DOI: 10.1002/chem.200901101

Ionic Liquids in Microemulsions—A Concept To Extend the Conventional Thermal Stability Range of Microemulsions

Oliver Zech,[a] Stefan Thomaier,[a] Agnes Kolodziejski,[a] Didier Touraud,[a] Isabelle Grillo,[b] and Werner Kunz*[a]

Ionic liquids (ILs) have attracted more and more attention in recent years, because of their unique properties, such as low vapor pressure, high thermal stability, and wide liquid range.[1] Beside the application of ILs as solvents for synthesis[2] or catalysis,[3] the feature of amphiphilic association structures to form micelles, microemulsions, vesicles, and lyotropic liquid-crystalline phases has been reviewed recently.[4] Eastoe et al. performed the first small-angle neutron scattering (SANS) experiments on microemulsions containing room-temperature ionic liquids (RTIL) and demonstrated the formation of surfactant-stabilized dispersed nanodroplets with IL cores.[5]

All studies concerning ILs in microemulsions described in literature have been performed below the boiling point of water. In the present study, we are interested in microemulsions that are stable over a wide temperature range at ambient pressure. For this purpose, water must be replaced by a RTIL.

The first RTIL, ethylammonium nitrate (EAN) with a melting point of 14 °C, was reported almost a century ago by Walden.[6] EAN is supposed to form three-dimensional hydrogen-bond networks.[7] Therefore, it is an appropriate component to replace water in microemulsions with high thermal stability. Atkin et al. recently characterized microemulsions composed of nonionic oligo-ethyleneoxide surfactants, alkanes, and EAN.[8] As the effect of temperature on microemulsions with nonionic surfactants is very pronounced, they are not favorable for formulating systems that are stable over a wide temperature range. Recently, we characterized microemulsions with EAN as the polar phase, dodecane as the continuous phase, 1-hexadecyl-3-methylimidazolium chloride ([C_{16}mim][Cl]), an IL that exhibits surfactant properties,[9] and decanol as cosurfactant at ambient temperature.[10] The minimum area/surfactant molecule of [C_{16}mim][Cl] at the solution–air interface in water[9b] was reported to be 0.49 nm^2 and 0.53 nm^2 in EAN.[9c] The immiscibility of the polar phase EAN with dodecane over the whole temperature range was confirmed by ^{1}H NMR spectroscopy and refractive index measurements (details are given in the Supporting Information). The interfacial tension at 30 °C between EAN and dodecane was determined to be 19.1 mN m^{-1}. All ingredients exhibit excellent thermal stability.

Herein, we demonstrate for the first time the existence of high-temperature stable microemulsions under ambient pressure. These systems show a thermal stability ranging from 30 °C up to at least 150 °C. We report on conductivity in combination with SANS experiments on EAN-in-dodecane (ionic liquid in oil) microemulsions within a temperature range between 30 and 150 °C.

The pseudo-ternary phase diagram at 30 °C has already been reported.[10] All experiments follow an experimental path, where the amount of surfactant and cosurfactant was kept constant at 40 wt %, while the amount of EAN was increased.

The conductivity of microemulsions is an important feature that gives information about their percolative or anti-percolative behavior.[11] For percolative systems the conductivity displays a remarkable change over several orders of magnitude. In fact, the high-temperature stable microemulsions show percolation phenomena over the whole investigated temperature range. This is illustrated in Figure 1, in which the specific conductivity is shown as a function of the volume fraction ϕ (details of the calculation of the volume fraction at different temperatures are given in the Supporting Information). In the insert of Figure 1 one can see clearly that the threshold, at which the conductivity increases re-

---

[a] O. Zech, Dr. S. Thomaier, A. Kolodziejski, Dr. D. Touraud,
Prof. Dr. W. Kunz
Institute of Physical and Theoretical Chemistry
University of Regensburg, 93040 Regensburg (Germany)
Fax: (+49) 941-943-4532
E-mail: werner.kunz@chemie.uni-regensburg.de

[b] Dr. I. Grillo
Institut Laue-Langevin, B.P.156, 38042 Grenoble Cedex 9 (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901101.

