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# Ethylammonium nitrate in high temperature stable microemulsions

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ABSTRACT

The increasing number of publications reflects the still growing interest in nonaqueous microemulsions containing room-temperature ionic liquids. Recently, we characterized microemulsions composed of the room-temperature ionic liquid ethylammonium nitrate (EAN) as polar phase, dodecane as continuous phase and 1-hexadecyl-3-methyl imidazolium chloride ([$C_{16}$mim][Cl]), an IL that exhibits surfactant properties, and decanol as cosurfactant at ambient temperature. We demonstrate here the high thermal stability of these microemulsions. Along an experimental path, no phase change could be observed visually within a temperature range between 30 °C and 150 °C. The microemulsions are characterized with quasi-elastic light scattering measurements at ambient temperature and temperature dependent small angle neutron scattering (SANS) experiments between 30 °C and 150 °C. DLS measurements at ambient temperature indicate a swelling of the formed structures with increasing amount of EAN up to a certain threshold. The SANS experiments were performed below this threshold. The data evaluation of such concentrated systems like microemulsions is possible with the "generalized indirect Fourier transformation" method (GIFT). We evaluated the small angle scattering data via the GIFT method, for comparison we also applied the model of Teubner and Strey (TS) which was often used to describe scattering curves of microemulsions. The GIFT method gives good fits throughout the experimental path, while the TS model gives relatively poor fits. Both, light scattering and SANS results are in agreement with the existence of EAN droplets stabilized by surfactant with dodecane as continuous phase along the whole investigated temperature range. Moreover, these results clearly demonstrate the possibility to formulate high temperature stable microemulsions with ionic liquids at ambient pressure.

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## 1. Introduction

Ionic liquids (ILs), especially imidazolium and pyridinium based ionic liquids have attracted more and more attention in recent years, because of their outstanding properties [1–3]. Beside these ionic liquids, there is also a growing interest in protic ionic liquids [4,5] and research towards greener ILs [6,7].

Particular attention has been paid to room-temperature ionic liquids (RTIL). The RTIL ethylammonium nitrate has been described almost a century ago by Walden [8]. This polar, colorless liquid exhibits a melting point of 14 °C [9] and is supposed to form three-dimensional hydrogen bonded networks [10,11]. The formation of amphiphilic association structures in and with ionic liquids, such as micelles, vesicles, microemulsions and liquid crystalline phases has been reviewed recently [12–14]. Evans et al. demonstrated the formation of micelles and liquid crystalline phases in EAN already in the 1980s [9–11]. We demonstrated the formation of [$C_{16}$mim][Cl] micelles, an ionic liquid surfactant, in EAN as well [15]. Recently, Araos et al. investigated the structure of nonionic surfactant micelles in EAN with SANS [16]. Furthermore, they observed the formation of lyotropic liquid crystals by nonionic surfactants in EAN [17]. The formation of Liquid crystalline phase of mixtures of [$C_{16}$mim][Cl] in EAN has also been reported lately [18]. Evans et al. proposed from static and dynamic light scattering measurements of ionic surfactant aggregates in EAN either small classical spherical micelles or spherical mixed micelles, where the ethylammonium ions act as cosurfactant [11]. Furthermore, the existence of amphiphilic nanostructures in pure protic ionic liquids, namely EAN and propylammonium nitrate (PAN) has been reported by Atkin and Warr [19]. They observed in the SANS spectra of selectively deuterated EAN and PAN structure peaks giving evidence of nanosegregation in the bulk. Kennedy et al. concluded from electrospray ionization mass spectrometry that selected PILs including EAN and PAN consist of a polydisperse mixture of aggregated ions [20].

Furthermore, EAN has also been applied as polar phase in nonaqueous microemulsions [21,22]. Atkin et al. characterized microemulsions composed of nonionic oligoethyleneoxide surfactants, alkanes and EAN [21]. For their microemulsions they observed a single broad small angle scattering peak as it was often described for aqueous microemulsions. The curves were analyzed with the

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Teubner–Strey model. Moreover, Warr and coworkers reported propylammonium nitrate (PAN) to promote self-assembly of nonionic surfactants into micelles, lyotropic liquid crystals and microemulsions [23]. They suggested from SANS contrast variation experiments that the propylammonium cation might act as cosurfactant in these self-assembled structures similar to the cosurfactant-like role proposed for the ethylammonium cation [11].

We are interested in high temperature stable nonaqueous microemulsions, because of the wide field of potential applications. Therefore, nonionic surfactants are not favorable as they are very sensitive towards temperature. Very recently, we investigated microemulsions with an ionic liquid surfactant and EAN as polar pseudo-phase at room-temperature [22]. Furthermore, we could demonstrate with conductivity measurements and few, preliminary SANS investigations the high thermal stability of the present systems at ambient pressure [24]. Now we present the results of detailed studies in order to get refined information on the temperature effect on microemulsion structure. We investigate here these systems with dynamic light scattering measurements at ambient temperature and temperature dependent SANS measurements between 30 °C and 150 °C.

