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Solubility data of zwitterions in water

Maciej Zawadzki [a, *], Marta Królikowska [a, b]

[a] Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warsaw, Poland
[b] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban, 4041, South Africa

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ABSTRACT

In this work a series of ammonium- and phosphonium-based zwitterions (ZIs) namely: 3-(triethylammonio)propane-1-sulfonate, $N_{222}C3S$, 4-(triethylammonio)butane-1-sulfonate, $N_{222}C4S$, 3-(tributylammonio)propane-1-sulfonate, $N_{444}C3S$, 4-(tributylammonio)butane-1-sulfonate, $N_{444}C4S$, 3-(trihexylammonio)propane-1-sulfonate, $N_{666}C3S$, 4-(trihexyl-ammonio)butane-1-sulfonate, $N_{666}C4S$, 3-(tributylphosphonio)propane-1-sulfonate, $P_{444}C3S$ and 4-(tributyl-phosphonio)butane-1-sulfonate, $P_{444}C4S$ have been synthesized. The structure and purity of these compounds were confirmed by ^1H NMR. The thermal properties such as temperature and enthalpy of (solid + solid) phase transition as well as the melting temperature of pure ZIs were evaluated by DSC technique. The (solid + liquid) and (liquid + liquid) phase equilibria measurements have been performed for eight binary systems of synthesized ZIs and one purchased 3-(1-pyridinio)-1-propanesulfonate [PyC3S] using the dynamic method and the experimental results were correlated using NRTL equation. Additionally, ternary system of {$N_{666}C3S$ (1) + $N_{444}C3S$ (2) + water (3)} with three different $N_{666}C3S$ to $N_{444}C3S$ initial molar fractions was determined.

1. Introduction

In the past few decades, ionic liquids (ILs) have been an object of interest for both academics and industry. Their unique properties which undoubtedly include: negligible vapor pressure, high chemical, and thermal stability, large liquidus range, total or partial solubility in polar or non-polar compounds, or good electrical conductivity [1] make them attractive for specific applications [2,3] in comparison with organic solvents. Moreover, the possibility of changing their properties by structural design of both cation and anion is considered one of their most interesting characteristics, which allows designing IL for specific purposes. The use of IL in liquid-liquid extraction [4] and other applications [5,6] were extensively investigated.

Other class of ionic compounds that gathers more attention are zwitterionic compounds (ZIs) [7]. These compounds have two charged groups that are linked together by a covalent alkyl chain. This prevents the different partition of ions when biphasic systems, used in extraction, are concerned. Ohno and co-workers [8] proposed increasing the content of water in IL organic phases by addition of ZIs in order to enhance the ability to dissolve and extract proteins [9]. Additionally, ZIs as well as ILs can form mixtures with both upper and lower critical solution temperatures (LCST, UCST) with water [10]. This kind of mixtures could find application in both separation processes [11], water purification [12], or enzymatic reactions. Similarly, to ILs, physicochemical properties of ZIs can be tuned by changing the chemical structure. Both ILs and ZIs can form aqueous biphasic systems [10] used in the separation of amino acid [13], proteins [14], or alkaloids [15].

This group of compounds has great potential and is relatively understudied. These compounds have a potential to be used as additives in IL mixtures and other solvent mixtures especially water to enhance their solvation properties. The aim of this work is to better understand these compounds and their interactions with water by means of solid + liquid and liquid + liquid phase equilibria measurements. Knowledge of thermodynamic behavior of ZIs and their molecular interactions with water will allow for better understanding and enable more accurate prediction of physicochemical properties.

* Corresponding author.
E-mail address: mzawadzki@ch.pw.edu.pl (M. Zawadzki).

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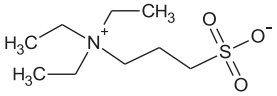
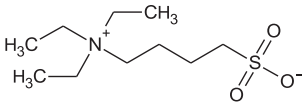
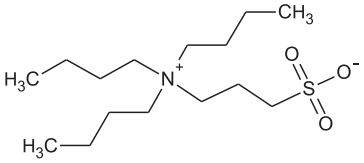
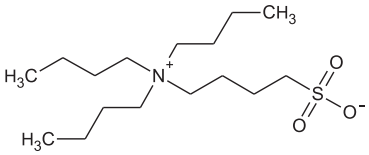
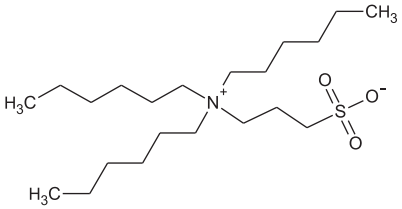
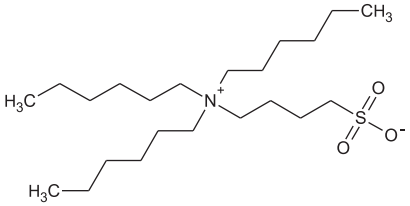
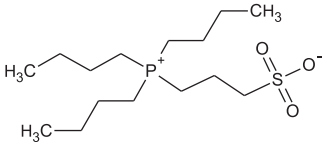
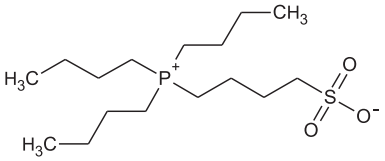
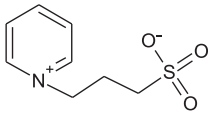
2. Experimental section

2.1. Materials

In this work, six ammonium-based and two phosphonium-based ZIs with different alkyl side chain lengths have been synthesized accordingly to a reported procedure [16]. The general description of the synthesis procedure is below, details are described in the SI. The chemical structures were confirmed by ^{1}H NMR and ^{13}C NMR analysis. The graphical results of these analyses are collected on Figs. S1 to S16 in Supplementary Material (SM). The 3-(1-pyridinio)-1-propanesulfonate was purchased from Sigma-Aldrich (>97%, used as received).

The structures, names, and abbreviations of the tested ZIs are

Table 1
Structures, abbreviations, and names, source and CAS No. for the compounds studied in this work.

Structure	Name, abbreviation, CAS No.	M/g·mol^{-1}
	3-(triethylammonio)propane-1-sulfonate $N_{222}C3S$, synthesis in our laboratory, CAS No. -;	223.33
	4-(triethylammonio)butane-1-sulfonate $N_{222}C4S$, synthesis in our laboratory, CAS No. -	237.36
	3-(tributylammonio)propane-1-sulfonate $N_{444}C3S$, synthesis in our laboratory, CAS No. -	307.49
	4-(tributylammonio)butane-1-sulfonate $N_{444}C4S$; synthesis in our laboratory, CAS No. -	321.52
	3-(trihexylammonio)propane-1-sulfonate $N_{666}C3S$; synthesis in our laboratory, CAS No. -	391.65
	4-(trihexylammonio)butane-1-sulfonate $N_{666}C4S$; synthesis in our laboratory, CAS No. -	405.68
	3-(tributylphosphonio)propane-1-sulfonate $P_{444}C3S$; synthesis in our laboratory, CAS No. -	324.46
	4-(tributylphosphonio)butane-1-sulfonate $P_{444}C4S$; synthesis in our laboratory, CAS No. -	338.49
	3-(1-pyridinio)-1-propanesulfonate PyC3S; Aldrich, ≥97.0% CAS No. 15471-17-7	201.24