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Polarity of the interface in ionic liquid in oil microemulsions

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ABSTRACT

Ionic liquid based microemulsions were characterized by absorption solvatochromic shifts, ^{1}H NMR and kinetic measurements in order to investigate the properties of the ionic liquid within the restricted geometry provided by microemulsions and the interactions of the ionic liquid with the interface. Experimental results show a significant difference between the interfaces of normal water and the new ionic liquid microemulsions. Absorption solvatochromic shift experiments and kinetic studies on the aminolysis of 4-nitrophenyl laurate by *n*-decylamine show that the polarity at the interface of the ionic liquid in oil microemulsions (IL/O) is higher than at the interface of water in oil microemulsions (W/O) despite the fact that the polarity of [bmim][BF_4^-] is lower than the polarity of water. ^{1}H NMR experiments showed that an increase in the ionic liquid content of the microemulsion led to an increase in the interaction between [bmim][BF_4^-] and TX-100. The reason for the higher polarity of the microemulsions with the ionic liquid can be explained in terms of the incorporation of higher levels of the ionic liquid at the interface of the microemulsions, as compared to water in the traditional systems.

1. Introduction

Microemulsions are thermodynamically stable, macroscopically homogeneous and optically transparent systems of two immiscible solvents in the presence of a suitable surfactant [1]. Typical water in oil microemulsions consist of nanoscopic pools of water dispersed in a nonpolar solvent stabilized by a surfactant monolayer. The possibility of simultaneously having a polar and a nonpolar solvent makes microemulsions attractive reaction media both for hydrophobic organic compounds and inorganic salts [2]. The properties of the confined water are very different from those of the bulk water due to the geometric size constraints of the environment and to intermolecular interactions at the micellar interface [3]. In these systems the nanodroplet size is directly proportional to the water content through the parameter W ($W = [H_2O]/[\text{Surfactant}]$) [4]. Recently, in order to prepare water in oil microemulsions with the desired properties we changed the surfactant [5] and the oil [6] and identified the kinetic repercussions. The focus of our study in the work reported here was the dispersed medium.

Microemulsions in which water is replaced by a polar solvent have attracted great interest and, in this context, the most common solvents used include formamide, dimethylformamide, dimethylacetamide, ethylene glycol, propylene glycol, and glycerol [7]. The reason for this interest is that there are a large number of organic reactions for which contact with water needs to be avoided. In this regard, nonaqueous ionic liquid (IL) microemulsions where the ILs are sequestrated by non-ionic surfactants represent an interesting area since they provide hydrophobic or hydrophilic microdomains that expand the potential uses of the ILs in microheterogeneous systems [8]. Eastoe et al. recently reported that the IL concentration acts as an effective interfacial curvature-control parameter, thus representing a new approach to tuning the formulation of microemulsions and emulsions [9]. Ionic liquids (ILs) are receiving significant attention as environmentally friendly media for reactions, separations, and multidisciplinary chemistry areas [10]. Physicochemical properties like high stability, nonvolatility, and wide electrochemical window make them interesting media in which to study chemical reactions [11]. The ionic liquids are made of ions rather than molecules, which leads to a different selectivity and reactivity compared with conventional organic solvents. Accordingly, the increased use of ILs instead of conventional organic solvents results in significantly less evaporation of volatile organic compounds. Despite the fact that ILs are often considered as green alternatives to organic solvents, notably chlorinated hydrocarbons, their toxicity and biodegradability properties [12] have not been completely determined and the preparation of ILs often involves a metathesis step, which limits their green credentials to some degree. However, in both of these areas major advances have been made in the understanding and design of cleaner routes for the preparation of ILs [13].

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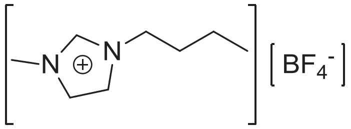


Scheme 1.

In the present work, we used 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], Scheme 1) as a solvent instead of water, Triton X100 (TX100) as a surfactant and cyclohexane as the continuous medium. The [bmim][BF_4] microemulsions were recently characterized by different experimental techniques: UV–VIS spectrophotometry (UV–VIS), electron microscopy (EM), laser light scattering (LLS), and small-angle neutron scattering (SANS) [14]. This system allowed us to study the properties of the ionic liquid within the restricted geometry of a microemulsion and, for the first time, to carry out kinetic experiments in [bmim][BF_4]/TX100/cyclohexane microemulsions.

The aminolysis of esters was the reaction studied and this is very well known in water, in various organic solvents, and in microemulsions. The amine (*n*-decylamine, DA) and the ester (nitrophenyl laurate, NPL) were chosen because of their hydrophobicity (Scheme 2). For the sake of comparison, the aminolysis of NPL in water/TX100/cyclohexane microemulsions was also studied.

2. Experimental

TX-100 was obtained from Fluka. According to a literature procedure, TX100 was evaporated under vacuum at 80 °C for 4 h to remove excess water before use [14c]. The ionic liquid [bmim][BF_4] was obtained from Solvent Innovation and, in an effort to avoid atmospheric water, the IL was manipulated under an inert atmosphere and fresh samples were used. *N*-decylamine and 4-nitrophenyl laurate (Aldrich) were of the highest available purity and were used as supplied.

