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Nonaqueous Microemulsions Containing Ionic Liquids – Properties and Applications

Oliver Zech,[1,2] Agnes Harrar,[1] and Werner Kunz[1]
[1]Institute of Physical and Theoretical Chemistry,
University of Regensburg, 93040 Regensburg,
[2]Current address: Max-Planck Institute of Colloids and Interfaces,
14424 Potsdam,
Germany

1. Introduction

There is a still growing interest in ionic liquids (ILs) in general and room temperature ionic liquids (RTILs) in particular resulting from their fascinating and outstanding properties and wide range of potential applications. The research field of ILs was almost entirely related to imidazolium, pyridinium and pyrrolidinium based substances in the last decade (Welton 1999; Earle & Seddon 2000; Wasserscheid & Keim 2000). Beside these classical aprotic ionic liquids, attention has been paid to protic (Greaves & Drummond 2007; Greaves et al., 2008 b) and to the development of less toxic ILs (Tao et al., 2006; Fukaya et al., 2007; Pernak et al., 2007; Zech et al., 2009 a). ILs are often considered as future solvents for catalysis (Welton 1999; Wasserscheid & Keim 2000; Pârvulescu & Hardacre 2007; van Rantwijk & Sheldon 2007), chemical reactions (Haumann & Riisager 2008; Martins et al., 2008), extractions (Blanchard et al., 1999), and electrochemical purposes (Hapiot & Lagrost 2008).

Apart from these applications, ILs also stimulated research in classical colloid and surface chemistry. The formation of amphiphilic association structures in and with ionic liquids, such as micelles, vesicles, microemulsions and liquid crystalline phases has been reviewed three times between 2007 (Hao & Zemb 2007) and 2008 (Qiu & Texter 2008; Greaves & Drummond 2008 a), reflecting the growing interest and progress in this field. In this review we focus on ILs in nonaqueous microemulsions, because significant new work has been reported in this field since these earlier reviews have been published.

Microemulsions are thermodynamically stable, isotropic transparent mixtures of at least a hydrophilic, a hydrophobic and an amphiphilic component. The first microemulsion structures termed at that time "oleophatic hydro-micelle" were discovered in 1943 by Hoar and Schulman (Hoar & Schulman 1943). The term microemulsion was introduced by Schulman and coworkers in 1959 describing optically isotropic transparent solutions consisting of water, oil, surfactant and alcohol (Schulman et al., 1959). A more recent definition was given by Danielsson and Lindman: "A microemulsion is a system of water, oil and an amphiphile which is a single optically isotropic and thermodynamically stable liquid solution" (Danielsson & Lindman 1981). Herein, "water" corresponds to a polar phase that is classically an aqueous solution that can contain electrolytes and other

additives. The word "amphiphile" from amphi (both sides) and philos (liking) was coined by Winsor (Winsor 1954) to describe substances with an affinity towards both non-polar and polar phases. In this context, surfactants are the most important amphiphiles, since their amphiphilic character is strong to drive them to the interface where the polar part is located in the polar phase and vice versa. The term "oil" refers to an organic phase that is immiscible or at least to a certain extend immiscible with the polar phase. Consequently, non-polar substances such as hydrocarbons, partially or totally chlorinated or fluorinated hydrocarbons, unbranched alkanes, cyclic or aromatic hydrocarbons, but also triglyceride natural oils can be used (Salager & Antón 1999). A great variety in structure of these single phase microemulsions is known in literature ranging from water-in-oil (w/o) over bicontinuous to oil-in-water (o/w) structures. In the case of a w/o microemulsion, oil is the continuous phase with water droplets stabilized by surfactant molecules and vice versa for o/w structures. The microemulsion structure depends on the volume fraction of oil, water and amphiphile as well as on the nature of the interfacial film. o/w microemulsion structures preferentially form when the oil volume fraction is low and vice versa for w/o microemulsions. Bicontinuous structures, which are networks of oil and water nanodomains separated and stabilized by a surfactant interfacial film with a net curvature close to zero, can be found at almost equal amounts of water and oil. When using non-ionic surfactants and ionic double-chain surfactants, such as sodium bis (2-ethylhexyl) sulfosuccinate (AOT) no cosurfactant is necessary for the formation of microemulsions (Angel et al., 1983). This results from the ability of these amphiphiles to reduce the interfacial tension between oil and water to a very low value, a requirement to form stable microemulsions. Many other surfactants like single-chain ionic surfactants do not exhibit this characteristic and hence cosurfactants, i.e. *n*-alcohols or *n*-amines, are indispensable to obtain the required low interfacial tension for the formation of stable microemulsions (Bellocq et al., 1984; Rakshit & Moulik 2009).

Another important phase classification that can often be found in literature has been introduced by Winsor (Winsor 1948), who found four general types of phase equilibria. A Winsor type IV phase corresponds to classical single phase microemulsions consistent with Hoar´s & Schulman´s definition (Hoar & Schulman 1943). A Winsor type I system denotes two phases in equilibrium, an o/w structure and an almost pure oil upper phase. On the contrary, in a Winsor type II system an aqueous phase containing surfactant is in equilibrium with an w/o microemulsion in the upper phase. Finally, Winsor type III structures equal a three-phase system consisting of a surfactant poor water phase, a bicontinuous middle phase, and an upper almost pure oil phase.

Apart from these classical microemulsions composed of water, oil, and surfactant (and cosurfactant, where appropriate), it has been demonstrated that the polar phase is not necessarily water and the non-polar phase not compulsorily oil. The idea of nonaqueous microemulsions is not new (Friberg & Podzimek 1984; Rico & Lattes 1984; Friberg & Liang 1987; Rico & Lattes 1987), for example water can be replaced by glycerol (Saidi et al., 1990), glycol or formamide (Ray & Moulik 1994). Efforts have further been made to replace water by a mixture of molten salts (nitrate mixtures of ethylenediamine / ammonia / potassium) in a system composed of sodium dodecyl sulfate (SDS), 1- pentanol and decane (Chang 1990).

These pioneer studies stimulated research on the formulation of nonaqueous microemulsions containing ionic liquids. This review focuses on nonaqueous microemulsions with ionic liquids with a subdivision of microemulsions containing aprotic and protic ionic liquids,

since they exhibit substantial differences with respect to phase behavior and microstructures. A strong emphasis has been placed on highlighting the differences of aqueous and ionic liquid microemulsions in general and regarding the effect of temperature in particular. Finally, an outlook concerning applications of these IL- microemulsions and future challenges and prospects is presented.

2. Ionic liquids in nonaqueous microemulsions

The definition of ionic liquids allows distinguishing them from a classical molten salt. A molten salt is mostly a high-melting, highly viscous and very corrosive substance while ionic liquids are already liquid at lower temperatures (< 100°C) and exhibit in most cases relatively low viscosities. Conventional ILs typically contain bulky organic cations with a low degree of symmetry such as imidazolium, pyrrolidinium, tetraalkylphosphonium, trialkylsulfonium or quaternary ammonium. These cations hinder the regular packing in a crystal lattice. Consequently, the solid crystalline state becomes energetically less favorable, leading to low melting points (Krossing et al., 2006). This effect can be enhanced further by the implementation of an anion with a delocalized charge, resulting in decreased interionic interactions (Xue et al., 2006).

Depending on the combination of the cation and the anion, ILs can have either hydrophilic or hydrophobic character. The most frequently investigated ILs are based on imidazolium cations. Anions such as halides, acetate, nitrate and ethylsufate form hydrophilic ILs while anions such as bis(trifluoromethylsulfonyl)imide and hexafluorophosphate lead to hydrophobic ILs. Apart from these aprotic imidazolium or pyridinium based ionic liquids there was recently a growing interest in protic ionic liquids (PILs). A comprehensive overview about types and physicochemical properties of PILs was currently given in a review of Greaves & Drummond (Greaves & Drummond 2007). Ethylammonium nitrate (EAN), which represents the first room temperature ionic liquid described in literature, has already been reported in 1914 (Walden 1914) and is nowadays probably the most frequently studied PIL.

