

Solid–liquid phase equilibria in binary mixtures of functionalized ionic liquids with sugar alcohols: New experimental data and modelling



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ABSTRACT

Solid–liquid equilibrium (SLE) phase diagrams of binary systems composed of dicyanamide ionic liquid and sugar alcohols (*meso*-erythritol, xylitol and D-sorbitol) are presented. The studied ionic liquids are based on imidazolium cations having in their structure functionalized side chains: allyl, 2-hydroxyethyl, 3-cyanopropyl, 2-chloroethyl. An impact of the terminal group is discussed in terms of molecular interactions (polarity, hydrogen bonding) between ionic liquids and sugar alcohol. Apparent thermodynamic functions of dissolution of sugar alcohols in ionic liquids were calculated with the Van't Hoff equation. Thermodynamic modelling of the studied SLE phase diagrams with perturbed-chain statistical associating fluid theory (PC-SAFT) is presented. It is proven that accurate correlations of the considered cross-associating systems can be obtained by using relatively simple molecular schemes applied for both ionic liquids and sugar alcohols.

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1. Introduction

A vast number of studies testing ionic liquids (henceforth denoted by ILs) as dissolving media has been performed by far [1,2]. First of all, this is due to the fact that several solvent properties of ILs can be relatively easily modified by means of an appropriate tailoring of chemical structure of ions constituting them. It has been established that properties like fusion temperature, liquid density, viscosity and other thermophysical properties of ILs can be changed by replacing cation core, switching anion from hygroscopic to hydrophilic, or increasing/decreasing the length, branching/cyclization, functionalization of side chains mostly attached to cations. In particular, it is desirable to understand both qualitative and quantitative relationship between the solubility of various materials in ILs and their chemical structure. Of course, they can be found by both experimental and theoretical means, including accurate physico-chemical measurements and modelling based on a great variety of tools, including computer simulations, quantum chemical methods and thermodynamic equations of state [3–8].

Recently, a significant amount of attention from both academic and industrial communities has been devoted to solubility of biomass-related compounds in ILs [9–14]. A motivation for works of this type is so-called biorefining concept, an approach for

chemical engineering based on biomass-derived substrates serving as feedstocks for chemical transformations (for instance into energy or various high value added products). Since the carbohydrates are the most abundant chemicals on Earth, it is natural that they are considered as a potential candidates belonging into biorefinery idea. Unfortunately, sugars and some of their derivatives (like sugar alcohols) are soluble in water and rather poorly soluble in organic solvents, whilst aqueous solutions are not suitable medium for chemical reactions involving organic compounds. This is the main obstacle hindering application of water as a dissolving agent in biorefining processes and that is why screening for alternative solvents for carbohydrates must be perceived as an important research goal. ILs seem to be very promising candidates for biorefineries as they additionally promote “greener” applications in chemical reactions and separations. Indeed, in recent years ILs have turned out to be promising candidates for dissolving biomaterials, particularly carbohydrates and lignocellulosic biomass [12]. In fact, ILs exhibit some unique features relevant from the environmental point of view, e.g. extremely low volatility, high heat capacity and enhanced (compared with volatile organic solvents and water) thermal stability.

Many efforts have been made aiming to measure and reporting solubility of sugars or sugar-derived compounds in ILs. The contributions until 2010 are described in detail elsewhere [15]. A great of majority of them presents single data points at fixed temperature. This is usually not sufficient information for practical applications, where solubility curves over wide range of temperature or even complete solid–liquid equilibrium (SLE) phase diagrams

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Nomenclature

a, A	Helmholtz free energy
A, B, \dots	associating sites
k	binary interaction parameter
k_B	Boltzmann constant
m	PC-SAFT parameter
N	number of molecules/sites/data points
P	pressure
T	absolute temperature
u	PC-SAFT parameter
x	mole fraction

Greek letters

γ	activity coefficient
ϵ	PC-SAFT parameter
κ	PC-SAFT parameter
σ	PC-SAFT parameter/root mean square deviation
φ	fugacity coefficient

Superscripts

calcd	calculated value
exptl	experimental value
LB	Lorentz–Berthelot combining rule
res	residual property
WS	Wolbach–Sandler combining rule

Subscripts

1	sugar alcohol
2	ionic liquid

are preferred for designing crystallization processes or dissolution conditions. Thus far, only several papers presenting solubility curves for the considered systems are available in open scientific literature [16–27]. Moreover, antisolvent precipitation of carbohydrates from several imidazolium ILs was investigated very recently [21,28].