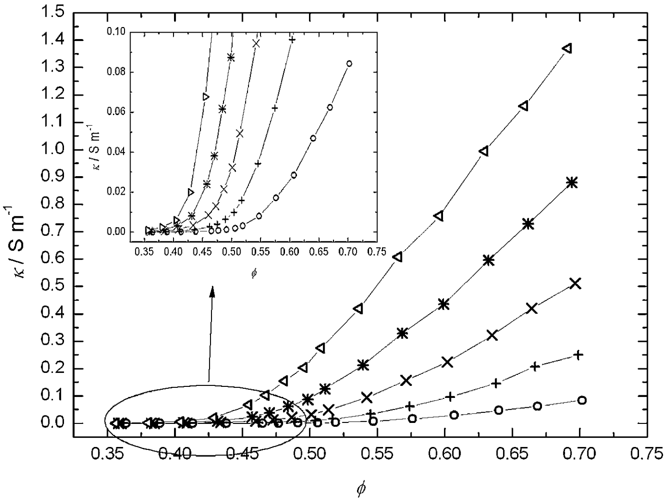

Figure 1. Specific conductivity as a function of the volume fraction ϕ, which demonstrates the percolative behavior at different temperatures (30 °C (○), 60 °C (+), 90 °C (×), 120 °C (*), and 150 °C (Δ)).

markably and percolation appears, is shifted with increasing temperature to the left hand side. This so-called percolation threshold volume fraction ϕ_p was calculated from the inflection point of the curve $\log(\kappa)=f(\phi)$ (for details see the Supporting Information).[12] ϕ_p values as a function of temperature are summarized in Table 1 and illustrated in Figure 2. Interestingly, ϕ_p decreases linearly with increasing temperature. This effect can be explained by the increased motion of the formed IL nanodomains when the temperature is raised. Hence, the probability that two RTIL pools meet each other is higher and the threshold is shifted to smaller ϕ. In addition, the conductivity measurements demonstrate the wide thermal stability of the microemulsions.

Table 1. Percolation threshold volume fraction ϕ_P as a function of temperature.

θ [°C]	30	60	90	120	150
ϕ_P	0.48	0.46	0.43	0.41	0.39

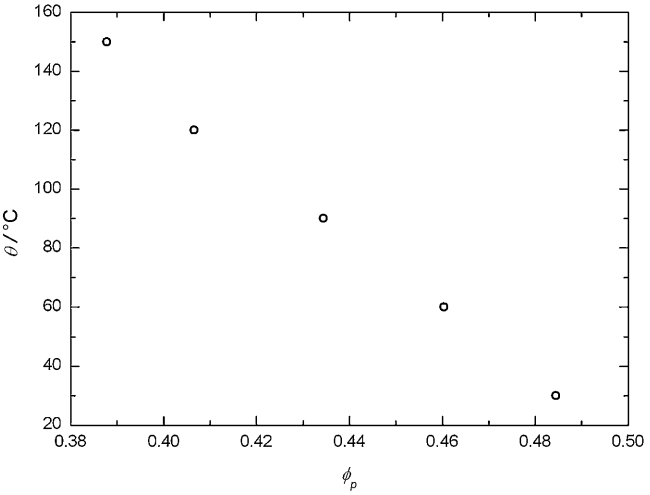

Figure 2. Temperature dependence of the percolation threshold volume fraction ϕ_P.

To confirm the high-temperature stability and the existence of microemulsions, we performed temperature-dependent SANS measurements. [D$_{26}$]Dodecane was used to improve the scattering contrast.