Prior to going into detail with ternary and quaternary systems, self-assembled structures in binary IL/surfactant mixtures remain to be discussed. As a matter of principle, solvents that promote the ability of amphiphiles to form micelles should exhibit a high dielectric constant, a high solvating power and should be highly structured (Lattes & Rico 1989). Micelle formation of alkyltrimethylammonium bromides, alkylpyridinium bromides and octylphenol ethoxylate (TX-100) in EAN was first reported almost 30 years ago (Evans et al., 1982; Evans et al., 1983 a). In addition to micellar structures in binary IL/EAN mixtures, liquid crystals of lipids in EAN have been found (Evans et al., 1983 b). There has been a renewed strong research interest in this field mainly in the past few years. ILs as solvents to promote self-assembly have been reviewed in 2005, where only few studies were available in literature (Baker & Pandey 2005) and more recently in 2007 (Hao & Zemb 2007) and 2008 (Greaves & Drummond 2008 a). Although a detailed discussion of the phase behavior of binary IL/surfactant mixtures is beyond the scope of this review, some general conclusions can be drawn. The critical micelle concentration (cmc) is significantly higher in ILs compared to water. For example Evans et al. found that the cmc of conventional surfactants in EAN is between 5 and 10 times higher compared to water (Evans et al., 1982). Greaves et al. studied the self-assembly behavior of amphiphiles in 22 different protic ILs (Greaves et al., 2008 b), fourteen of those were found to promote self-assembly of amphiphiles. The

concept of the Gordon parameter, which represents a measure of the cohesive energy density of a solvent and hence the driving force of a solvent as promoter for self-assembly was applied to these systems. Whilom it was generally accepted that no amphiphilic aggregation exists for solvents with a Gordon parameter below 1.3 J m^{-3} (Evans & Wennerström 1998). Nowadays, ethylammonium butyrate with a value of 0.576 J m^{-3} is the solvent with the lowest Gordon parameter known to promote self-assembly of amphiphiles (Greaves et al., 2007). The self-assembly is not restricted to protic ILs, it has been documented for several aprotic ILs as well (Anderson et al., 2003; Hao et al., 2005; Patrascu et al., 2006). In addition to the extensive amount of research conducted into binary IL/surfactant mixtures progress has been made in the formulation and characterization of nonaqueous microemulsions, the actual topic of this review.

2.1 Aprotic ionic liquids

Studies concerning the use of aprotic ILs in microemulsions are almost entirely related to imidazolium based substances. Herein, the most extensively studied microemulsions comprise the RTIL 1-butyl-3-methyimidazolium tetrafluoroborate ([bmim][BF$_4$]) as water substitute, the non-ionic surfactant TX-100 and oil as apolar phase.

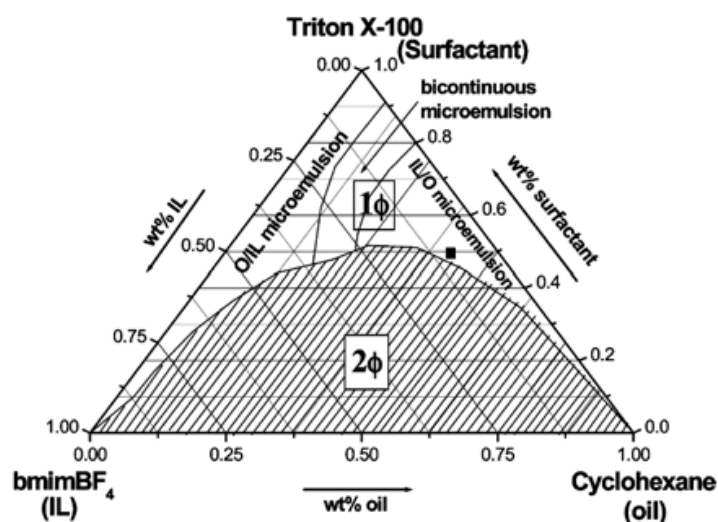Fig. 1. Ternary phase diagram of [bmim][BF$_4$]/TX-100/cyclohexane at 23 °C. (Reproduced from (Gao et al., 2008) with permission, copyright American Chemical Society, 2008).

The first microemulsion, where water has been replaced by an RTIL has been reported by Gao et al. (Gao et al., 2004). They replaced water by [bmim][BF$_4$], while cylcohexane has been used as apolar phase and TX-100 as surfactant. The corresponding ternary phase diagram at 35°C has been recorded, while the phase diagram for the identical system has been reported by Li et al. at 25 °C (Li et al., 2008) and by Gao et al. at 23°C (Gao et al., 2008). Since the phase diagrams do not differ significantly between 23°C and 35°C, the phase diagram at 23 °C is exemplarily illustrated in Figure 1.

In the following, the state of research on [bmim][BF$_4$]/TX-100/cyclohexane microemulsions is discussed in detail. Different microemulsion subregions have been identified by means of conductivity measurements (Gao et al., 2004). Typical cuts in the phase diagram have been made, where the weight fraction of [bmim][BF$_4$]/TX-100 was kept constant while the amount of cyclohexane increases. Consistent with microstructures known for aqueous

microemulsions, oil-in-IL (o/IL) microregions at low amounts of cyclohexane, followed by bicontinuous and IL-in-oil (IL/o) structures with increasing oil content have been identified via conductivity measurements. Further, freeze fracture transmission electron micrographs (FF-TEM) in the IL/o microregion indicated droplet structures with increasing size when R value, defined as the molar ratio of [bmim][BF$_4$]/surfactant, was rised. The results are consistent with apparent hydrodynamic radii extracted from dynamic light scattering (DLS) measurements. Nonetheless, the droplet sizes inferred from DLS measurements of the order of 0.1 μm at R = 1.5 appear to be extraordinary large and are outside the range of conventional microemulsions. These outstandingly large droplet dimensions may be related to collective scattering effects that have not been taken into account (Qiu & Texter 2008).
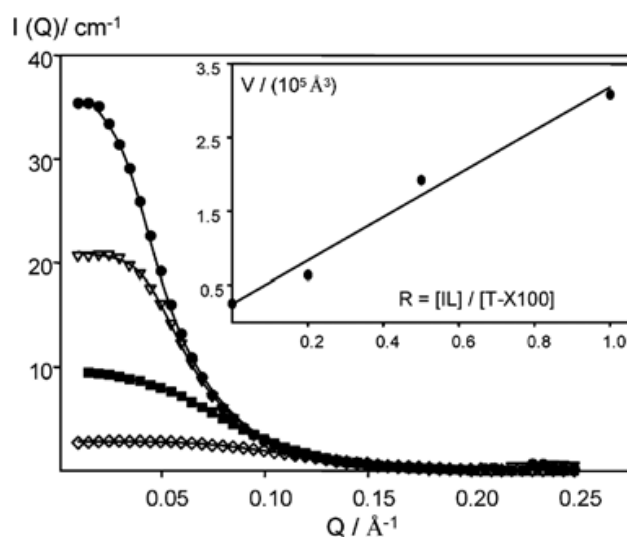

Fig. 2. SANS from single-phase [h-bmim][BF4] in cyclohexane-d_{12} microemulsions at 55°C. R = 0 (◊), 0.2 (■), 0.5 (Δ), and 1.0 (•); ϕ_{TX-100} =0.41. The fits shown as lines are to a form factor for homogeneous ellipsoids. Inset shows the micelle swelling behavior in terms of the ellipsoid volume V as a function of added IL. (Reproduced from (Eastoe et al., 2005), with permission, copyright American Chemical Society, 2008).

Eastoe et al. performed small angle neutron scattering (SANS) experiments on the same systems at 55°C, except that cyclohexane-d_{12} was used to improve the scattering contrast (Eastoe et al., 2005). The scattering curves for different R values, comparable to the R values investigated by Gao et al. (Gao et al., 2004) could well be described by a model of homogeneous diluted ellipsoidal particles, which was in agreement with IL/o structures. A swelling behavior of the IL nanodomains with increasing R value was observed consistent with the observations of Gao et al. The SANS curves with the corresponding fits for ellipsoidal structures are illustrated in Figure 2. By contrast, the extracted sizes were in the typical range of aqueous microemulsions arguing strongly against the DLS radii reported by Gao et al.

