Scientific paper

Specification of Zwitterionic or Non-Zwitterionic Structures of Amphoteric Compounds by Using Ionic Liquids

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Abstract

Some imidazolium-based ionic liquids were used to determine zwitterionic or non-zwitterionic structures of glycine and p-amino benzoic acid, as model amphoteric compounds, in their corresponding isoelectric point. To do this, the partitioning behaviors of both compounds between the ionic liquid and aqueous phase at different pH values were investigated. The results revealed that due to having different pH-dependent chemical structures, each compound showed different partitioning behavior. This observation was considered as a basis for introducing a green technique for understanding the real chemical structures (species), i.e. zwitterionic or non-zwitterionic structures of amphoteric compounds such as amino acids in the aqueous solutions. This study revealed the existence of a non-zwitterionic (neutral) structure for p-amino benzoic acid and a zwitterionic structure for glycine in their corresponding isoelectric points.

Keywords: p-Amino benzoic acid; Glycine; Ionic liquid; Partition coefficient; Zwitterion

1. Introduction

Charge characterization and speciation of amino acids is of interest not only in biological sciences for better understanding of the metabolic processes in tissue membranes but also in analytical chemistry for improving and designing new separation and measurement procedures. Generally, knowing the chemical forms, including the charged structures, of a compound as it really exists in a sample would help revealing its true impact on human or the environment. Speciation analysis plays a unique role in studies of biogeochemical cycles of chemical compound, determination of toxicity as well as ecotoxicity of selected elements, quality control of food products, control of medicines and pharmaceutical products, technological process control, and clinical analysis. For instance, zwitterions, used widely in chemical, biological and medicinal fields, show distinct physicochemical properties relative to ordinary ampholytes, which largely decide their bioavailability and biological activities.1 Many studies including computational protocols have been done about charge characterization of peptides and proteins (to interpret their mass spectrometry data)2 as well as amino acids in gas phase.3-8 However, few studies about the charged structures of amino acids in aqueous phase are available for checking the studies reported by many authors. In 1916, Adams showed that an amino acid might possess a zwitterionic structure, i.e. \( \text{+NH}_3\text{–R–COO}^- \), rather than a non-zwitterionic classical structure, i.e. \( \text{NH}_2\text{–R–COOH} \), in aqueous solutions.9 However, opposite ideas also were reported.10 In this regard, in 1930, Harris was able to provide direct evidence through doing many titrations and experiments to show that an amino acid molecule does possess, in preponderant proportion, a zwitterionic rather than a non-zwitterionic classical structure.11 In a recent study, amino acids were considered as neutral species,12 while previous studies showed that they can exist in zwitterionic form. So it is necessary to investigate the real amino acid species in aqueous solutions.

Klotz and Gruen performed many experiments and compared the ionization constants of the amino groups in \( p \)-amino benzoic acid (PABA) and its esteric compounds to reveal that PABA is primarily neutral (i.e. free of any charge) in its isoelectric point (pI = 3.68).13 Other studies
showed that PABA exists in neutral and not in zwitterionic form in its isoelectric point in aqueous solutions. Yet to have further evidence, alternative procedures are required for confirming the above mentioned assumptions as that presented in this article.

Room temperature ionic liquids (RTILs) are known as green solvents and applied in different chemical scopes, such as electrochemistry, batteries and fuel cells investigations, chemicals synthesis, catalytic processes, and separation sciences. Also, interactions of chemical compounds with ILs can be considered as models of bio-membranes for studying the membrane permeability or structure-activity relationships. It has been reported that the distribution coefficients of ionized forms of solutes in ILs are between one and three orders of magnitude lower than those of the molecular substances. So, studying the partitioning behaviors of different compounds, specifically the amphoteric substances, in IL/H2O system would be a way to obtain information about their different charged species including the zwitterions.

In this work, a simple and efficient methodology is introduced to characterize zwitterionic or non-zwitterionic structure of glycine, as a model amino acid, as well as that of PABA in the isoelectric points by studying their partitioning behaviors between aqueous and ionic liquid phases. The ionic liquids used in this study have imidazolium-based chemical structures: 1-butyl-3-methylimidazolium hexafluorophosphate, [C8mim][BF4]; 1-octyl-3-methylimidazolium tetrafluoroborate, [C4mim][BF4], and 1-octyl-3-methylimidazolium hexafluorophosphate, [C8mim][PF6].

2. Experimental

2.1. Instrument

The UV-Vis absorption spectra were recorded against the solvent blank at room temperature, using a U-3500 spectrophotometer (Shimadzu, Kyoto, Japan). A Metrohm 780 pH-meter was applied for pH measurements. The NMR spectra were recorded using a Bruker-Advanced DPX/250 (1H NMR 250 MHz and 13C NMR 62.9 MHz) spectrophotometer.