The SANS spectra at different temperatures for 6 wt % EAN, a EAN concentration below ϕ_P at ambient temperature, are shown in Figure 3. A small-angle scattering peak could be observed at 30, 60, and 90 °C, as has been reported in classical aqueous microemulsions.[13–15] At 150 °C the correlation peak is less pronounced. The peak maxima are shifted to smaller q with increasing temperature. The evaluation of such concentrated systems is possible with the "generalized indirect Fourier transformation" (GIFT) method.[16] Using the GIFT method it is possible to determine the form factor $P(q)$ and the structure factor $S(q)$, which takes particle interaction into account, simultaneously. The GIFT method enables the extraction of $P(q)$ in a model free way and was applied successfully to aqueous microemulsions.[14,17]

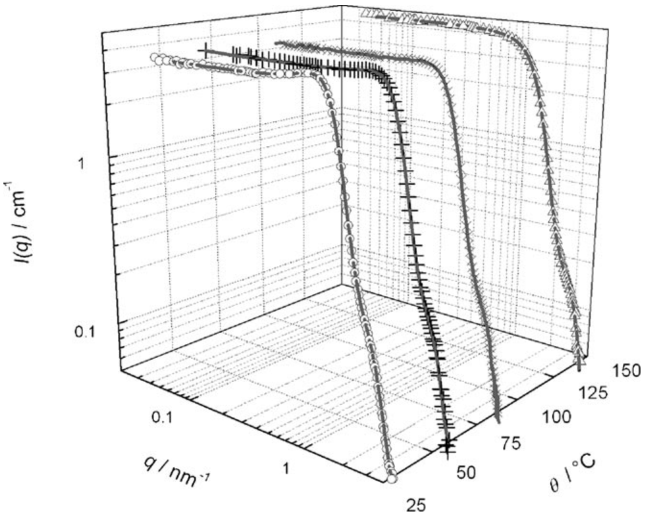

Figure 3. SANS for 6 wt % EAN, 40 wt % surfactant+cosurfactant and 54 wt % [D$_{26}$]dodecane at different temperatures (30 °C (○), 60 °C (+), 90 °C (×), and 150 °C (Δ)); full lines are fit curves from the GIFT evaluation using the Percus–Yevick effective structure factor.

For the data evaluation, we used a Percus–Yevick effective structure factor $S_{eff}(q)$ and assumed a Schulz distribution. $S_{eff}(q)$ is described by the parameters volume fraction, radius, and polydispersity. Note that polydispersity and volume fraction cannot be modeled independently; a unrealistically high polydispersity would lead to a too high volume fraction and vice versa.[18] It is known that the polydispersity in common microemulsions is about 25 %, and thus we fixed it at this level.[18] Furthermore, a wavelength distribution of $\delta\lambda/\lambda$ of 10 % was taken into account. The fit quality of the data evaluation with GIFT is very good as can be seen in

Figure 3 (full lines). The maxima r^{Ai}_{max} of the pair distance distribution functions $p(r)$ can be interpreted in terms of particle dimensions.[18] These functions are shown in Figure 4. Interestingly, r^{Ai}_{max} values do not change significantly between 30 °C and 90 °C (2.34 nm) and increase slightly for 150 °C (2.54 nm). The $p(r)$ functions for the latter is broader than the $p(r)$ functions at lower temperatures. Nevertheless, there is no significant change in the shape of these functions with increasing temperature. Evidently, there is no essential structural variation within the measured temperature range.

