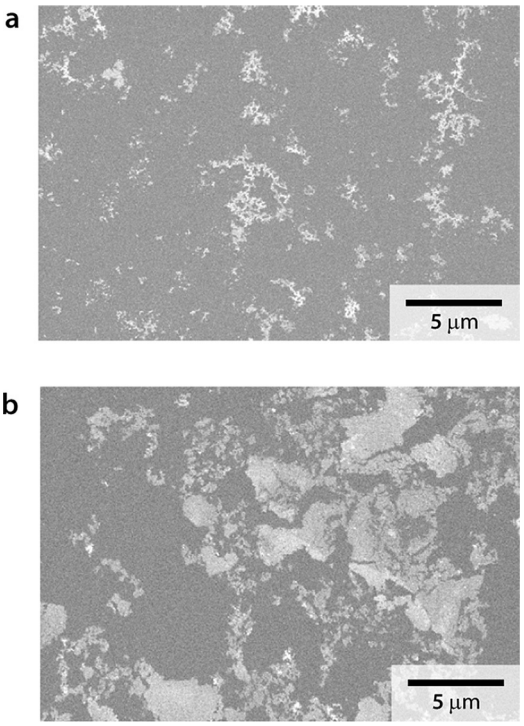


Figure 4. FE-SEM images of the mixture of fructose, sulfuric acid and ionic liquids with a) trace amounts and b) a large amount of added water.

solvent–solute pair properties. The detected droplets, particle-like structures, and meshwork were similar to those shown in Figure 2 (see the Supporting Information for FE-SEM images of the systems described in Table 1). In order to confirm that the observed structures were not the artifacts of electron microscopy, we carried out IR spectroscopy and dynamic light scattering (DLS) measurements (see the Supporting Information for details).

Finally, we used the developed technique to monitor chemical reactions in ionic liquids. The industrially relevant conversion of biomass to 5-HMF has been investigated as a process to form this highly valuable platform chemical.[18] We performed the conversion of fructose to 5-HMF, and the samples taken directly from the reaction mixture were studied by FE-SEM. The presence of water had a notable impact on the outcome of the acid-catalyzed transformation of fructose to 5-HMF in ionic liquids (Scheme 1). A higher conversion of 66% and a higher selectivity of approximately 10:1 were observed in the reaction with trace water. A larger amount (10 wt%, approximately 12 vol%) of water resulted in a much lower conversion of fructose (20%) and a poor selectivity of 2:1.

An electron microscopy study showed two types of systems. With a trace amount of water, small particles of approximately 20–30 nm in diameter, arranged into aggregates with the characteristic sizes of 1–5 μm, were formed (Figure 4 a). With a large amount of added water, the observed morphology significantly changed. The aggregates became denser, and their size increased to more than 10 μm (Figure 4 b). Thus, the addition of water to the reaction mixture led to alteration of the morphology. The formation of the bulk microscale phase with relatively low surface-to-volume ratio led to the poor substrate accessibility and, as a result, to a reduced carbohydrate conversion.

Several assumptions concerning the influence at the molecular level can be made. The presence of water in the reaction mixture can shift the equilibrium between two forms of fructose (i.e., open-chain and furanose forms) and change the contributions of the cyclic and acyclic pathways to the overall process.[19] The formation of the dehydration products can be suppressed by the addition of a large amount of water.[20] The effect of the media may influence acidic properties, which are of key importance in carbohydrate

conversion.[21] Finally, water can act at the microscopic level and change the microphase composition of the reaction mixture. Of course, it would be of interest to determine the mechanistic origin for these observations at the nano- and molecular scales. The distribution of intermediates and products between observed phases and localization of dehydration process are also still be resolved. We anticipate further studies on the subject in the near future.

In summary, we have described the direct observation of the micro-heterogeneity in ionic liquid/water and ionic liquid/alcohol two-component systems by means of scanning electron microscopy. A variety of complex structures with nanoscale and microscale organizations were revealed. The remarkable flexibility of these structures creates opportunities for the control of the reactions in water-containing systems at the microscopic level. The possibility has been demonstrated in the present study by utilizing electron-beam irradiation as a tool for microstructure shaping. The described methodology has been successfully applied to perform the FE-SEM monitoring of the chemical reaction of fructose conversion to the valuable platform chemical 5-HMF. Higher conversions and better selectivity were observed in the ionic liquid system containing a nanostructured meshwork. The loss of the nanostructured organization negatively influenced the transformation.

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