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Aqueous two-phase systems containing imidazolium ionic liquids and a Tween surfactant

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ABSTRACT

Two imidazolium-based ionic liquids, 1-ethyl-3-methyl imidazolium methylsufate ($C_2C_1imC_1SO_4$) and 1-ethyl-3-methyl imidazolium ethylsulfate ($C_2C_1imC_2SO_4$), were tested as contenders for phase segregation in aqueous solutions of a non-ionic surfactant belonging to Tween family (Tween 20). Several empirical equations were used to correlate the binodal results which were previously obtained by means of the cloud point method at temperatures ranging from $T = (298.15–333.15)$ K. The tie-lines have been determined by means of density and refractive indices measurement, and the Othmer-Tobias model was used to elucidate the thermodynamic consistence of these experimental values.

1. Introduction

Due to their unique properties, ionic liquids have superseded conventional volatile and toxic organic solvents for the development of more environmentally friendly industrial processes.

On account of the variety of possible anions and cations, the resulting number of ionic liquids with different chemical-physical properties is very high [1]. Then, it is possible to design the "flawless ionic liquid" depending on the application to perform. In fact, the variety of research works has bloomed in the last years, encompassing a broad range of fields [2] such as the development of an ultra-fast ionic liquid-based rechargeable battery [3]. They have also been proposed at an industrial scale in companies such as BASF, Institut Français du Pétrole, or Degussa, and the annual production of some of them (mostly belonging to imidazolium family) exceeds the tonne per year [2,4].

Phase segregation in systems containing aqueous solutions of ionic liquids is a testing ground since Gutowski and co-workers reported the first work on the ability of ionic liquids to form Aqueous Two-Phase Systems (ATPS) [5]. However, following this line, many authors have applied this kind of systems for the separation of molecules with different nature like biomolecules [6,7], antibiotics [8] or radiological isotopes [9], among others.

On the other hand, the use of non-ionic surfactants in several fields like food, detergents, biocatalyst, *etc.* is attributed to their advantages in terms of cost, biodegradability, lower interface tension, thermal stability, negligible flammability and volatility [10] could be a good bet in order to design more competitive ionic liquid-based ATPS. Among the most commonly used surfactants, the Tween family, has been highlighted in many reports, as a non-toxic and efficient alternative, and it was even demonstrated to act as carbon source in culture broths [11]. In this context, we have recently reported for the first time the ability of imidazolium-based ionic liquids to promote phase splitting in aqueous solutions of surface active compounds [12]. Therefore, in view of the above the necessity for looking into new possibilities/combinations of these ionic liquid-based ATPS is clear.

The aim of this work was to study the immiscibility windows for the systems {Tween 20 + $C_2C_1imC_nSO_{4\ (n\,=\,1,2)}$ + H_2O} at several temperatures. The solubility data were modelled with empirical equations including a variation of Merchuk model [13]. The segregation capacity was also evaluated in terms of tie-line data, tackling the tie-line length (*TLL*) and the slope (*S*). The use of Othmer-Tobias equation [14] helped to elucidate the coherence of the experimental *TL* results.

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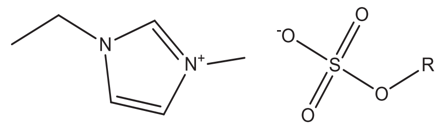
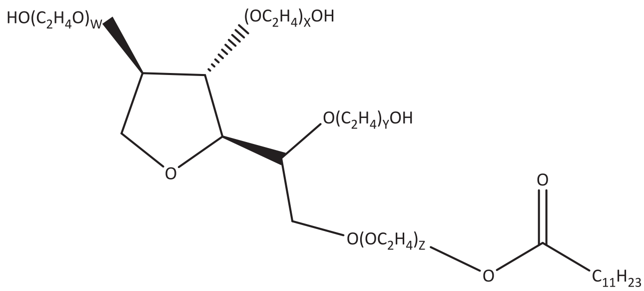
Table 1
Chemical characteristics and provenance.