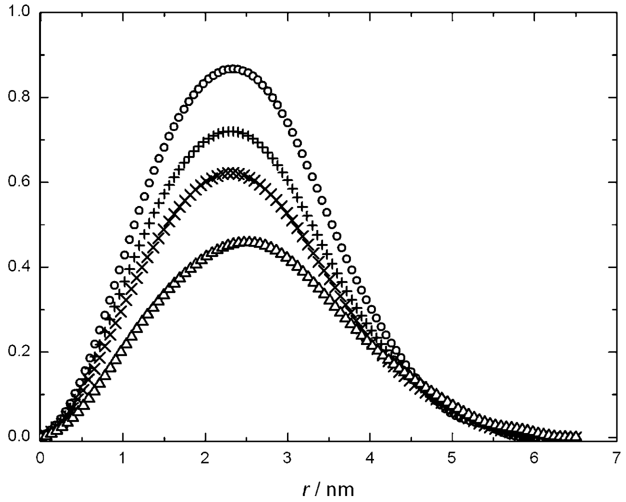

Figure 4. Pair distance distribution functions $p(r)$, extracted from the GIFT method for 6 wt% EAN, 40 wt% surfactant+cosurfactant, and 54 wt% [D$_{26}$]dodecane at different temperatures (30 °C (○), 60 °C (+), 90 °C (×), and 150 °C (Δ)).

In conclusion we demonstrated that ionic liquids in microemulsions extend the conventional thermal stability range of microemulsions at ambient pressure. It is possible to formulate nonaqueous microemulsions containing ionic liquids that exhibit a thermal stability range between 30 °C and 150 °C. Both conductivity and SANS measurements are in agreement with the existence of a L$_2$ phase (ionic liquid in oil). Dynamic light scattering and temperature-dependent SANS experiments for different EAN concentrations show that swelling behavior with an increasing amount of EAN occurs. This will be discussed in detail in a forthcoming publication. It should be stressed that here we have chosen only model systems. We believe that this concept can be extended to other ionic liquids and, depending on the system, the thermal stability range can probably be enlarged much more by appropriately chosing the components. These high-temperature stable microemulsions open a wide field of potential applications, such as for nanoparticle synthesis, new reaction media, or lubricant formulations.

Experimental Section

Dodecane and [D$_{26}$]dodecane were obtained from Aldrich (99%) and Euriso-Top (98%), respectively. 1-Decanol was obtained from Aldrich (98%). EAN and [C$_{16}$mim][Cl] were prepared and stored as documented elesewhere.[10] The ionic liquids were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by ESI MS. No impurities could be detected. The water content of EAN, which was determined by means of a Karl-Fischer titration using an Abimed MCI analyser (model CA-02), was less than 100 ppm.

Densities of the pure EAN, dodecane, and the densities of the [C$_{16}$mim][Cl]+decanol mixture (1:4, molar ratio) were measured with a pyknometer between 30 °C and 150 °C in steps of 10 °C. The obtained linear density–temperature relationships are given in the Supporting Information.

Conductivity measurements were carried out with an in-house built symmetrical Wheatstone bridge with a Wagner earth, sine generator, and resistance decade.[19] The electrolyte resistances were measured at frequencies between 240 Hz and 10 kHz and extrapolated to infinite frequency. Cells with cell constants ranging from 0.02 to 11.60 cm^{-1} were used.

SANS experiments were carried out on the instrument D22 at the Institut Laue-Langevin, Grenoble, France. Quartz cells from Hellma were used, which offer a thermal stability of 8 bar at 300 °C with a height of 50 mm, a length of 40 mm, and a thickness of 1 mm. Three configurations were used to cover a q-range from 0.07 nm^{-1} to 4.0 nm^{-1}.

The interfacial tension between EAN and dodecane was measured with a tensiometer (K100 Krüss, Germany) under an Ar atmosphere. Samples were thermostatted at 30 °C, the mean value of ten measurement points was taken.

Acknowledgements

The authors thank the Institut Laue-Langevin for the allocation of beam time and Dr. R. Schupfner (University of Regensburg) for help with radiation protection questions. The authors thank further Dipl. Ing. H. Hilbinger (University of Regensburg) for discussions concerning the conductivity measurements and Dr. W. Wachter (University of Graz) for help with the GIFT software.

Keywords: ionic liquids · microemulsions · percolation · small-angle neutron scattering · thermal stability

---

[1] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084; b) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; c) T. J. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206–237.