The solvation dynamics and rotational relaxation of Coumarin 153, a rigid molecule having a single low-lying excited state and simple solvatochromic behavior (Maroncelli & Fleming 1987) has been investigated for the same system by Chakrabarty et al. (Chakrabarty et al., 2005). With steady state and time resolved fluorescence spectroscopy measurements at different R values they observed a red shift in the emission spectra with increasing [bmim][BF$_4$] content indicating the formation of RTIL pools. The solvation times in the RTIL pools were found to be nearly independent of [bmim][BF$_4$] content and size of the

microemulsion droplets. By contrast, a decrease in solvation time in aqueous reverse microemulsions with increasing R values has been documented in literature (Sarkar et al., 1996; Riter et al., 1998). Using isothermal titration microcalorimetry Li et al. determined the heat of dilution and extracted the second virial coefficient, b_2 of these microemulsions (Li et al., 2008). Both heat of dilution and b_2 are significantly larger compared to conventional aqueous microemulsions (Chen et al., 2000). From these studies Li et al. deduced substantial stronger interactions of the IL nanodroplets compared to aqueous systems. Further, the data suggested weakened interdroplet interactions with increasing temperature. With respect to the influence of temperature important results have been obtained studying temperature induced microstructural changes with DLS, freeze-fracture transmission electron microscopy (FF-TEM) and two-dimensional nuclear Overhauser effect (ROESY) experiments (Gao et al., 2009 a). By visual inspection a single phase microemulsions has been observed up to 74°C, which corresponds to the boiling point of cyclohexane. DLS measurements indicate an increase in droplet size with rising temperature within (24 – 44)°C with diameters between 54 nm (24°C) and 153 nm (44°C). Gao et. al proposed that the formation of microemulsions in a system consisting of [bmim][BF$_4$] and TX-100 is driven by the electrostatic attraction between the positively charged [bmim]$^+$ cation and the ethylene oxide (EO) units in TX-100 (Gao et al., 2006 b). Hence, the effective interaction area of EO units is higher than in water resulting in an increased size of the reverse microemulsion droplets (Gao et al., 2009 a). FF-TEM images confirmed the existence of a droplet structure within (25 – 55)°C and are in agreement with increasing droplet size with rising temperature. 2D ROESY spectra indicated structures with [bmim][BF$_4$] domains, stabilized by a surfactant interfacial film in a continuous oil phase. Further, it was proposed that EO moieties penetrate into the RTIL interior with the hydrophobic chain pointing towards the continuous oil phase. Moreover, an increase in droplet size with rising temperature is related to a decrease in interfacial curvature of the surfactant film. Gao et al. supposed that the electrostatic interaction between the [bmim]$^+$ cation and the EO units is relatively temperature independent while the solubility of the hydrophobic surfactant chain is temperature sensitive and thus causes the change in interfacial curvature (Gao et al., 2009 a). A schematic picture of the proposed microemulsion structure in dependence of temperature including the change in interfacial curvature is illustrated in Scheme 1. However, these microemulsions are relatively temperature insensitive compared to common nonionic surfactant based aqueous microemulsions (Wormuth et al., 2002) highlighting fundamental differences between IL and water based microemulsions. The temperature sensitivity of aqueous microemulsions with nonionic surfactants is related to the interaction of water molecules with the EO moieties of the nonionic surfactant. Hence, a temperature change can provoke transitions from w/o to bicontinuous and o/w structures (Wormuth et al., 2002).

For [bmim][BF$_4$]/TX-100/oil microemulsions the influence of replacing the oil phase has been extensively studied as well. Beside cyclohexane as described in the previous paragraph, phase diagrams with toluene (Gao et al., 2006 a; Li et al., 2007), p-xylene (Gao et al., 2006 b) and even benzene (Gao et al., 2007 a; Gao et al., 2007 b) have been reported. The resulting phase diagrams are comparable to the phase diagram shown in Figure 1 indicating that there is no major influence of the type of the oil with respect to the single phase region and type of occurring microstructures. Similar to the systems described for cyclohexane transition from o/IL over bicontinuous to IL/o structures with increasing toluene (Gao et al., 2006 a), p-xylene (Gao et al., 2006 b) and benzene content (Gao et al., 2009 b), respectively have been detected with conductivity measurements. Further, a swelling of the IL
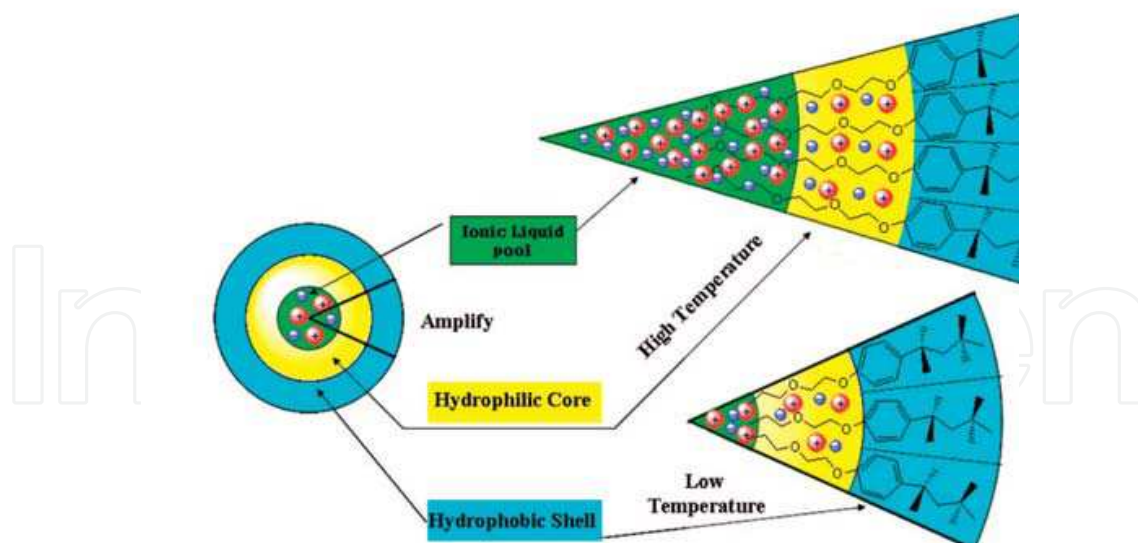
Scheme 1. Schematic illustration of the [bmimBF$_4$]/o microemulsion structure, accompanied by the curvature change of TX-100 interfacial film at [bmimBF$_4$]/o two phases with changing temperature. (Reproduced from (Gao et al., 2009 a) with permission, copyright American Chemical Society, 2009).

nanodomains with increasing amount of [bmim][BF$_4$] has been verified by DLS measurements for the [bmim][BF$_4$]/p-xylene microemulsions (Gao et al., 2006 b). The micropolarity of [bmim][BF$_4$]/TX-100/toluene has been studied via UV-vis spectroscopy and methyl orange (MO) as probe. With increasing amount of [bmim][BF$_4$] the absorption spectra were red shifted indicating an increase in micropolarity until a plateau was reached when the RTIL pool was formed. Similar results have been reported by Han and coworkers for [bmim][BF$_4$]/TX-100/cyclohexane systems (Gao et al., 2004). Fu et al. studied the electrochemical properties with toluene as oil phase using cyclic voltammetry (CV) and electrochemical impendence with potassium ferricyanide as electroactive probe (Fu et al., 2008). Their measurements indicated that the reversibility of [Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4-}$ electrode reaction in the o/IL microemulsion was enhanced compared to IL/o structures and the neat IL, respectively. Concerning the effect of temperature an increase in droplet size with increasing temperature was reported with toluene as continuous phase similar to the systems with cyclohexane (Gao et al., 2009 a). Recently, FF-TEM was used to detect the swelling process of o/IL microemulsions. Herein, bicontinuous IL containing microemulsions have been visualized for the first time with FF-TEM (Gao et al., 2009 b). The structural evolution monitored by FF-TEM is illustrated exemplarily for the [bmim][BF$_4$]/TX-100/toluene system in Figure 3.