Compound	Chemical structure	Mass fraction purity	Supplier
$C_2C_1imRSO_4$ (R = methyl or ethyl)		0.97	IoLiTec
Tween 20 (w + x + y + z = 20)		0.98	Sigma-Aldrich

2. Experimental

2.1. Chemicals

The non-ionic surfactant polyethoxylted sorbitan laurate (Tween 20), was supplied by Sigma-Aldrich, and used as received without further purification. The ionic liquids $C_2C_1imC_1SO_4$ and $C_2C_1imC_2SO_4$ were purchased from IoLiTec. Possible traces of solvents and moisture were removed by vacuum drying ($P = 2 \times 10^{-1}$ Pa) and moderate temperature ($T = 323.15$ K) for several days. Then, it was stored under inert atmosphere until use. The chemical structures of the compounds used are shown in Table 1.

2.2. Experimental procedure

The binodal curves were performed in a jacketed glass vessel containing a magnetic stirrer at different temperatures from $T = (298.15–333.15)$ K, which were controlled with a F200 ASL digital thermometer with an uncertainty of ±0.01 K. The solubility curves were ascertained through the widely employed cloud point titration method [15]. In short, water was added to binary mixtures containing ionic liquid and surfactant (with known mass fraction) until the detection of a cloudy solution. Afterwards, drops of water were carefully added until a clear solution was obtained, and the immiscibility region was fully characterized. All the samples were weighed in an analytical Sartorius Cubis MSA balance (125P-100-DA, $\pm 10^{-5}$ g). Additionally, the binodal curve was characterized by measuring the density and refractive indices at the selected temperature range. An Anton Paar DSA-48 digital vibrating tube densimeter with an uncertainty of $\pm 2 \cdot 10^{-4}\ g \cdot cm^{-3}$ was used for density measurements. Refractive indices were determined by means of a Dr. Kernchen ABBEMAT WR refractometer (uncertainty of $\pm 4 \times 10^{-5}$). Previously both densimeter and refractometer were calibrated following the manufacturer recommendations.

The tie-lines (*TLs*) were experimentally determined by mixing an appropriate ternary mixture within the immiscibility region.

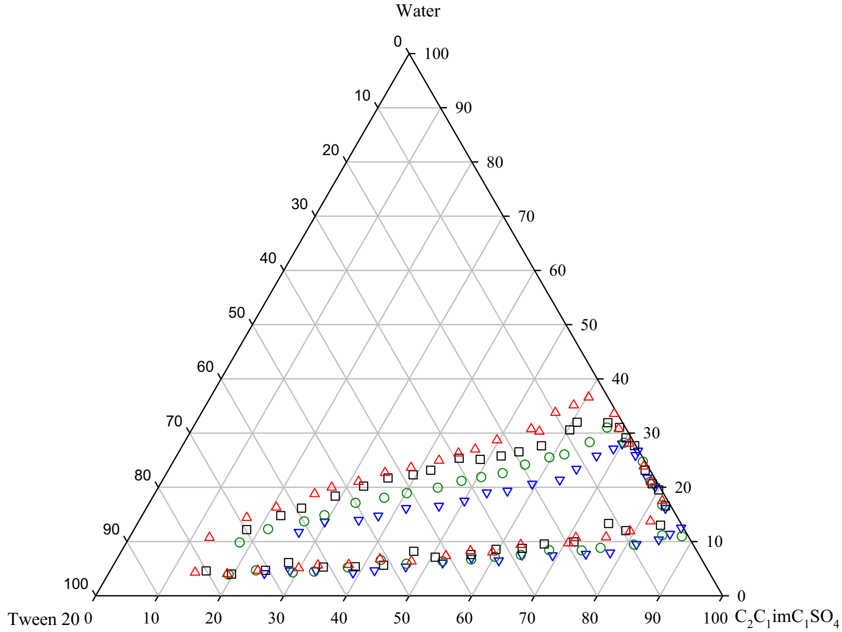


Fig. 1. Binodal results for the system {Tween 20 (1) + $C_2C_1imC_1SO_4$ (2) + H_2O (3)} at $T = 298.15$ K (▽), 313.15 K (○), 323.15 K (□), 333.15 K (△) and $P = 101.33$ kPa.