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Effect of 1-carboxymethyl-3-methylimidazolium chloride ionic liquid on thermodynamic and solubility of L-threonine in water at 298.15 K and atmospheric pressure

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ABSTRACT

Vapor–liquid equilibrium data (water activity, vapor pressure and osmotic coefficient) of the mixed aqueous solutions, L-threonine + 1-carboxymethyl-3-methylimidazolium chloride and the corresponding binary aqueous amino acid solutions have been measured by the isopiestic method at temperature 298.15 K and atmospheric pressure. The experimental data for the activity of water were accurately correlated with segment-based local composition models of the Wilson, NRTL, modified NRTL and NRF-NRTL. From these data, the corresponding activity coefficients have been calculated. For the same system, the solubility of the L-threonine at various ionic liquid (IL) concentrations was measured at 298.15 K using gravimetric method. Also the above local composition models were used to describe the solubility of amino acid in pure water and in aqueous IL solutions. To provide information regarding solute–solute interactions, transfer Gibbs free energies (ΔG_{tr}) of amino acid from water to aqueous IL solutions have been determined from the solubility measurements and activity coefficient of amino acid in water and [Cmmim][Cl] + water solutions calculated from different models, as a function of IL concentration at 298.15 K.

1. Introduction

The biological and industrial importance of amino acids is well known as well as the knowledge of their physical and chemical properties. Amino acids are the basic building blocks of proteins and peptides, and the development of more accurate and efficient processes for their separation, concentration and purification of those has been a subject of main interest, particularly for pharmaceutical and food industries [1]. On the other hand, the reverse micellar extraction of proteins or amino acids with an electrolyte or an organic solvent has been recently considered of great interest. The importance of studying the behavior of biomolecules in aqueous systems containing electrolytes will be evident when the high cost of their separation and purification processes is considered [2,3]. To design these processes, the fundamental physical properties of biomolecules, such as solubility and activity coefficient, must be obtained [4]. The effects of co-solvents on the solubility and conformational stability of proteins have been of intense interest for decades. Obviously, the stability of biomolecules under co-solvent conditions is dependent on the nature of the co-solvent; which can alter a protein's properties and structural effects through biomolecular interactions between its functional groups and the co-solvent particles [5]. Ionic liquids (ILs) are a new class of organic salts and as green solvents have significant effect in many biochemical and chemical processes. The introduction of structural functionalities on the cationic or anionic part has made it possible to design new ILs with targeted properties. A new kind of ionic liquid has been developed recently, and these are called "task specific" ionic liquids. In task specific ionic liquids the alkyl group is functionalized [6]. We guess that the functionalized IL, which is studied in the present work, by virtue of its functional group, promotes remarkable changes in the solubility of the studied amino acid due to new interactions may arise between IL and amino acid. The solubility behavior of biomolecules in aqueous electrolyte solutions assumes a very important role in the life sciences and biotechnological developments [7]. The successful representation of the solubility is directly related to the ability to correlate and predict the activity coefficients of amino acids in solution. One of the important tools to investigate the interactions between ionic salts and amino acids is thermodynamic transfer properties such as free energy, entropy and enthalpy, of amino acids in aqueous IL solutions. These results lead to the conclusion that some of the electrolytes can

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Nomenclature

A_x	Pitzer–Debye–Hückel constant
a	activity or binary parameter in the NRTL, mNRTL, NRF-NRTL model
A	amino acid
a, b, c	coefficients of Eq. (14)
B	second virial coefficient
C	coordination number
D	dielectric constant
Dev	relative percentage deviation
E	binary parameter in the Wilson model
f	fugacity of the amino acid
ΔG	transfer Gibbs free energy of the amino acid
e	electronic charge
G	binary parameter in the NRTL, mNRTL, NRF-NRTL model
g	Gibbs energy of interaction or Gibbs energy
H	binary parameter in the Wilson model
h	enthalpy of interaction
I_x	ionic strength on the mole fraction scale
k	Boltzmann constant
K_s	equilibrium constant
m	molality
M	molar mass
N_A	Avogadro's number
NP	number of experimental data
OF	objective function
P	vapor pressure
R	gas constant
S	solubility of amino acid
T	temperature
V	molar volume
x	mole fraction
X	effective mole fraction
Z	charge number

Greek letters

α	nonrandomness factor
ε	permitivity of vacuum
ν	stoichiometric parameter
ρ	closest approach parameter
γ	activity coefficient
τ	binary parameter in the NRTL, mNRTL, NRF-NRTL model
ϕ	osmotic coefficient
μ	chemical potential

Superscripts

bin	binary system
cal	calculated value
ex	excess
exp	experimental value
LR	long-range
m	molality base
PDH	Pitzer's extension of Debye–Hückel function
SR	short-range
ter	ternary system
x	mole fraction base
*	unsymmetric convention
±	zwitterion
°	pure solvent
′	apparent transfer properties

Subscripts

a and *c*	anion and cation
ca	electrolyte (ionic liquid)
i, *j*, *k*	any species, amino acid, ions and water
m	amino acid
NRTL	non-random two liquid
mNRTL	modified NRTL model
NRF	non-random factor model
tr	transfer
w	water
Wilson	Wilson model

Table 1
A brief summary of the purity of the used materials.

Material[a]	Mass fraction purity
NaCl L-threonine	(GR, min99.5%)>0.99
N-methylimidazole	>0.99
Choloroacetic acid	>0.99
Acetonitrile	>0.99
Methanol	>0.99

[a] All materials were supplied from Merck.

stabilize biological important molecules such as proteins. From the Gibbs free energy of transfer (ΔG_{tr}) studies obtained from solubility of amino acid we can elucidate the effect of ionic liquid on protein stability [8]. For calculating ΔG_{tr} values the vapor–liquid equilibrium (VLE) and solubility of amino acids data are required. Only a few measurements, however, have been performed on VLE and solubility of amino acids in ILs [5,9,10]. In calculation of ΔG_{tr} values a suitable correlation equations for the measured properties are also necessary. An overview of thermodynamic equations which can be used for correlating VLE and solubility of an amino acid in aqueous ionic liquid solution was given in a previous publication [9].

In continuation of our previous work, in this work the vapor–liquid equilibria of ternary system {L-threonine + 1-carboxymethyl-3-methylimidazolium chloride [Cmmim][Cl] + H_2O} and the corresponding binary aqueous L-threonine system have been measured using the improved isopiestic method at T = 298.15 K. Another objective of this study is the presentation of new experimental data for the solubility of L-threonine in aqueous [Cmmim][Cl] solutions at 298.15 K using the gravimetric method. These data permit us to investigate the role of studied IL, [Cmmim][Cl], on the solubility of L-threonine. The obtained experimental data for the water activity and solubility in this work were correlated with the segment-based local composition models such as Wilson [11], NRTL [12], modified NRTL (mNRTL) [13] and NRF-NRTL [14] models.

To obtain more thermodynamic information about these kinds of systems, we also calculated the transfer Gibbs free energies (ΔG_{tr}) of L-threonine from water to various concentrations of ionic liquid [Cmmim][Cl].

2. Experimental setup

2.1. Materials

Sodium chloride (solute for the isopiestic reference standard solution) was dried in the electrical oven about 383.15 K for 24 h prior to use. L-Threonine was used without further purification. The reagents used for the synthesis of [Cmmim][Cl] were *N*-methylimidazole, choloroacetic acid, acetonitrile and methanol purchased from Merck. The purity of the used materials is shown in