Therein, the R value was kept constant at $R = 0.5$, while the organic solvent weight fraction F successively increases. For $F \leq 0.25$ a nearly spherical droplet structure could be detected, while the o/IL diameter increased with F confirming the swelling behavior. Moreover, the aggregates changed from spherical structures ($F \leq 0.25$) to droplet clusters and larger aggregates. At a toluene weight fraction of $F = 0.30$, a bicontinuous structure could be detected. A comparable structural evolution has been observed for the [bmim][BF$_4$]/TX-100/p-xylene microemulsions ranging from droplet structures over droplet clusters to bicontinuous systems. By contrast, bicontinuous structures could not be identified for [bmim][BF$_4$]/TX-100/cyclohexane systems since phase separation occurred at higher cyclohexane weight fractions.
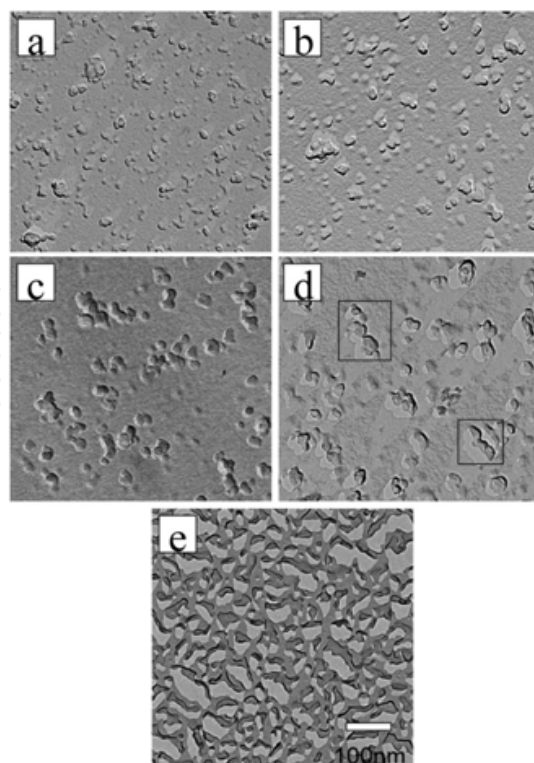
Fig. 3. FF-TEM images of the toluene/[bmim][BF$_4$] microemulsion aggregates with R = 0.5 and F = 0.10 (a), 0.15 (b), 0.20 (c), 0.25 (d), and 0.30 (e). Scale bar is 100 nm for all samples in the figure. (Reproduced from (Gao et al., 2009 b) with permission, copyright American Chemical Society, 2009).

Adhikari et al. investigated microemulsions comprising 1-pentyl-3-methylimidazolium tetrafluoroborate ([pmim][BF$_4$])/TX-100/benzene (Adhikari et al., 2007; Adhikari et al., 2009). Surprisingly, the ternary phase diagram has not yet been documented in literature. However, interesting results have been obtained studying the solvation dynamics in different subregions of these microemulsions with Coumarin 480 (C480) as probe. The probe can be distributed in both polar and apolar regions of the microemulsions. Since the solute absorption and emission spectra are dependent on the polarity of the solvent, the probe can be excited selectively by a variation of the excitation wavelength λ_{ex}. A so-called red edge exication shift (REEs) denotes the shift in the wavelength of maximum fluorescence emission towards higher wavelengths, caused by a shift in the excitation wavelength towards the red edge of the absorption band (Demchenko 1982; Mukherjee & Chattopadhyay 2005). For the RTIL microemulsion faster solvation dynamics and a slower anisotropy decay with increasing λ_{ex} has been reported (Adhikari et al., 2007). The authors explained these observations by a higher viscosity and polarity of the core of the reverse microemulsion compared to that at the interface. Therefore, a long λ_{ex} accompanied with slow anisotropy decay probes a highly viscous core. Moreover, fluorescence resonance energy transfer (FRET) from C480 and rhodamine 6G (R6G) has been studied in the same microemulsion by picosecond and femtosecond emission spectroscopy (Adhikari et al., 2009). Three different time scales of FRET of (1, 250 and 3000) ps have been found. It was proposed that in the highly polar IL pool FRET is very fast based on the close proximity of the donor and the acceptor species. The 250 ps component could be allocated to FRET from

a donor inside the surfactant chains and the long component was assigned to FRET from a donor in the continuous phase and an acceptor in the RTIL core. Further, Mojumdar et al. studied the proton transfer of pyranine via femtosecond up-conversion (Mojumdar et al., 2010) in the same microemulsions.

In the previous paragraphs the state of research concerning microemulsions with [bmim][BF$_4$] and [pmim][BF$_4$] as polar phase has been summarized. Li et al. varied the ionic liquid representing the polar phase in nonaqueous microemulsions (Li et al., 2005). They replaced water by 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]). The idea of using [bmim][PF$_6$] as polar phase represents an unconventional idea and important progress, since [bmim][PF$_6$] is considered as apolar and not miscible with water. The single-phase region of the ternary phase diagram toluene/TX-100/[bmim][PF$_6$] covered an area about 75% of the phase diagram. Different subregions could be detected via conductivity measurements. With increasing weight fraction of TX-100 + [bmim][PF$_6$] a transition from a [bmim][PF$_6$]/o microstructure via a bicontinuous region to an o/[bmim][PF$_6$] microstructure has been reported. Small angle X-ray scattering (SAXS) experiments that have been performed in the [bmim][PF$_6$]/o sub-region indicated a swelling of the droplet structure with increasing amount of RTIL. The apparent gyration radii (R_g) extracted from Guinier analyses lay in a typical size range for microemulsions between (4.4 and 6.2) nm at different R values ($0.3 \leq R \leq 0.98$). Zheng et al. investigated microemulsions consisting of toluene/Tween 80/ [bmim][PF$_6$] (Zheng & Eli 2009; Zheng et al., 2009). These systems have been characterized via conductivity and FTIR spectroscopy (Zheng et al., 2009), the micropolarity has been monitored via UV- VIS spectroscopy (Zheng & Eli 2009). Conductivity measurements indicated a transition from o/[bmim][PF$_6$] via bicontinuous to [bmim][PF$_6$]/o microregions with increasing toluene weight fraction at a fixed R value. The transitions monitored by conductivity measurements, exemplarily shown for these systems, are illustrated in Figure 4. Since Figure 4 represents a typical example for phase transitions in microemulsions that can be detected with conductivity measurements, the characteristics of the curve will be discussed in the following. The increase in conductivity along the curve from point A to B can be allocated to an o/RTIL microstructure. With increasing amount of
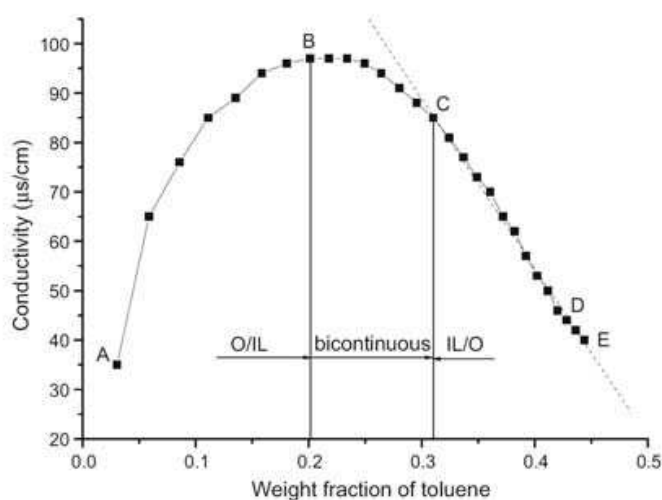

Fig. 4. Electrical conductivity of the microemulsions toluene/Tween80/[bmim][PF$_6$] as a function of toluene content, [bmim][PF$_6$]/Tween 80 = 1.9. (Reproduced from (Zheng et al., 2009) with permission copyright Springer-Verlag, 2009).

oil (toluene) the conductivity increases, which correlates with an increase in the mobility of charge carriers. The addition of a cosolvent, in the present case toluene, increases the mobility of charge carriers, because less of ion pairs are then present in the solution. With increasing toluene content the volume of the microdroplets rises correlating with an improved ionic mobility due to the dissociation of ion pairs in the solution. From point B to C the conductivity decreases slightly indicating a change in microemulsion structure. This subregion can be assigned to a bicontinuous structure. When the oil content is further increased a significant decrease in conductivity can be observed between point C and E representing a typical IL/ o structure. The authors attributed the change in conductivity from point D to E to a percolation phenomenon that might be present in this system, but to our opinion this can not clearly be confirmed from these data.

FTIR spectra indicated the presence of hydrogen-bonds between [bmim][PF$_6$] and Tween 80. Zheng et al. reported hydrogen-bond interactions between the C2-H of the [bmim]$^+$ cation and the EO units in Tween 80 and an interaction of the [PF$_6$]$^-$ anion with the terminal hydroxyl group of Tween 80 (Zheng et al., 2009). The authors suggested that these hydrogen-bonded interactions between [bmim][PF$_6$] and Tween 80 might be the driving force for the solubilization of the RTIL into the core of the Tween 80 aggregates.