2.2. Reagents

Ammonium hexafluorophosphate and sodium tetrafluoroborate were purchased from Fluka; 1-bromobutane, 1-bromooctane, 1-methylimidazolium, glycine, p-aminobenzoic acid (PABA), ninhydrin, and hydrindantin dihydrate were purchased from Merck Chemical Company with the highest available purity and were used without further purification. The ionic liquids (Table 1): 1-butyl-3-methylimidazolium hexafluorophosphate, [C8mim][BF4]; 1-octyl-3-methylimidazolium tetrafluoroborate, [C8mim][BF4]; and 1-octyl-3-methylimidazolium hexafluorophosphate, [C8mim][PF6], were synthesized as described in literature and their chemical structures were verified by using NMR spectroscopy. The obtained NMR spectra of ILs were in good agreement with the previously reported spectra and no traces of impurities were observed. Distilled deionized water was used throughout this work.

2.3. Procedure

Individual aqueous solutions containing 1.0×10⁻³ mol L⁻¹ of either glycine or PABA (each with a volume of 500 µL) were brought into contact with 50 µL of IL at room temperature in a stoppered glass test tube. The ionic strengths of aqueous solutions were kept constant using the 0.10 mol L⁻¹ KCl solution for all pH values. Each system was vigorously stirred with a magnetic stirrer for 30 minutes and then both phases were carefully separated using a centrifugation device. The partition coefficients of both glycine and PABA between the IL phase and aqueous solution (IL/H2O system) were calculated according to the following equation: KIL/AW = [(CIL − CIW)/(CVIL)]/[(CIAW)/(VIL)], where CI and CF, respectively, refer to the initial and final concentrations of each compound in aqueous phase; VAW and Vil refer to the aqueous and IL phase volumes, respectively. Final concentration of PABA in the aqueous phase was determined by using UV-Vis spectrophotometry. Final concentration of glycine in aqueous phase was determined by ninhydrine method. Generally, in this method the glycine solution is mixed with a solution prepared by dissolving 2.0 g ninhydrin and 0.30 g hydrindantin in 75 mL DMSO and 25 mL of sodium acetate buffer in pH 6.4. The mixture is heated up in a boiling water bath for a period of 5 minutes. Afterward, it is immediately cooled in an ice-bath. The absorbance of the mixture is measured with a spectrophotometer at 575 nm.

It is stressed that each point presented on charts in Figures 1 and 2 is the average of triplicate measurement.

3. Results and Discussion

3.1. Partitioning of Glycine Into Imidazolium-based ILs

As it is shown in Figure 1, comparison at different pHs, partition coefficient of glycine is relatively high in the pH region where its cationic (A⁺) and anionic (A⁻) species (Table 1) are dominant. However, the K value for distribution of glycine between water and [C4mim][BF4] is higher (up to K = 2.0) at low pH. Electrostatic interactions of A⁺ and A⁻, respectively, with the anionic and cationic parts of the studied ILs are responsible for showing this behavior. Partition coefficient of the species with net zero-charge (i.e., either a zwitterionic species with both positive and negative charges in the aqueous and IL phases) is lower than that of the charged species.
One molecule, or a neutral species that does not have any charge) of glycine (A±) is the lowest as a consequence of diminishing of its electrostatic interactions with IL due to the presence of a net zero-charge on the molecule. Moreover, in spite of simultaneous presence of two ionized groups, i.e. “NH₃ and COO⁻, the hydrophobicity of glycine molecule decreases so that a lower partition coefficient of its zwitterionic form, A±, in the pH range 4.0–8.0 is achieved. This behavior showed that the net zero-charge of glycine species at its isoelectric point (pH 6.06) has a zwitterionic (not neutral) structure; because of this, hydrophobicity and consequently its extraction into IL phase is the lowest.

These results show that the number of ionized groups in a molecule is a determining factor for its extraction into the IL phase. Since glycine has two ionized groups (“NH₃ and COO⁻”) in its isoelectric point, but in acidic or basic conditions has only one of these ionized groups (i.e. “NH₃ or COO⁻, respectively, in acidic and basic solutions), partitioning of its zwitterionic form into IL phase is not better compared to its other two forms. These results confirm that glycine has a zwitterionic structure in its isoelectric point which was also already verified by Harris.¹¹

If glycine is neutral (instead of being zwitterion) in its isoelectric point, then it will be expected to have a higher partition coefficient due to a more hydrophobic character in comparison to its both cationic (A⁺) and anionic forms (A⁻).