Besides experimental work done in the field of SLE phase diagrams of mixtures of ILs with sugars or sugar alcohols, several authors attempted to perform a thermodynamic modelling of these systems. In particular, simple local composition idea based excess Gibbs energy (G^E) models like NRTL, e-NRTL and UNIQUAC [21,24,25,29] have been shown to be reliable tools for solubility curves representation. Unfortunately, those models are purely correlative so that their parameters can not be used to calculate SLE curves for systems other than to which they are assigned. More advanced model, namely, perturbed-chain statistical associating fluid theory (PC-SAFT), has been also intensively studied by a few research groups [16,18,19,22]. First of all, this model is formulated as an equation of state and therefore it can be used to capture both pure fluid and mixture properties. Moreover, contrary to G^E models it can be applied in purely predictive mode in the case of mixture properties, including solubility. In our previous papers we showed, however, that the predictive capacity of PC-SAFT for systems composed of ILs and sugar or sugar alcohols is limited and satisfactory results can be achieved only when binary interactions parameters are implemented [16,18,19]. Similar observations were made by other authors as well [22].

This work presents another contribution to our systematic investigations of solubility of sugars and sugar alcohols in various ILs. Solubility curves of *meso*-erythritol, xylitol and D-sorbitol in four ILs based on and functionalized imidazolium cations were determined. In our previous paper [16], a similar study has been

reported for systems with glucose. All the sugar alcohols selected for this study are very important food additives [30] (mostly as artificial sweeteners) having also some health care (sugar-free and dietary drinks and foods) and cosmetic applications. Furthermore, D-sorbitol or xylitol (i.e., the most representative sugar alcohols) were placed the U.S. Department of Energy on the list of twelve building block chemicals for biorefinery [31]. Summing up, the data for twelve binary systems {IL + sugar alcohol} are reported over wide range of temperature and IL concentration. The cations of ILs under study are as follows: 1-allyl-3-methylimidazolium dicyanamide, 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide, 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide and 1-(2-chloroethyl)-3-methylimidazolium dicyanamide. Thermodynamic modelling of the investigated systems with the PC-SAFT equation of state is demonstrated as well.

2. Experimental

2.1. Materials

The chemical structures and abbreviations used in further text for cations and anion constituting the investigated ILs as well as the chemical structures of sugar alcohols are shown in Fig. 1. Before the measurements all samples were dried and degassed by applying vacuum (approx. 1 mbar) at moderate temperature (approx. 323 K) for approximately 48 h. All the compounds were stored under vacuum in desiccator over freshly activated molecular sieves and phosphorus pentoxide used as drying agents. Water content in ILs

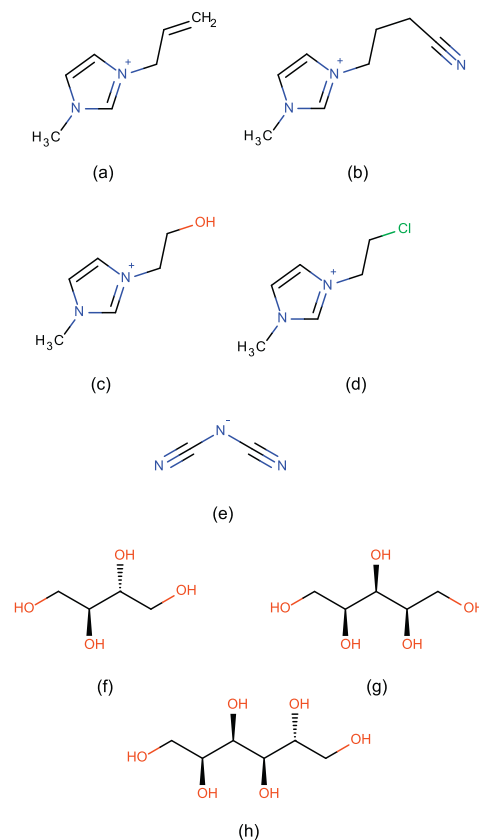


Fig. 1. The chemical structure of the ions forming the ionic liquids and sugar alcohols considered in this study: (a) 1-allyl-3-methylimidazolium cation, $[C_{1=C}C_1Im]$; (b) 1-(2-hydroxyethyl)-3-methylimidazolium cation, $[C_{2OH}C_1Im]$; (c) 1-(3-cyanopropyl)-3-methylimidazolium cation, $[C_{3CN}C_1Im]$; (d) 1-(2-chloroethyl)-3-methylimidazolium cation, $[C_{2Cl}C_1Im]$; (e) dicyanamide anion, $[N(CN)_2]$; (f) *meso*-erythritol; (g) xylitol; (h) D-sorbitol.

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