Cheng et al. investigated promising systems consisting of ethylene glycol (EG) as polar phase, [bmim][PF$_6$] as oil substituent and TX-100 as surfactant (Cheng et al., 2007 a). Since the vapor pressure of both EG and [bmim][PF$_6$] are very low at ambient temperature, these microemulsions represent an important step towards systems consisting entirely of non-volatile components. The microemulsions have been studied by means of conductivity, DLS, UV-Vis and FF-TEM measurements. With conductivity measurements [bmim][PF$_6$]/EG, bicontinuous and EG/[bmim][PF$_6$] subregions could be identified. The [bmim][PF$_6$]/EG subregion has further been characterized by DLS measurements, for different R values (0 ≤ R ≤ 0.28) apparent hydrodynamic radii between (5 – 19) nm have been extracted confirming a swelling behavior with increasing amount of RTIL. Further, the radii extracted from CONTIN analysis (Provencher 1982 a; Provencher 1982 b) are consistent with a swelling law for spherical microemulsions, where the size of the droplets should be a linear function of R (Zhu et al., 1992). The swelling law can be expressed as $R_H{}^{app} = 3\, V_{disp}\, R\, A_h{}^{-1}$, where $R_H{}^{app}$ is the apparent droplet radius, V_{disp} the molecular volume of the dipersed phase and A_h the effective area per headgroup at the interface (Cheng et al., 2007 a). The [bmim][PF$_6$]/EG microemulsions obeyed this swelling law confirming a spherical droplet structure. FF-TEM images further confirmed the existence of spherical [bmim][PF$_6$]/EG microregions, while the sizes agreed reasonably well with the droplet dimensions extracted from DLS measurements. Using MO as probe, UV-Vis measurements indicated an increasing micropolarity of the EG domains with rising amount of EG in the EG/[bmim][PF$_6$] subregion.

Most studies concerning aprotic ionic liquids in microemulsions are attendant on the use of nonionic surfactants. In contrast, we reported microemulsions consisting of the ionic surfactant 1-hexadecyl-3- methylimidazolium chloride ([C$_{16}$mim][Cl]), which is at the same time an ionic liquid (Zech et al., 2009 b). Further, [bmim][BF$_4$] has been used as polar phase, dodecane as apolar phase and decanol as cosurfactant. Along an experimental path in the corresponding phase diagram, these systems have been characterized by means of conductivity, viscosity and SAXS measurements. Moreover, we have directly compared microemulsions with the aprotic ionic liquid [bmim][BF$_4$] and the protic ionic liquid ethylammonium nitrate (EAN). The major advantage of using ionic surfactants is that the

microemulsions become even less sensitive towards temperature. A detailed comparison of the [bmim][BF$_4$] systems with the protic RTIL EAN is given in section 2.2.

Rabe & Koetz investigated phase diagrams of 1-ethyl-3-methylimidazolium ethylsulfate ([emim][etSO$_4$])/cetyltrimetyhlammonium bromide (CTAB)/toluene+pentanol and 1-ethyl-3-methylimidazolium hexylsulfate ([emim][hexSO$_4$])/CTAB/toluene+pentanol, respectively (Rabe & Koetz 2010). They studied the phase behavior of these systems in dependence of oil/cosurfactant ratio and temperature. Interesting results have been obtained although these systems are on the boarderline of nonaqueous microemulsions, since the authors reported water contents in the IL up to 5wt%. To our opinion terming an IL with 5wt% water "nearby water-free" (Rabe & Koetz 2010) is questionable, since 5wt% of water correspond for example for [emim][hexSO$_4$] to a water molar ratio of $x_{H2O} = 46\%$! For the system [emim][etSO$_4$]/CTAB/toluene+pentanol different toluene/pentanol ratios have been investigated ranging from 1:1 to 20:1 at ambient temperature. In the absence of cosurfactant two separated isotropic phase channels could be found, where one was attributed to an IL/o structure and the second to an o/IL microstructure. With increasing amount of cosurfactant the area of these single phase regions increased until they became connected at a toluene:pentanol ratio of 1:1. Further, the effect of temperature on the pseudo-ternary phase diagrams was studied. For a ratio toluene:pentanol of 5:1 the two separated phase channels present at ambient temperature were connected at 50°C, with increasing temperature (80°C) the area of the one phase region further augmented. These temperature dependent phase diagrams are illustrated in Figure 5. With conductivity measurements a typical percolation phenomenon with increasing amount of IL in the IL/o region was observed, the threshold was found to be relatively independent of the IL anion chain length. The percolation behavior was further confirmed with viscosity measurements. From DLS measurements two separate peaks were extracted in the intensity plot with sizes in the typical range for microemulsions. Cryo scanning electron microscopy (cryo-SEM) images below the percolation threshold indicate separated spherical structures which were attributed to IL/o microstructures. An increase in droplet size with increasing amount of IL was further confirmed by cryo-SEM.
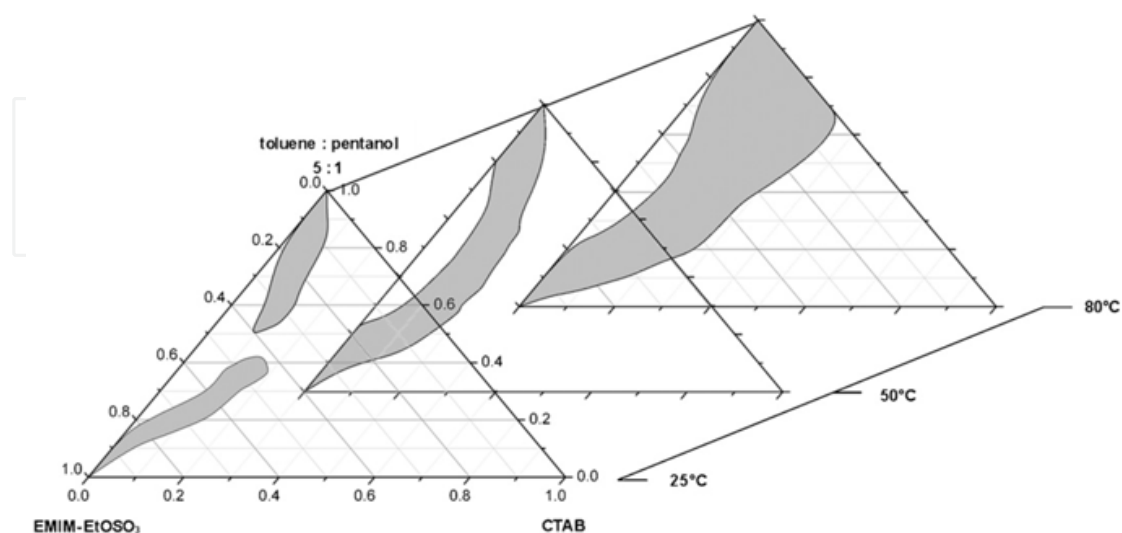

Fig. 5. Pseudo ternary phase diagrams of CTAB/toluene+pentanol/[emim][etSO$_4$] between (25 – 80)°C. (Reproduced from (Rabe & Koetz 2010), with permission, copyright Elsevier, 2010).

Gayet et al. characterized microemulsions composed of benzylpyridinium bis-(trifluoromethanesulfonyl)imide ([bnpyr][NTf$_2$])/TX-100/toluene (Gayet et al., 2009). The microstructure has been investigated with DLS, SANS, viscosity and pulse field gradient spin-echo (PGSE) NMR measurements. A transition of o/IL over bicontinuous to IL/o microstructures with increasing toluene content has been identified by means of conductivity measurements. Relative self-diffusion coefficients determined via PGSE NMR measurements were in line with the existence of IL/o structures. Hydrodynamic radii in the IL/o regime were in the typical order of magnitude for microemulsion structures, while radii from DLS measurements ($2.2 \leq R_h \leq 3.4$) nm were slightly larger compared to the PGSE NMR measurements ($1.8 \leq R_h \leq 1.9$) nm. SANS and SANS contrast variation data in the IL/o regime could be described using a polydisperse homogeneous ellipsoid model, while for the bicontinuous regime the domain size D^* was evaluated via the Bragg relation $D^* = 2\,\pi\,q_{max}^{-1}$ where q_{max} corresponds to the position of the correlation peak.