It is noticeable that charge densities of the ionic constituents of IL phase may affect its extracting ability when it interacts with different forms of an amino acid such as glycine. For instance, the electrostatic interaction of cationic form of glycine (A⁺) with the anionic part of an IL, i.e. BF₄⁻ or PF₆⁻, depends on the value of the charge density of these ions. Table 2 provides the calculated charge densities of constituent ions of the ILs used in this study.³⁴ As it is shown in this table, the charge density of BF₄⁻ is higher than PF₆⁻; also quantum chemical calculations indicated that the effective negative charge in BF₄⁻ is much higher than in PF₆⁻.³⁵ Therefore, stronger electrostatic interaction between the cationic form of glycine and BF₄⁻, and consequently a higher extraction of A⁺ into BF₄⁻-based ILs, is expected as demonstrated in Figure 1.

It has been reported that the presence of water in ionic liquids may have important implications on the properties of room temperature ILs as solvents, such as conductivity, viscosity and diffusivity.³⁶ The water content of ILs is an important parameter that must be taken into consideration for evaluating the different extraction behaviors of ILs. But, before continuing the following discussion, it should be mentioned that in this text, the water contents of ILs refers to the amount of water that ILs are capable to absorb during their contact time with aqueous phase for a duration of 30 min in all the experiments. In this contact, the ion-pair association between cationic and anionic constituents of an IL is partially disrupted in the presence of water due to the development of H-bonding between water and the anionic part of the IL. For imidazolium-based ILs, it has been reported³⁷ that water molecules (in the content range of 0.2–1.0 mole water per liter of IL) are mostly in free (not self-associated) state but could bind to the anionic constituent, i.e. PF₆⁻ or BF₄⁻, of the IL. Furthermore, the
bulky cations of ILs containing long alkyl chains can organize water molecules around themselves. These types of ILs undergo hydrophobic hydration in water that is usually known as the formation of more oriented and rigid structures of water surrounding the ILs.\textsuperscript{38,39} In this situation, the interaction between anionic and cationic constituents of the IL decreases; however, the electrostatic interactions between cationic form of glycine (A\textsuperscript{+}) and anionic part of IL enhances. Therefore, the partition coefficients of glycine in the pH values that exists in its cationic form directly depend on the water content of IL.

According to literature,\textsuperscript{40} the water contents of ILs decrease in the order of [C\textsubscript{8}mim][BF\textsubscript{4}] > [C\textsubscript{4}mim][PF\textsubscript{6}] > [C\textsubscript{8}mim][PF\textsubscript{6}], which exactly follows the same order found for ILs in the extraction of cationic form of glycine (Figure 1). It is to be noticed that the partition coefficient of glycine, when [C\textsubscript{8}mim][PF\textsubscript{6}] was used as IL, was so low that it could not be shown in Figure 1.

In brief, both water contents of ILs as well as charge density of their anionic parts make cationic form of glycine to be extracted into IL phase in an order of [C\textsubscript{8}mim][BF\textsubscript{4}] > [C\textsubscript{4}mim][PF\textsubscript{6}] > [C\textsubscript{8}mim][PF\textsubscript{6}]. (Figure 1).

At pHs ≥ 7 (Figure 1) where anionic form of glycine (A\textsuperscript{−}) is dominant, water content and charge density of the cationic form of IL (i.e. the imidazolium ion) could be examined as the possible driving forces for extraction of A\textsuperscript{−} into the IL phase. It should be noticed again that the partition coefficients, when [C\textsubscript{8}mim][PF\textsubscript{6}] was used as IL, were so low that they are not shown in this figure. However, the order of ILs for partitioning of A\textsuperscript{−} could be considered as [C\textsubscript{4}mim][PF\textsubscript{6}] > [C\textsubscript{8}mim][BF\textsubscript{4}] > [C\textsubscript{8}mim][PF\textsubscript{6}] based on data shown in Figure 1. This is in agreement with the order of charge densities of cationic parts of ILs (Table 2).

The [C\textsubscript{8}mim][PF\textsubscript{6}], with both higher charge density in its cationic part and lower water content than [C\textsubscript{4}mim][BF\textsubscript{4}], has provided higher partitioning for the anionic forms of glycine. This observation shows that charge density of cationic part of ILs is favorable for extraction of glycine. It seems that the extraction of A\textsuperscript{−} is favored by the water content of the IL when ILs have similar cationic constituents but different water contents.

Extraction of A\textsuperscript{−} into [C\textsubscript{8}mim][BF\textsubscript{4}], with a higher water content, was found to be higher than that of [C\textsubscript{4}mim][PF\textsubscript{6}], which has the least water content. The results obtained for partition coefficients of A\textsuperscript{−} in different ILs reveal that both charge density of the cationic part of IL and its water content are responsible for the extraction of A\textsuperscript{−} but they may counteract. As it is shown in Figure 1, the differences in the values of the partition coefficients of A\textsuperscript{−} in different ILs are not as remarkable as those observed for A\textsuperscript{+} in different ILs. It should be mentioned that [C\textsubscript{8}mim][BF\textsubscript{4}] could not be studied in this work as it is soluble in water.

