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Evaluating the transfer free energies of amino acids from water to ammonium-based ionic liquids at 298.15 K

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ABSTRACT

The interactions between ionic liquids (ILs) and amino acids (AA_s) can easily be quantified using the apparent transfer free energy ($\Delta G'_{tr}$) values that can be used to interpret the stability of the proteins in the same solvent medium. In this study, $\Delta G'_{tr}$ values of AA_s such as phenylalanine (Phe), histidine (His), threonine (Thr), glutamine (Gln) and serine (Ser) from the water to ILs have been obtained from the solubility measurements, as a function of IL concentration at 298.15 K under atmospheric pressure. The investigated ILs contain diethylammonium acetate (DEAA), diethylammonium hydrogen sulfate (DEAS), triethylammonium acetate (TEAA), triethylammonium hydrogen sulfate (TEAS), triethylammonium dihydrogen phosphate (TEAP), and trimethylammonium acetate (TMAA). The results reveal that the IL effect was specific and independent for each AA in the aqueous medium. Apparently, we observed a positive as well as negative $\Delta G'_{tr}$ values for Phe, His, Glu, Thr, and Ser AA_s in the ammonium-based ILs.

1. Introduction

Ammonium-based ionic liquids (ILs) belong to a class of protic ionic liquids (PILs) that have been accepted as a new revolutionary, "Green Solvents" that have attracted the attention of both academia and chemical industries [1]. The novel property that distinguishes PILs from the rest of the ILs is the proton transfer from the acid to the base that leads to the build-up of a hydrogen-bonded network, which is similar to the effects that occur in protein aqueous solutions [2,3]. Undoubtedly, the use of PILs can reduce the use of hazardous and polluting organic solvents due to their unique physical properties.

The ammonium-based ILs are less viscous and easy to handle [1], and are very attractive solvent media for the assay of protein stability [4,5]. Additionally, prevention of protein self aggregation in aqueous solutions containing ammonium-based ILs has been successfully reported by our research group [6]. Moreover, literatures reveal that the ammonium-based ILs act as best stabilizers for the protein structure. Lau et al. [7] reported that in the presence of triethylmethyl ammonium methylsulfate ([Et_3NMe][MeSO4]) IL, the activity of Candida Antarctica Lipase B (CALB) almost resembled that of its native state. Similarly, de Diego et al. [8] observed that in the presence of an IL such as butyltrimethylammonium bis(trifluoromethylsulfonyl) imide ([btma][NTf2]) improved the stability of CALB. In the same fashion, ethyl ammonium nitrate (EAN) prevents the aggregation of denatured protein lysozyme, bringing back its activity up to 75% [9]. This outstanding property of ammonium-based IL was further supported by Byrne et al. [10], where EAN permitted the refolding of a thermally unfolded lysozyme and also provided long term stabilization without aggregation. Mann et al. [11] reported the thermal stability and activity of lysozyme in four ammonium-based ILs such as ethylammonium formate (EAF), propylammonium formate (PAF), 2-methoxyethylammonium formate (MOEAF) and ethanolammonium formate (EtAF). Their report revealed that the PILs (EAF, PAF, MOEAF and EtAF) were effective stabilizers for the protein against thermal unfolding. Further, Wei and Danielson [12] observed that the structural stability of cytochrome c (cyt c) is improved in methyl ammonium formate (MAF) and ethyl ammonium formate (EAF).

The basic concept of stability of proteins in ILs originates through understanding the thermodynamic properties such as apparent transfer free energy ($\Delta G'_{tr}$) which is obtained through the analysis of the solubility properties of individual amino acids (AA_s) in aqueous solution of ILs [13,14]. Apparently, the sign and magnitude of the measured $\Delta G'_{tr}$ quantify the protein response to changes in solvent quality. By definition, if the values are $\Delta G'_{tr} > 0$, means that the protein is stable, whereas a low value of transfer free energy, $\Delta G'_{tr} < 0$, represents that the protein becomes unfolded to a solvent. Our group is significantly involved in predicting the $\Delta G'_{tr}$ of the AA_s with ILs that strongly appeal the mode of interactions between the ILs and AA_s [13–17]. In this context, AA_s such as glycine (Gly), tryptophan (Trp), tyrosine (Tyr), histidine (His), valine (Val), alanine (Ala), and leucine (Leu) have been studied and the thermodynamic contribution of the peptide backbone unit and dipeptide units such as diglycine (Gly_2), triglycine (Gly_3) and tetraglycine

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