Electronic supplementary information

Fundamentals of percolation theory

Conventional microemulsion systems containing organic solvent as a continuous phase and water droplets as a dispersed phase exhibit extremely low conductivities, since continuum is an insulating medium. However, with increase of water content, above certain threshold conductivity begins to increase rapidly. This phenomenon is called electrical percolation and is a result of microemulsion droplets being no longer totally separated from each other, but able participate in a mass transfer. This mechanism can be of two types: static[1], where bicontinuous structure is formed, and dynamic[2], when consecutive fusion and fission of droplets takes place. Both theories state, that percolation transition occurs at certain threshold and specific conductivity, before and after percolation threshold follows the scaling laws:

$$\kappa = A(\phi_p - w_{H_2O})^{-s} \qquad \text{for } w_{H2O} < \varphi_p$$

$$\kappa = B(w_{H_2O} - \phi_p)^t \qquad \text{for } w_{H2O} > \varphi_p$$

where: κ is the specific conductivity, w_{H2O} is the content of water, ϕ_p is the critical content of the conducting phase (percolation threshold), and A, B, s, and t are constants. In static percolation in conventional MEs, critical parameter was observed to be in close to 0.6^3 and 0.7^4, whereas in dynamic one is higher, usually 1.2^4, 1.3^5.

Although, ionic liquid microemulsion differs significantly from conventional systems, that percolation theory was designed for, to some extent it can be applied for both nonaqueous[6] and aqueous[4] IL-MEs, too. The percolation thresholds in conductivity, ϕp, can be obtained from the inflection point of $d\kappa/dwH_2O = f(wH_2O)$ function (at times, $dln\kappa/dwH_2O = f(H_2O)$ is also applied[5]) and are indicated in figures 2A and 2B in the article.

Values of exponent "*s*" in the scaling law were obtained from ln – ln plot of conductivity versus reduced water content before percolation threshold (figure S1) and were approximate to values predicted by the static percolation theory (0.57 and 0.56 for [BMIM][PF$_6$] and [BMIM][Tf$_2$N]

respectively). Therefore, values determined in this study to some extent reveal formation of the bicontinuous structure[4] in the area where more intense increase of conductivity. Formation of bicontinuous structure was further confirmed by measurements of diffusion coefficients with cyclic voltammetry.
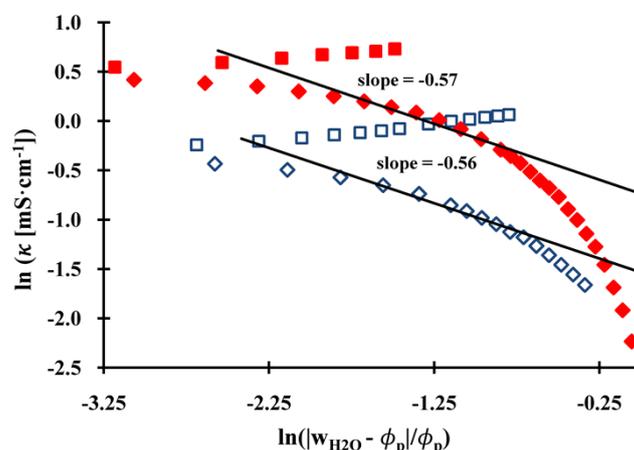

Figure S1. The scaling dependence of the specific conductivity of the microemulsions with [BMIM][Tf$_2$N] (empty), [BMIM][PF$_6$] (full symbols), below (◆) and after (O) percolation threshold. Slopes indicate exponents of scaling laws.

Nevertheless, t parameters being lower than 0.2 significantly differs from literature values determined for conventional ME since for the post-percolation region constant t generally ranges $1.1 \leq t \leq 1.6$ up to even 2.0[7]. It is the result of incomplete fulfilment of percolation theory assumptions - the amount of surfactant is high, the apolar component is highly conductive, its interaction with other components is significant, and the mechanism of charge transport differ. Therefore, percolation mechanism in such systems is still open to debate and its quantitative description needs serious enhancements.

Conductivity

Changes of conductivity slope well corresponds with results obtained from cyclic voltammetry (Figure 8B of the manusctipt). Although formation of bicontinuous structure generally results in more pronounced increment of conductivity with addition of water, presence of cosurfactant

does change the trend. This is explained in "Influence of the cosurfactant addition" section. Overlap of microstructural transitions obtained from apparent diffusion coefficients and changes of conductivity slope confirms, that conductivity measurements can be used to differentiate microstructures even if sharp increase in slope does not occur.
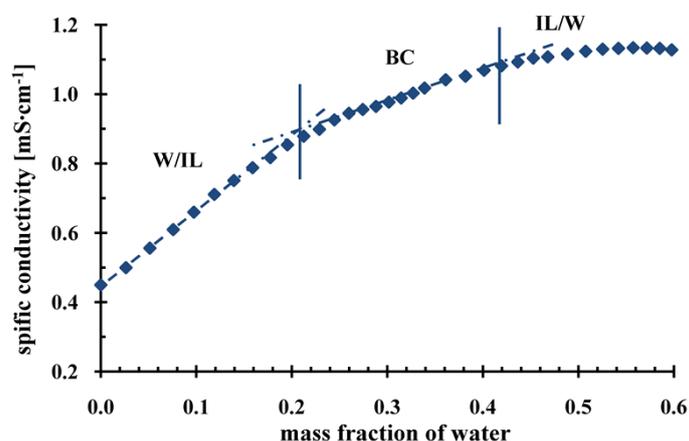

Figure S2. Specific conductivity of [BMIM][Tf$_2$N]/TX-100-BuOH/H$_2$O systems in a function of water content at constant IL-to-mixed surfactant mass ratio equal to 0.15:0.85.