Cheng et al. highlighted a major contribution towards the formulation of nonaqueous microemulsions with two types of ionic liquids (Cheng et al., 2007 b). For the first time they reported ionic liquid in ionic liquid (IL/IL) structures. For this purpose, the hydrophobic ionic liquid [bmim][PF$_6$] and the hydrophilic protic ionic liquid propylammonium formate (PAF) were used as apolar and polar phase, respectively. Moreover, these microemulsions contained the anionic surfactant sodium bis (2-ethylhexyl) sulfosuccinate (AOT). One
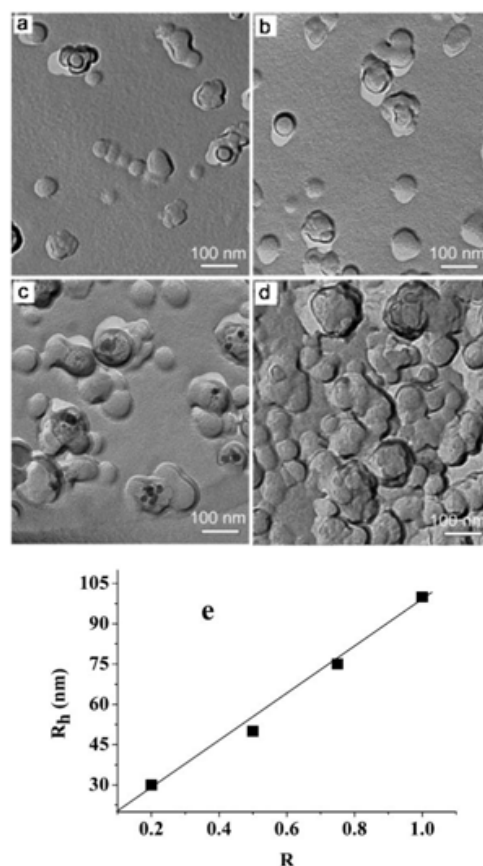

Fig. 6. TEM images of FFEM replicas of [bmim][PF$_6$]–AOT–PAF microemulsions. (a) R = 0.2, (b) R = 0.5, (c) R = 0.75, (d) R = 1.0 (weight fraction of AOT is 0.16); (e) dependence of the droplet diameter (R_h) on [bmim][PF$_6$]-to-AOT molar ratio (R). (Reproduced from (Cheng et al., 2007 b), with permission, copyright Royal Society of Chemistry, 2007).

important precondition for the formation of stable microemulsions is that the polar and the apolar phase do not mix. By the tricky combination of PAF and [bmim][PF$_6$], whose solubility in PAF was less than 0.1 wt% under ambient conditions (Cheng et al., 2007 b) this requirement could be fulfilled. However, the single phase region in the ternary phase diagram was exceptionally small. FF-TEM images at different R values and a constant amount of surfactant indicated droplet like structures with droplet radii ranging from (15 – 50) nm as illustrated in Figure 6. The authors proposed [bmim][PF$_6$]/PAF structures, the extracted radii increased linearly with *R*.

For a better overview, the different microemulsion systems with aprotic ionic liquids, the methods used to characterize them and the corresponding references are summarized in Table 1.

microemulsion system	methods	references
[bmim][BF$_4$] TX-100 cyclohexane	conductivity, FF-TEM, DLS, UV-Vis SANS DLS, FTIR, ^{1}H-NMR, ITC, conductivity ITC steady-state and picosecond time resolved emission spectroscopy IT-microcalorimetry, conductivity DLS, FF-TEM, ROESY conductivity, ROESY, FF-TEM	(Gao et al., 2004) (Eastoe et al., 2005) (Gao et al., 2008) (Li et al., 2008) (Chakrabarty et al., 2005) (Chen et al., 2000) (Gao et al., 2009 a) (Gao et al., 2009 b)
[bmim][BF$_4$] TX-100 p-xylene	conductivity, DLS, ^{1}H-NMR, FTIR, UV-Vis conductivity, ROESY, FF-TEM	(Gao et al., 2006 b) (Gao et al., 2009 b)
[bmim][BF$_4$] TX-100 toluene	conductivity, CV conductivity, DLS, UV-Vis conductivity, CV, impendance spectroscopy DLS, FF-TEM, ROESY conductivity, ROESY, FF-TEM	(Gao et al., 2006 a) (Li et al., 2007) (Fu et al., 2008) (Gao et al., 2009 a) (Gao et al., 2009 b)
[bmim][BF$_4$] TX-100 benzene	FTIR, ^{1}H-NMR, ^{19}F-NMR, DLS conductivity, ROESY, FF-TEM	(Gao et al., 2007 a) (Gao et al., 2009 b)
[pmim][BF$_4$] TX-100 benzene	femtosecond up-conversion, DLS FRET femtosecond up-conversion	(Adhikari et al., 2007) (Adhikari et al., 2009) (Mojumdar et al., 2010)
[bmim][PF$_6$] TX-100 toluene	conductivity, SAXS	(Li et al., 2005)
[bmim][PF$_6$] Tween 80 toluene	UV-Vis, conductivity conductivity, FTIR	(Zheng & Eli 2009) (Zheng et al., 2009)
ethylene glycol	conductivity, DLS, FF-TEM, UV-Vis	(Cheng et al., 2007 a)

TX-100 [bmim][PF$_6$]		
[bmim][BF$_4$] [C$_{16}$mim][Cl]+1-decanol dodecane	conductivity, viscosity, SAXS	(Zech et al., 2009 b)
[emim][etSO$_4$] or [emim][hexSO$_4$] CTAB toluene+pentanol	conductivity, viscosity, oscillation measurements, DLS, cryo-SEM	(Rabe & Koetz 2010)
[bnpyr][NTf2] TX-100 toluene	conductivity, PGSE NMR, DLS, SANS	(Gayet et al., 2009)
PAF AOT [bmim][PF$_6$]	surface tension, FF-TEM	(Cheng et al., 2007 b)

Table 1. Summary of the different microemulsions systems with aprotic ionic liquids together with the references and methods used.

2.2 Protic ionic liquids

Atkin & Warr reported microemulsions composed of nonionic alkyl oligoethyleneoxide surfactants (C$_i$E$_j$), alkanes and EAN as polar phase (Atkin & Warr 2007). They studied the phase behavior of the ternary mixtures by applying typical slices through the phase prism at a 1:1 oil to water ratio while the amount of surfactant was varied. Since phase prisms of microemulsions with nonionic surfactants, where the dependence of temperature is taken into account are relatively complicated and difficult to interpret, greater understanding comes from going back to two-dimensional space by taking slices through the phase prisms. The phase diagram, where the mass fraction of surfactant is shown as a function of temperature, takes the shape of a fish. These so-called fish cuts are the most often used two-dimensional phase diagrams concerning microemulsions with non-ionic surfactants and have been studied systematically for aqueous microemulsions by Kahlweit et al. (Kahlweit et al., 1988; Kahlweit et al., 1989). Atkin and Warr presented fish-cuts obtained for an equal ratio of water to oil for surfactants with increasing amphiphilicity (C$_8$E$_2$, C$_{12}$E$_3$, C$_{14}$E$_4$). With dodecane as oil the phase diagrams were very similar to the corresponding aqueous systems (Kahlweit et al., 1993). A tricritical point (Kahlweit et al., 1985; Kahlweit et al., 1986), where the formation of a three phase body occurred was found for the EAN/C$_i$E$_j$/dodecane systems at amphiphilicities between C$_8$E$_2$ and C$_{12}$E$_3$. Compared to water (Kahlweit et al., 1986) and formamide (Schubert et al., 1993) the tricritical point was shifted for EAN to higher amphiphilicities i.e. longer alkyl chain lengths. Additionally, Atkin & Warr studied the microemulsions phase behavior as a function of the oil alkyl length (octane, decane, dodecane, tetradecane and hexadecane) and headgroup size. Exemplarily fish-cuts for EAN microemulsions with dodecane and tetradecane are illustrated in Figure 7.

