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Extended abstract

EXTENDED ABSTRACT

Liquid–liquid equilibria in solutions with potential ecological importance

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Abstract: In the last three years, our research follows two main issues, defined by the slogans: “green meets toxic” and “green meets green”. The first issue considers the potential use of ambient friendly solvents for toxic organic compounds of industrial and practical importance. The other is related to liquid phase behavior in solutions of ecologically sustainable substances. The “green” solvents studied are: ionic liquids, liquid poly(ethylene glycol), glycerol and 1,2- and 1,3-propanediol.

Keywords: sustainable solvents; phase equilibria, poly(ethylene glycol); glycerol; propanediols; ionic liquids.

In the past ten years, Portugal has rapidly advanced in scientific research and development, showing a consistent state strategy in this respect. Statistics and facts obviously speak in favor to this claim:[1] *i*) in 2008, Portugal invested over 2,513,000,000 Euro for this purpose, *i.e.*, 1.51 % of the gross national product (GNP), which is the highest level ever, surpassing those of Ireland and Spain; *ii*) within the aforementioned funds, nearly a half came from the private sector and this increase is enormous – almost three times more compared to 2005; *iii*) the number of researchers per thousand active members of the population reached 7.2, being now over the average in the European Union; *iv*) Portugal probably has one of the best stimulation politics for private investments in research – companies could have tax reductions of up to 82.5 % of their scientific input; *v*) in the period 2004–2008, Portugal had one of the best increase rates of scientific production – the number of publication per million inhabitants in journals acknowledged by the Information Sciences Institute (ISI) list, increased from 373 to 626 (nearly 70 %).

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This favorable scientific environment enabled us, and still does, the realization of good and productive scientific investigations. In the last three years, two main research topics – or slogans – emerged: "green meets toxic" and "green meets green". The first considers ambient friendly solvents for toxic organic compounds (generally solvents as well) of industrial and practical importance. However, the other topic is related to liquid phase behavior in solutions of "green" – ecologically sustainable – substances.

Ambient friendly solvents of our interest are ionic liquids, liquid poly(ethylene glycol), glycerol, 1,2- and 1,3-propandiol.

Ionic liquids constitute a class of compounds the number of which – already enormous (over 1,000,000 known class members)[2] – is constantly rising. The present definition is that they are ionic compounds (salts) that possess glass transition and/or melting points below 100 °C.[3] The complex but diverse structure and versatile solvent properties of ionic liquids offer wide possibilities for both fundamental studies and practical applications.[2,4] Their high asymmetry, robust (ugly) cations (and sometimes anions as well) contribute to their low melting points. Some of the "green" aspects of ionic liquids – toxicity and biodegradebility – are still under discussion,[3] while achieving good purity remains a challenging task.[5,6] However, their favorable properties, extremely low volatility,[7–9] in principle zero flammability[10] and relative thermal stability[11] yet makes them good candidates for alternative solvents. Due to their dual nature – they consist of polar and non-polar domains – they have versatile solvent–solute properties and exhibit a rich phase behavior.[12]

Liquid poly(ethylene glycol) (PEG) (average molar weight 200 and 400 g mol^{-1}) is a good polar solvent which acts both as a proton donor and proton acceptor.[13] It is ambient friendly since it has a rather high boiling point but has a very low toxicity as well and is biodegradable to a large extent.[14] Another interesting aspect of PEG is that it may change its polarity depending on the polarity of the other component in a solution[15] – this aspect obviously contributes to its diversity as a solvent.

1,2- and 1,3-Propandiol and glycerol have high boiling points as well and thus present ecologically sustainable substances. Generally, their toxicity is low, particularly that of glycerol which is practically edible. All these polyalcohols are quite polar and good hydrogen bonding solvents.

Within the aforementioned slogan "green meets toxic", the first issue that was considered is solutions of a highly toxic compound – nicotine – and ionic liquids. In this respect, ionic liquids, 1-alkyl-3-methyl-imidazolium bis(trifluoromethyl sulfonyl) amide ($[C_n mim][NTf_2]$, n = 2–10)) and 1-ethyl-3-methyl-imidazolium ethyl sulfate ($[C_2 mim][EtSO_4]$ – ECOENG212) were initially studied. It was found that ionic liquids of the first series were all completely miscible with nicotine over a wide range of temperatures. However, the solubility tests in the

case of ECOENG212 showed a very limited miscibility – a "wall-like" phase diagram was obtained.[16] The latter presents an extremely narrow one-phase region on the nicotine-rich side and a much higher miscibility on the ionic liquid-rich side. Thus, it was decided to combine the two ionic liquids with the same cation [C_2mim][NTf_2] and [C_2mim][$EtSO_4$] (these are completely miscible) to form a combined solvent. For distinct molar ratios of these two ionic liquids (actually ratios of two different anions), it was possible to fine-tune the temperature-composition phase diagram for the system (nicotine + combined solvent) – the solvent compositions that provide complete miscibility at ambient temperatures were determined.[16]

The same strategy was applied when the ionic liquids 1-alkyl-3-methyl-imidazolium chloride ([$C_n$mim][Cl], n = 6–10) were applied.[16] When the number of the carbon atoms in the cation (n) is 10, the ionic liquid is a very good solvent for nicotine – the upper critical solution temperature (UCST) is below 298.15 K. However, as the carbon number n decreases, the mutual miscibility in the system is reduced. Therefore, in these cases, the combined solvents for tuning the nicotine phase diagrams were practically distinct mixtures of imidazolium cations and a commonly – chlorides.