The order of ILs for partitioning of zwitterionic form of glycine is as follows: [C\textsubscript{8}mim][BF\textsubscript{4}] > [C\textsubscript{4}mim][PF\textsubscript{6}] > [C\textsubscript{8}mim][PF\textsubscript{6}]. Polarity and water content of ILs are concluded to be the effective parameters that could explain the above observation. Partition coefficient is more dependent on the charge density of the ionic components of ILs than on its water content (which in a way reflects the polarity of IL). As [C\textsubscript{8}mim][PF\textsubscript{6}] is a least polar IL with least water content, it is expected that glycine as a polar compound (log\textsubscript{K} in octanol is around −3) would have the smallest K in this IL.

### 3.2. Partitioning of p-amino Benzoic Acid Into Imidazolium-Based ILs

Partitioning behavior of PABA between water and imidazolium-based IL phases, at different aqueous pH values, was investigated. As shown in Figure 2, partition coefficient of PABA was the highest at its isoelectric point showing that the hydrophobicity of PABA could be the reason for its higher extraction in the IL phase. This consequently proves that PABA exists in a neutral rather than in a zwitterionic form at its isoelectric point. At pH values higher or lower than the isoelectric pH, ionic forms of PABA (PA\textsuperscript{−} and PA\textsuperscript{+}), with lower hydrophobicity than its neutral form (PA), have lower tendency for transporting into the IL phase. Therefore, the electrostatic interactions of PA\textsuperscript{−} and PA\textsuperscript{+} with ILs are the driving forces for extraction of PABA into IL phase. It is remarkable that the extraction of PABA into the studied ILs is in the order of [C\textsubscript{8}mim][BF\textsubscript{4}] > [C\textsubscript{4}mim][PF\textsubscript{6}] > [C\textsubscript{8}mim][PF\textsubscript{6}], which is in agreement with the order of water content of ILs as was mentioned previously. Furthermore, higher ability of BF\textsubscript{4}\textsuperscript{−} than PF\textsubscript{6}\textsuperscript{−} for H-bond formation with –COOH and –NH\textsubscript{2} groups\textsuperscript{35} of PABA could be another reason for higher extraction of PABA into [C\textsubscript{8}mim][BF\textsubscript{4}].

Thus hydrophobicity and electrostatic interactions of solutes with ILs are two driving forces for their partitioning into IL phase. It seems that the effect of hydrophobicity is more significant than that of the electrostatic interactions, because anionic molecule despite of having ability for elec-
trostatic interactions with ILs, is less hydrophobic than a neutral molecule and its extraction into IL phase is lower.

The partitioning behaviors of either glycine (Figure 1) or PABA (Figure 2) were found to follow a similar pattern in all the studied ILs as is demonstrated by their corresponding curves. This indicates that each of the studied ILs can be utilized for investigating the partitioning behavior of a target amphoteric compound such as glycine and PABA in order to specify either its zwitterionic or non-zwitterionic structures.

It is noticeable that according to previous reports, an ion-exchange mechanism could be proposed for extraction of ionic forms of amphoteric compounds into IL phase.30,34 So extracted ionic forms of glycine or PABA into IL phase could be as [RNH₃⁺][BF₄⁻], [RNH₃⁺][PF₆⁻] or [Rmim⁺][CO₃⁻] forms.

4. Conclusion

Partitioning behaviors of glycine and p-amino benzoic acid, as two model substances for amphoteric compounds, into imidazolium-based ILs [C₈mim][BF₄], [C₈mim][PF₆], and [C₈mim][PF₆] was studied. The pH-dependent partition coefficients of both compounds revealed the zwitterionic structures of glycine and non-zwitterionic (neutral) structure of p-amino benzoic acid in their isoelectric points. Specification of zwitterionic or non-zwitterionic structures of amphoteric compounds through their partitioning between water and IL phases was found to be a simple, fast and reliable method in comparison to the past reported procedures.

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6. References

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Povzetek

Študirali smo porazdelitvene koeficienta glicina in p-aminobenzojske kisline, dveh modelnih amfoternih spojin, v ion-
ske tekočine (IL) na osnovi imidazola, to so \([\text{C}_8\text{mim}]\text{[BF}_4]\), \([\text{C}_4\text{mim}]\text{[PF}_6]\), and \([\text{C}_8\text{mim}]\text{[PF}_6]\). Porazdelitveni koeficienti so pokazali, da ima glicin dvoionsko (zwitterionsko) strukturo, medtem ko ima p-aminobenzojska kislina nevtralno (ne-zwitterionsko) strukturo v izoelektrični točki. Pokazali smo, da je določitev dvoionske ali neionske strukture amfoternih snovi na osnovi njihovega porazdeljevanja med vodno in IL fazo, enstavna, hitra in zanesljiva metoda v primerjavi z metodami, o katerih so poročali v pretekosti.

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