The phase behavior response to these changes was found to be broadly consistent with aqueous systems, while the effective area of interaction for each EO unit was found to be significantly higher in EAN compared to aqueous systems. $\overline{X}$ defines the point of the
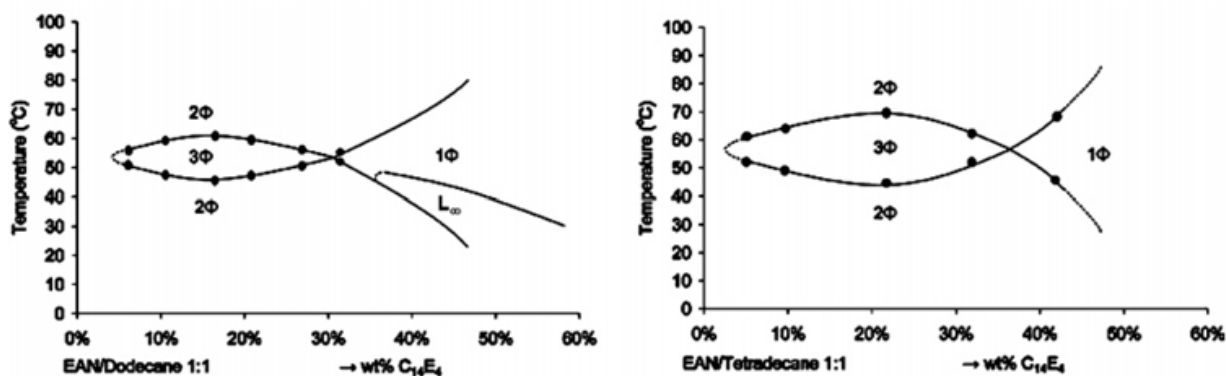
Fig. 7. Vertical section through the phase prisms for $C_{14}E_4$/EAN/alkane systems with equal masses of EAN and alkane. (Reproduced from (Atkin & Warr 2007), with permission, copyright American Chemical Society, 2007).

maximum surfactant efficiency i.e. the minimum amount of surfactant required to solubilize two immiscible solvents. SAXS curves near $\overline{X}$ exhibit a single broad scattering peak followed by a q^{-4} decay at large q values. The curves could well be described with the Teubner-Strey model (Teubner & Strey 1987). The oil and water regimes are coupled via the surfactant film resulting in a broad scattering peak. Both, the scattering peak and the q^{-4} dependence at large q can be described with the TS formula and two characteristic length scales, the domain size d and the correlation length ξ can be extracted. From the SAXS experiments the authors concluded that the changes in d and ξ with amphiphilicity and oil alkyl chain length are consistent with observations made for aqueous systems. Nevertheless, the SAXS data suggested that the structuring in EAN microemulsions is higher compared to their aqueous counterparts. Zemb interpreted the SAXS data of Atkin and Warr on the C_iE_j/EAN/alkane systems in terms of a dimensionless dilution plot (Zemb 2009). Data have been compared to predictions of the models of de Gennes and Taupin (De Gennes & Taupin 1982), disordered open connected (DOC) cylinders and DOC lamellar structures (Zemb et al., 1990; Zemb 1997). None of the existing models was compatible with the experimental results. Nevertheless, a simple random microstructure without local order could be excluded, the data suggested that a connected microstructure is more likely to exist. Recently, Atkin et al. studied microemulsions composed of propylammonium nitrate (PAN), C_iE_j and different alkanes (Atkin et al., 2009). Although no cloud points of nonionic surfactants could be found in PAN, the phase behavior of ternary systems equals that of EAN and water based systems. Conductivity measurements and phase behavior of PAN/C_iE_j/oil microemulsions indicated that the microemulsions are weakly structured up to surfactant chain length of C_{18}. SANS data could well be described by the TS formula. Further, SANS contrast variation revealed a cosurfactant like role of the propylammonium cation in these ternary microemulsions.

Beside the implementation of protic ILs in microemulsions with nonionic surfactants, pseudo-ternary systems with ionic surfactants have been reported as well. We compared microemulsions composed of [C_{16}mim][Cl]+decanol/ RTIL/dodecane with EAN and [bmim][BF$_4$] as polar phase, respectively at ambient temperature (Zech et al., 2009 b). A significant difference with respect to phase behavior and microemulsions structure has been found. The area of the one phase region was considerably larger in the case of EAN than for microemulsions with [bmim][BF$_4$]. For the microemulsions with EAN a typical percolation behavior for the EAN/o region with increasing EAN content has been found. DLS

measurements indicated a swelling with increasing EAN content, which was further confirmed by SAXS measurements. At low EAN content a droplet EAN/o structures followed by the formation of larger connected EAN/o aggregates were supposed, while in the case of [bmim][BF$_4$] a bicontinuous structure is more likely to exist. Since all ingredients show an excellent thermal stability combined with high boiling points and decomposition temperatures, respectively, we have recently investigated the thermal stability of the [C$_{16}$mim][Cl]+decanol/ EAN/dodecane microemulsions. It could be demonstrated that these microemulsions were stable within a temperature range between (30 – 150)°C. Therefore, these microemulsions represent the first high temperature microemulsions with ILs, exhibiting a thermal stability that cannot be achieved with their aqueous counterparts (Zech et al., 2010 a). The percolation behavior in the EAN/o region could be observed over the whole investigated temperature range, as illustrated in Figure 8, where the specific conductivity is shown as a function of the volume fraction ϕ. From the inset of the plot in Figure 8 it is obvious that the threshold, where the conductivity increases remarkably and percolation appears, is shifted with increasing temperature to the left hand side i.e. to lower volume fractions. The corresponding percolation threshold volume fraction ϕ_P was shifted continuously with increasing temperature to lower volume fractions. This effect can be explained by the increased motion of the formed IL nanodomains when the temperature is rised. Hence, the probability that two RTIL pools meet each other is higher and the threshold is shifted to smaller ϕ. DLS measurements at 30°C indicated a swelling of the EAN/o nanodroplets with increasing amount of EAN, until a bimodal decay was observed in the intensity normalized autocorrelation functions. The threshold, where a bimodal decay occurred was consistent with the percolation threshold extracted from conductivity measurements (Zech et al., 2010 b). The high thermal stability was further confirmed by temperature dependent SANS experiments (Zech et al., 2010 b). Below the percolation threshold, the data treated by generalized indirect Fourier transformation (Brunner-Popela & Glatter 1997; Weyerich et al., 1999) (GIFT) analysis suggest a droplet like EAN/o microemulsion structure. The resulting pair distance distribution functions $p(r)$ were interpreted in a classical way as histogram of distances inside the particle. The maxima of
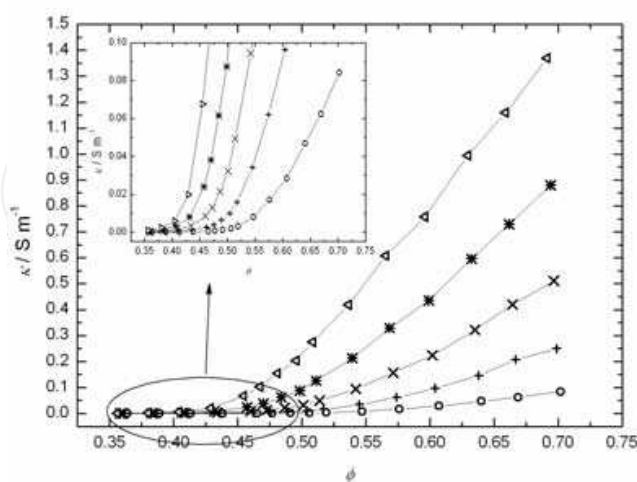

Fig. 8. Specific conductivity as a function of the volume fraction ϕ demonstrating the percolative behavior at different temperatures (30°C (○), 60°C (+), 90°C (×), 120°C () and 150°C (Δ)) (Reproduced from (Zech et al., 2010 a) with permission, copyright Wiley-VCH Verlag, 2010).

these bell shaped functions are related to half of the diameter. Within (30 - 150)°C bell shaped *p(r)* functions were obtained, consistent with a swelling of the EAN/o nanodomains with increasing amount of IL. Further, the size of the EAN nanodroplets stabilized by surfactant remained constant at a given EAN content within (30 – 90)°C and increased slightly for 150°C. For a concentration series the shape of the *p(r)* functions did not change significantly. The same was valid for the shape at 30°C and 150°C. Consequently, the SANS data demonstrated that that there is no essential structural variation within the measured concentration (below ϕ_P) and within the measured temperature range. However, the conductivity and SANS studies clearly demonstrated that one major benefit of the formulation of nonaqueous microemulsions with ILs is the extraordinary thermal stability that can be achieved. These systems represented the first high temperature microemulsions with ionic liquids with thermal stabilities far above the boiling point of water at ambient pressure.