Following the other slogan "green meets green", ionic liquids and aqueous (high average molecular mass) polyethylene glycol solutions were combined.[17] The main issue was to use ionic liquids as salts to eventually provoke a salting--out effect – low critical solution temperature (LCST) decreases – in PEG solutions with water, following the long-known pattern with inorganic salts that is applied in extraction and separation processes, mainly in biochemistry.[18–20] In this respect, 1-alkyl-3-methyl-imidazolium chloride ([$C_n$mim][Cl], n = 2–10) and ECOENG212 were studied. However, although ionic liquids are salts (molten salts), their behavior towards aqueous PEG solutions was shown to be much more complex than that of inorganic salts. While ionic liquids with short alkyl chains provoked a salting-out effect, those with long ones realized the opposite, the so-called salting-in phenomenon – PEG solubility in water, and thus the LCST of the solution, increased. To be more precise ECOENG212 provoked both effects – the initial salting-in effect was followed by the salting out. The results revealed the possibility of combining ionic liquids and inorganic salts to adjust liquid phase demixing (salting-in or salting-out) effects in aqueous PEG solutions.

Another study that is related to the "green" issue is connected to solutions of imidazolium ionic liquids with polyalcohols. In this work,[21] liquid–liquid equilibria (LLE) of solutions of imidazolium-based ionic liquids with either bistriflamide ([$C_n$mim][NTf_2], n = 2 and 10) or triflate anions ([C_2mim][OTf]), with 1--propanol, 1,2-propanediol, 1,3-propanediol and glycerol (1,2,3-propanetriol) were studied. The obtained phase diagrams showed a remarkable difference in solva-

tion properties between the ionic liquids with NTf_2 or OTf anions towards the aforementioned alcohols; thus, while [C_2mim][NTf_2] constantly exhibited partial miscibility, [C_2mim][OTf] was always completely miscible. This divergence is likely to be related to the distinct abilities of NTf_2 and OTf anions towards hydrogen bonding. There are more than a few evidences and/or facts – based on distinct liquid phase behavior, anion basicity or spectroscopic studies – that speak in favor of this claim (in this respect see ref. 21 and references cited therein). The results of this work enabled speculation on the possibility of using a combined solvent – a mixture of [C_2mim][NTf_2] and [C_2mim][OTf] ionic liquids (or, again, actually a mixture of two anions and a common cation) for a practical purpose – to separate 1,3-propanediol from glycerol and water. Namely, 1,3-propanediol is an important substance in the production of some polymers (polyesters, polyethers and polyurethanes).[22] One of the methods for its production is fermentation from glycerol and the most costly part of this process is the separation of the diol from the fermentation broth. This presents quite a technological challenge, since 1,3-propanediol and glycerol both have high boiling points – the hitherto applied separation methods all have questionable efficiency and/or high energy consumption.[22] Therefore, in this work, a phase diagram was presented that clearly indicates the possibility to realize the aforementioned separation by a sustainable process under ambient conditions.

Our near-future research is also attempting to combine ecologically favorable compounds, ionic liquids, liquid polymers and glycerol – this time in an attempt to obtain hybrid sustainable materials. These studies are to be pursued within our project “green meets green” – “Sustainable hybrid solvents or materials based on ionic liquids, glycerol and liquid polymers”, that has been approved by the Foundation for Science and Technology (FCT) of the Portuguese Ministry of Science, Technology and High Education (MCTES).[23]

ИЗВОД

РАВНОТЕЖА ТЕЧНОСТ–ТЕЧНОСТ У РАСТВОРИМА ОД ПОТЕНЦИЈАЛНОГ ЕКОЛОШКОГ ЗНАЧАЈА

ЗОРАН П. ВИШАК

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Наша истраживања у последње три године иду у два правца: а) повезивања еколошких растварача и токсичних једињења и б) повезивања еколошких растварача и нетоксичних, подношљивих компоненти. Прва линија истраживања подразумева потенцијално коришћење “зелених” растварача за органске, токсичне супстанце од индустријског и лабораторијског значаја. Друга се односи на понашање течних, еколошких, раствора. Проучавани еколошки растварачи су: јонске течности, течни поли(етилен-гликол), глицерол, 1,2- и 1,3-пропандиол.

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