

Transfer Free Energies of Peptide Backbone Unit from Water to Aqueous Electrolyte Solutions at 298.15 K

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Transfer free energies (ΔG_{tr}) of amino acids from water to aqueous electrolyte solutions have been determined from the solubility measurements, as a function of salt concentration at 298.15 K under atmospheric pressure. The investigated aqueous systems contain one of the amino acids of zwitterionic glycine peptides: glycine (Gly), diglycine (Gly₂), triglycine (Gly₃), and tetraglycine (Gly₄) and cyclic glycylglycine (c(GG)) with an electrolyte compound of potassium chloride (KCl), potassium bromide (KBr) or potassium acetate (KAc). The solubilities of glycine and diglycine in aqueous solution decrease with increasing the concentration of salts (salting-out effect), whereas those of triglycine and tetraglycine increase with increasing the concentration of salts (salting-in effect). Furthermore, salting-in effect was found in aqueous c(GG)/KBr system, while salting-out effect was observed in aqueous c(GG)/KCl or c(GG)/KAc system. The experimental results were used to estimate the transfer free energies (Δg_{tr}) of the peptide backbone unit ($-\text{CH}_2\text{C}(\text{O})\text{NH}-$) from water to the aqueous electrolyte solutions. We developed a new trail to determine the activity coefficients (γ) for aqueous and aqueous electrolyte solutions using an activity coefficient model, with which the total contribution of transfer free energy between solute and the solvent was calculated. We compared the difference between neglecting and using the activity coefficients term in predicting ΔG_{tr} . Since the transfer free energy contribution is negative, interactions between the ionic salts and the peptide backbone unit of zwitterionic glycine peptides are favorable and thus the ionic salts destabilize these amino acids. It was also found that KBr stabilizes c(GG), whereas KCl and KAc destabilize c(GG). These results provide evidence for the existence of interactions between the amide unit and ionic salts, in aqueous solution, which may be of importance in maintaining protein structure as well as in protein-solute and protein-solvent interactions.