Moreover, we could demonstrate that biodiesel can act as oil phase in high temperature microemulsions highlighting a way towards the formulation of biocompatible microemulsions (Zech et al., 2010 c). These model systems can be extended to other ILs, with [bmim][BF$_4$] instead of EAN as polar phase, where a remarkable thermal stability can be achieved as well (Zech 2010). The different microemulsions containing protic ionic liquids, the methods used to characterize them and the corresponding references are summarized in Table 2.

microemulsion system	methods	references
EAN C$_i$E$_j$ *n*-alkane	fish cuts, SAXS	(Atkin & Warr 2007)
PAN C$_i$E$_j$ *n*-alkane	fish cuts, conductivity, SANS	(Atkin et al., 2009)
EAN [C$_{16}$mim][Cl]+1-decanol dodecane	conductivity, viscosity, DLS, SAXS conductivity, SANS DLS, SANS	(Zech et al., 2009 b) (Zech et al., 2010 a) (Zech et al., 2010 b)
EAN [C$_{16}$mim][Cl]+1-decanol biodiesel	conductivity, viscosity, SAXS	(Zech et al., 2010 c)

Table 2. Summary of the different microemulsions systems with protic ionic liquids together with the references and methods used.

2.3 Applications

Applications in the field of nonaqueous microemulsions containing ionic liquids are still scarce up to date. Nevertheless, the few studies available in the open literature demonstrate the great potential of these microemulsions in a diversity of different fields.

The synthesis of nanoparticles is one of the most promising potential applications of these new systems. Zhao et al. used benzene/TX-100/[bmim][BF$_4$] microemulsions as template for the synthesis of silica nanoparticles under both basic and acidic conditions (Zhao et al., 2009). Herein, ellipsoidal nanoparticles have been obtained under acidic conditions, while hollow silica spheres were formed under alkaline conditions.

Moniruzzaman et al. reported a strategy for transdermal drug delivery by nonaqueous microemulsions with ILs (Moniruzzaman et al., 2010). A large number of drugs are sparingly soluble in both water and most organic solvents. Since the solubility of several drugs is remarkably higher in ILs, IL microemulsions can provide an effective carrier for transdermal drug delivery. In particular they studied the topical (into the skin) and transdermal (across the skin) delivery of acyclovir (ACV), which is an effective antiviral drug. Figure 9 shows the topological and transdermal delivery of ACV for various formulations. Figure 9 demonstrates that by using IL/o microemulsions as drug carrier the skin permeability of Yucatan hairless micropig skin to ACV was increased by several orders of magnitude. Moreover, IL/o microemulsions as drug carrier induced significant transdermal permeation of ACV. However, there is still necessity of improvement with respect to the cytoxicity of several ILs.

Gayet et al. studied the efficiency of Matsuda-Heck coupling in reverse microemulsions by replacing the ionic liquid [bnpyr][NTf$_2$] by a chiral structural analogue, 1-phenylethylpyridinium bis(trifluoromethanesulfonyl)imide ([pyr*][NTf$_2$]) in the system [bnpyr][NTf$_2$]/TX-100/toluene described in section 2.1. (Gayet et al., 2009). The efficiency of the Matsuda-Heck reaction between p-methoxyphenyldiazonium salt and 2,3-dihydrofurane and a palladium catalyst in neat IL, the bicontinuous and the Il/o regime was evaluated. The reaction was regioselective regardless of the nature of the media, while the yields were increased when the amount of IL was rised. However, no enantiomeric excess of one of the products could be detected although "chiral" microemulsions with [R-(+)-pyr*][NTf$_2$] and [S-(-)-pyr*][NTf$_2$] were used.
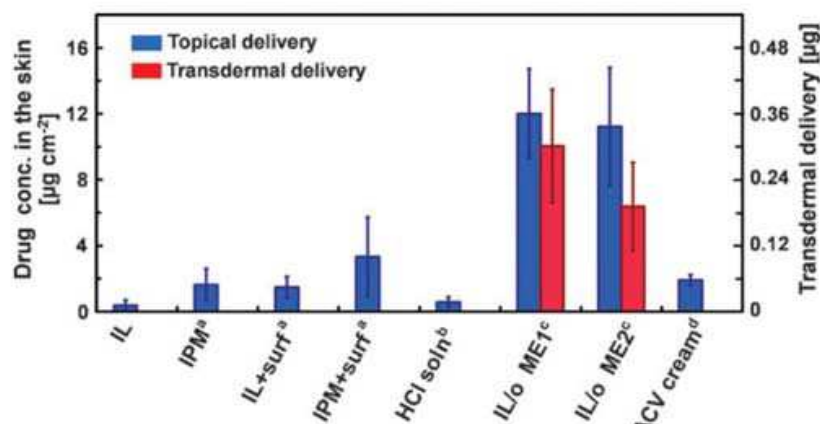

Fig. 9. Penetration of ACV from drug carriers into Yucatan hairless micropig skin under in vitro conditions. [ACV] = 5 mg mL^{-1}, weight fraction of surfactant was 0.2 (Tween-80:Span-20 = 3:1 (w/w)). [a] Almost all ACV remained as suspended powders in formulations. [b] HCl concentration was 0.1 M. [c] R = 0.7 and surfactant fractions were 0.2 and 0.3 for ME1 and ME2, respectively. [d] ACV herpecia topical cream (equivalent to 5 mg ACV) used for penetration study. The data represent the average of three experiments and the errors bars indicate the standard deviation. (Reproduced from (Moniruzzaman et al., 2010) with permission, copyright Royal Chemical Society, 2010).

IL microemulsions have also been used for the fabrication of polymer electrolyte membranes (Yan et al., 2009). These nonaqueous proton conducting membranes have been prepared via the polymerization of microemulsions comprising PILs, surfactant and a

polymerizable oil, which was a mixture of styrene and acetonitrile. Although the resulting vinyl polymers were insoluble in the IL, nanodomains were found to be uniform, transparent and flexible. A conductivity of these membranes up to 0.1 S m^{-1} was found due to connected PIL nanochannels preserved in the membrane. Further, these proton conducting membranes offered good mechanical properties, thermal and chemical stability. On the other side, there exists a progressive release of the PIL that may affect the long-term stability of these new promising materials.

Chen et al. used microemulsions composed of methyl methacrylate (MMA)/1-dodeyl-3-methylimidazolium bromide/[bmim][BF$_4$] microemulsions for free radical and atom transfer radical polymerizations (Chen et al., 2010). Polymers with reproducible size, well controlled molecular weight and low polydispersity could be produced. After the polymerization process, the remaining components could be recycled and reused.

3. Conclusions and outlook

In this review we have focused on nonaqueous microemulsions containing ionic liquids. A large diversity in phase diagrams and microstructures can be obtained in dependence of the ingredients and their proportions. Ionic liquids can act as polar phase to replace water, as oil substitute, as surfactant and they may even act as cosurfactant. It was further highlighted that the choice of the ionic liquid influences the phase behavior in general and the microstructure in particular. Many similarities compared to aqueous microemulsions have been found, but also some differences that underline the great potential of these systems with respect to applications. One obvious drawback is that the area of the single phase regions of ternary phase diagrams is smaller for ionic liquid microemulsions compared to their aqueous counterparts. Moreover, to reach the point of optimum formulation the amount of surfactant required is generally higher. Generally spoken ILs are less polar compared to water and hence the amount of surfactant (or its amphiphilicity, respectively) necessary to form micelles and microemulsions increases. Note that several studies can be found in literature, where the IL represents the apolar phase in aqueous microemulsions. Moreover, miscellaneous investigations report a remarkable effect when small amounts of water are added into the polar IL phase. However, this review has been focused on nonaqueous microemulsions and thence systems containing water were not implemented. One major point is that the stiffness of the interfacial film and the phase behavior can be tuned by the choice of the IL. For nonaqueous microemulsions containing ionic liquids it can be generalized that the temperature sensitivity is reduced. We believe that mainly the effect of temperature demonstrates one of the eminent benefits of these new colloidal systems. Since the vapor pressure of ILs is very low, systems can be designed that are stable far above the temperature range of conventional microemulsions, which may represent extraordinary reaction media. Further, it is obvious that by the choice of the components the stability range could also be extended towards low temperature microemulsions. One future challenge in this field will surely be the formulation and characterization of microemulsions that solely consist of ionic liquids. Moreover, more detailed investigations concerning the curvature, the rigidity of the interfacial and bending energies will be useful to provide a deeper understanding of these new promising systems. Although applications in this field are still scarce so far, it is evident that nonaqueous microemulsions will attract considerable interest in manifold fields. A strong future growth area might probably be their application as template materials or in nanoparticle synthesis. Furthermore, these systems are promising

candidates for chemical reactions in water-free organic or inorganic reactions. Moreover, they might find applications on separation science, encapsulation or nanocontainers, as well as in catalysis and biocatalysis.

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