The aminolysis reactions were followed by monitoring the UV–VIS absorbance of products using a Cary 500 scan UV–VIS–NIR spectrophotometer fitted with thermostatted cell holders. In all experiments the wavelengths used for the kinetic studies were in the range 400–425 nm. In all experiments the NPL concentration, typically $[NPL] = 5.00 \times 10^{-5}$ M, was much smaller than that of DA, and the temperature was kept constant at 35 °C. For the kinetic experiments the microemulsions were prepared using a solution of DA, $[DA] = 5.00 \times 10^{-2}$ M in cyclohexane. The integrated first-order rate expression was fitted to the absorbance-time data by linear regression ($r = 0.999$) in all cases. The observed rate constants, k_{obs}, could be reproduced with a margin of error of 5%. All experiments were carried out at 35.0 ± 0.1 °C.

The solvatochromic probe 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate [$E_T(33)$], also known as Reichardt's betaine dye, was obtained from Sigma–Aldrich and used as received. UV–VIS absorbance spectra were recorded on a Cary 500 scan UV–VIS–NIR spectrophotometer fitted with thermostated cell holders. The polarity was expressed on the E_T scale, one of the most widely used empirical solvent parameter scales. Aliquots of Reichardt's dye solution in methanol were added to a glass tube and the methanol was evaporated off under vacuum. The final concentration of the dye was 0.33 mM. The wavelength of maximum absorbance (λ_{max}) of the mixture was determined by UV spectrophotometry and $E_T(33)$ was calculated as: $E_T(33)$ (kcal/mol) = $28{,}591/\lambda_{max}$ (nm).

NMR spectra were recorded with the aid of a coaxial tube filled with DMSO-*d6* (Aldrich, 99.9%) to lock onto the deuterium signal. The signal of tetramethylsilane was used as ^{1}H NMR reference. All spectra were recorded on a Bruker AM 500 MHz spectrometer.

3. Results and discussion

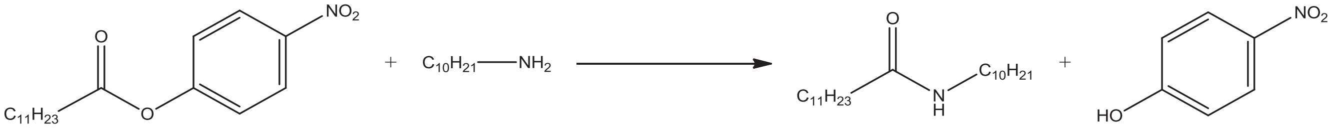
A kinetic study was carried out on the influence of the composition of the microemulsion on the aminolysis reaction between NPL and DA. The phase diagram of the H_2O/TX100/cyclohexane ternary system and [bmim][BF_4]/TX100/cyclohexane ternary system are illustrated in Fig. 1. The region labeled "Two phase region" was turbid and the region marked "Single phase region" was transparent. A mixture in the single-phase region can be considered as microemulsion. The analysis of phase behavior of microemulsions is an important part of microemulsions investigations. The difference between both systems is that in IL/O microemulsions the IL play the role of water in W/O microemulsions. The temperature of 35 °C and the compositions were selected with the purpose of covering a wide composition range. For W/O microemulsions the ratio W ($W = [H_2O][TX100]$) was varied between 0.5 and 7 and the surfactant concentration was varied between 0.1 M and 0.8 M, this implies that the content of TX100 was varied between 8.2–55% (w/w), that of water between 0.1–11% (w/w) and that of cyclohexane between 34–92% (w/w). For IL microemulsions the ratio W ($W = [IL]/[TX100]$) was varied between 0.13 and 0.81 and the surfactant concentration was varied between 0.71 M and 1.49 M, this implies that the content of TX100 was varied in the range 48–91% (w/w); that of IL between 2.8% and 21% (w/w) and that of the cyclohexane between 4.8% and 39% (w/w). These composition ranges provided a wide variation in properties such as polarity, viscosity, hydrogen bond donation capacity, and saline content.

The influence of the microemulsion composition on the observed rate constant for the aminolysis reaction of NPL with DA was studied. Experiments were carried out by varying the surfactant concentration and keeping the W parameter constant. These experiments were optimized for different W values and, therefore, the water content of the system was varied from W = 0.5–7 for W/O microemulsions ($W = [H_2O]/[TX100]$) and between W = 0.07 and W = 0.81 for IL microemulsions ($W = [IL]/[TX100]$).

It can be seen from Fig. 2 that an increase in the surfactant concentration leads to an increase in the observed rate constant (k_{obs}) in experiments in which the W parameter is kept constant. It can also be observed that the value of k_{obs} increases on decreasing the W parameter for W/O microemulsions. However, for IL microemulsions k_{obs} decreases as the IL content of the microemulsion decreases. The different properties of the two systems mean that the kinetic behavior in the microemulsions is different. Therefore, the results as a function of the system used will be presented separately.

3.1. Water/TX100/cyclohexane microemulsions

Reactivity in microemulsions can be quantitatively interpreted only if local reagent concentrations and intrinsic rate constants



Scheme 2.