## 2. Experimental

### 2.1. Materials

Dodecane and dodecane-$d_{26}$ 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 elsewhere [22]. The final water content of EAN was <100 ppm (m/m), no yellow discoloration resulting from nitrous oxide impurities [21] could be observed. The purity of the ionic liquids was controlled with $^1$H, $^{13}$C-NMR and ESI-MS. No impurities could be detected.

### 2.2. Experimental path

In a previous study, we investigated microemulsions composed of EAN, [$C_{16}$mim][Cl], dodecane and 1-decanol. A huge clear and isotropic single phase region was observed. At ambient temperature, we chose an experimental path, where the amount of surfactant plus cosurfactant was kept constant at 30 wt.% ($P_S$ = 30) [22].

By visual observation we noticed that a higher amount of surfactant plus cosurfactant is necessary for a thermal stability up to 150 °C at ambient pressure. Very recently, we demonstrated the high thermal stability with temperature dependent conductivity measurements and preliminary SANS investigations between 30 °C and 150 °C where the amount of surfactant plus cosurfactant was kept constant at 40 wt.% ($P_S$ = 40) [24]. All experiments described here follow this experimental path.

### 2.3. Apparatus and procedures

SANS experiments were carried out on the instrument D22 at the Institut Laue-Langevin. Quartz cells from Hellma were used, which offer a thermal stability of 8 bars at 300 °C with a height of 50 mm, a length of 40 mm and a thickness of 1 mm. SANS spectra along the experimental path at 30 °C, 60 °C, 90 °C and 150 °C were recorded. Three configurations were used to cover a $q$-range between 0.07 nm$^{-1}$ and 4.0 nm$^{-1}$. Experiments were carried out at a wavelength of 0.6 nm with a relative wavelength spread $\Delta\lambda/\lambda$ of 10% [25].

All dynamic light scattering (DLS) experiments have been performed at a scattering angle of 90 °C with a goniometer CGS-II from ALV (Germany). The samples were thermostated to 30 °C.

## 3. Results and discussion

### 3.1. Dynamic light scattering

It is well known that dynamic light scattering experiments of highly diluted solutions yield the free particle translational diffusion coefficient, $D_0$. $D_0$ is related through the Stokes–Einstein equation (Eq. (1)) to the hydrodynamic radius $R_H$, where $k$ is the Boltzmann constant, $\eta$ the viscosity of the solvent and $T$ the absolute temperature.

$$D_0 = \frac{kT}{6\pi\eta R_H} \tag{1}$$

The diffusion coefficient of particles in solution is concentration dependent due to particle interactions. For highly concentrated solutions like microemulsions the free particle diffusion coefficient $D_0$ must be replaced by the so-called effective diffusion coefficient $D_{eff}$. Consequently, the hydrodynamic radius must be replaced by an apparent hydrodynamic radius $R_{Happ}$. The problem of particle interaction and multiple scattering in microemulsions is a recurrent problem for the interpretation of dynamic light scattering results of microemulsions. Further, it is well known that the polydispersity in aqueous microemulsions is high [26]. Nevertheless, the $R_{Happ}$ give at least an idea of a dimension and can be compared to the small angle neutron scattering results.

For the DLS measurements the amount of EAN was varied between 0 wt.% and 36 wt.%. For EAN concentrations between 0% and 15% a single exponential decay of the autocorrelation function was observed. For higher EAN contents a bimodal decay was detected. Exemplarily, the intensity correlation functions versus time are illustrated in Fig. 1 for 12 wt.% and 30 wt.% EAN. To each curve a single exponential decay (Eq. (2)) was fitted as it is shown by full lines in Fig. 1.

$$(g^{(2)} - 1) = a_0 + (a_1 \cdot \exp(-a_2 \cdot \tau))^2 \tag{2}$$

For 12 wt.% EAN the intensity autocorrelation function could be well fitted with the single exponential decay. For 30 wt.% EAN a single exponential decay is not sufficient, the curve is bimodal. This gives first evidences for a structural variation at higher EAN weight fractions. In a previous study we reported percolative behavior at 30 °C along the same experimental path [24]. Interestingly, the percolation threshold is very close to the amount of EAN where a bimodal decay was observed. For the calculation of $R_{Happ}$ we used the viscosity of dodecane ($\eta$ = 1.236 cP) [27] at 30 °C as it is the continuous phase. By calculating the apparent hydrodynamic radii of the samples, where monomodal decay was reported (0 wt.% EAN–18 wt.% EAN), a regular increase of the size with increasing amount of EAN was observed. This regular swelling is shown in Fig. 2. The polydispersity indices ranged between 0.24 and 0.30, no tendency in the variation of the polydispersity indices with increasing EAN content could be detected.

To get more insight into the structure, particularly for those, where the intensity correlation function did not show a single exponential decay, we used a nonlinear data analysis provided by ALV. The data analysis program fits an integral type model function using a constrained regularization method.

This regularization method (Contin) described by Provencher [28,29] is beside the non-negatively constrained least-squares method (NNLS) [30], the most often used one [31]. In Fig. 3, distribution functions along the whole experimental path, at low EAN content are illustrated, the regular swelling is confirmed, above 18 wt.% EAN a second peak appears. One possible explanation for this second peak at higher amounts of EAN is the formation of droplet clusters or the formation of more elongated structures. Such hypotheses are in agreement with the conductivity measure-

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