[2] a) N. Haumann, A. Riisager, *Chem. Rev.* **2008**, *108*, 1474–1497; b) M. A. P. Martins, C. P. Frizzo, D. N. Moreira, N. Zanatta, H. G. Bonacorso, *Chem. Rev.* **2008**, *108*, 2015–2050.

[3] a) F. van Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757–2785; b) V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615–2665.

[4] a) J. Hao, T. Zemb, *Curr. Opin. Colloid Interface Sci.* **2007**, *12*, 129–137; b) Z. Qiu, J. Texter, *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 252–262; c) T. L. Greaves, C. J. Drummond, *Chem. Soc. Rev.* **2008**, *37*, 1709–1726.

[5] J. Eastoe, S. Gold, S. E. Rogers, A. Paul, T. Welton, R. K. Heenan, I. Grillo, *J. Am. Chem. Soc.* **2005**, *127*, 7302–7303.

[6] P. Walden, *Bull. Acad. Imp. Sci. St.-Petersbourg* **1914**, 1800.

[7] a) D. F. Evans, S.-H. Chen, G. W. Schriver, E. M. Arnett, *J. Am. Chem. Soc.* **1981**, *103*, 481–482; b) D. F. Evans, A. Yamauchi, R. Roman, E. Z. Casassa, *J. Colloid Interface Sci.* **1982**, *88*, 89–95; c) D. F. Evans, A. Yamauchi, G. J. Wei, A. Bloomfield, *J. Phys. Chem.* **1983**, *87*, 3537–3541.

[8] R. Atkin, G. G. Warr, *J. Phys. Chem. B* **2007**, *111*, 9309–9316.

[9] a) S. Thomaier, W. Kunz, *J. Mol. Liq.* **2007**, *130*, 104–107; b) O. El Seoud, P. Pires, T. Abdel- Moghny, E. J. Bastos, *J. Colloid Inter-*

face Sci. **2007**, *313*, 296–304; c) S. Thomaier, Ph. D. Thesis, University of Regensburg **2009**.

[10] O. Zech, S. Thomaier, P. Bauduin, T. Rück, D. Touraud, W. Kunz, *J. Phys. Chem. B* **2009**, *113*, 465–473.

[11] B. Lagourette, C. Peyrelasse, C. Boned, M. Clausse, *Nature* **1979**, *281*, 60.

[12] a) C. Boned, Z. Zaidi, P. Xans, J. Peyrelasse, *Phys. Rev. E* **1994**, *49*, 5295–5302; b) C. Blattner, J. Bittner, G. Schmeer, W. Kunz, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1921–1927.

[13] F. Lichterfeld, T. Schmeling, R. Strey, *J. Phys. Chem.* **1986**, *90*, 5762–5766.

[14] J. Brunner-Popela, R. Mittelbach, R. Strey, K.-V. Schubert, E. W. Kaler , O. Glatter, *J. Chem. Phys.* **1999**, *110*, 10623- 10632.

[15] T. Zemb, *Neutrons, X-ray and light: scattering methods applied to soft matter*, (Eds.: P. Lindner, T. Zemb), North Holland, Amsterdam, chap. 13, **2002**, pp. 317–350.

[16] a) O. Glatter, *J. Appl. Crystallogr.* **1997**, *30*, 415–421; b) J. Brunner-Popela, O. Glatter, *J. Appl. Crystallogr.* **1997**, *30*, 431–442; c) A. Bergmann, G. Fritz, O. Glatter, *J. Appl. Crystallogr.* **2000**, *33*, 1212–1216.

[17] R. Strey, O. Glatter, K.-V. Schubert, E. W. Kaler, *J. Chem. Phys.* **1996**, *105*, 1175–1188.

[18] N. Freiberger, C. Moitzi, L. de Campo, O. Glatter, *J. Colloid Interface Sci.* **2006**, *293-304*, 59–67.

[19] R. Wachter, J. Barthel, *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 634–642.

Received: April 26, 2009
Revised: October 1, 2009