Note, that decrease of conductivity slope in bicontinuous region is the more pronounced, the higher the ratio.
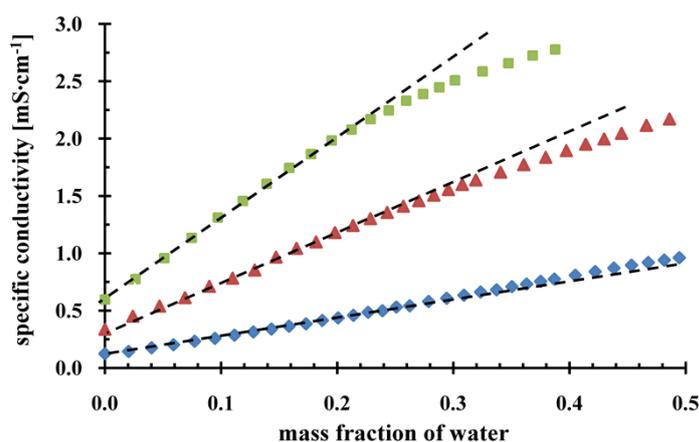

Figure S3. Specific conductivity dependence of [BMIM][PF$_6$]/TX-100:BuOH/H2O system on water content at (◆) 0.05:0.95, (□) 0.15:0.85 and (■) 0.25:0.75 IL-to-mixed surfactant mass ratios.
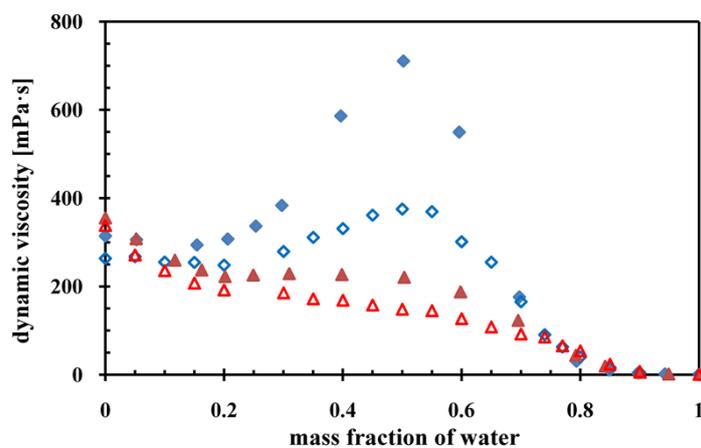
Dynamic viscosity

Figure S4. Viscosity dependence of the [BMIM][Tf₂N]/TX-100/H₂O system on water content at IL-to-surfactant ratios: ($\blacklozenge$) *0.05/0.95,* ($\lozenge$) *0.10/0.90,* ($\blacksquare$) *0.15/0.85,* ($\square$) *0.20/0.80*

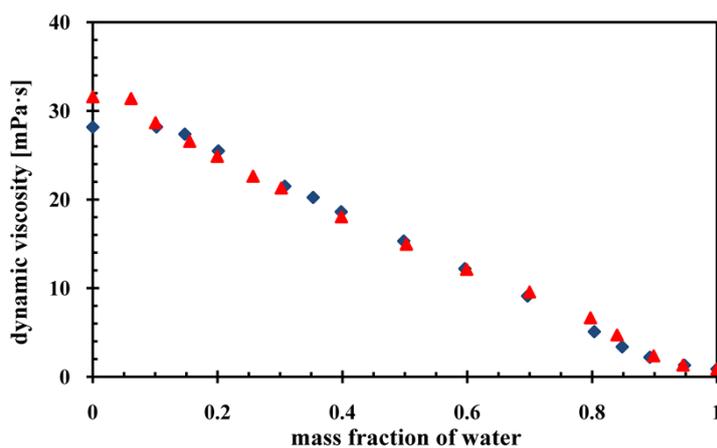*Figure S5. Viscosity dependence of the [BMIM][Tf₂N]/TX-100-BuOH(2:1)/H₂O system on water content at IL-to-mixed surfactant ratios:* ($\blacklozenge$) *0.05/0.95,* ($\square$) *0.15/0.85.*
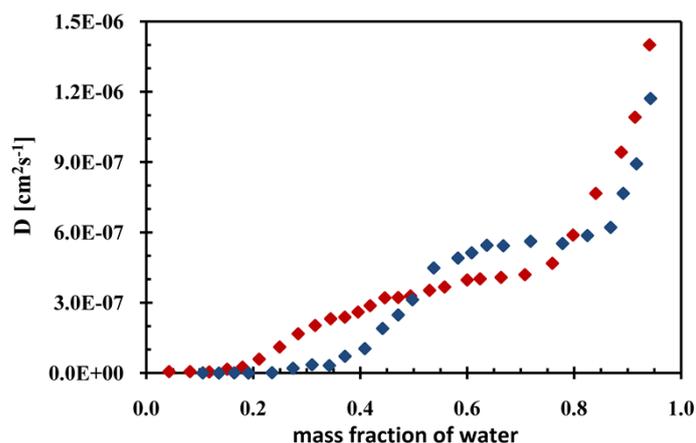
Cyclic voltamperometry

Figure S6. Apparent diffusion coefficients of $K_3Fe(CN)_6$ dissolved in (A) [BMIM][PF_6]/TX-100/H_2O and (B) [BMIM][Tf_2N]/TX-100/H_2O microemulsions at IL/TX-100 mass ratio 0.15/0.85 in a function of water content.

**References*:*

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