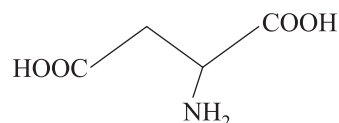


AMINO ACIDS & PEPTIDES

Section - 2

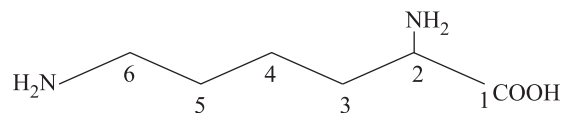
Amino Acids : Amino acids are the bifunctional compounds that contain both a carboxyl group, $-\text{COOH}$, as well as an amine group $-\text{NH}_2$. They are derivatives of carboxylic acids in which one hydrogen atom of carbon chain is substituted by amino group. They are classified as acidic, basic or neutral according to the number of amino and carboxyl groups in a molecule.

1. Acidic Amino acids : These contain a second carboxyl group or a potential carboxyl group in the form of carboxamide.



2-Amino Succinic acid

2. Basic Amino acids : These contain a second basic group which may be an amino group.



2, 6 - Diaminohexanoic acid

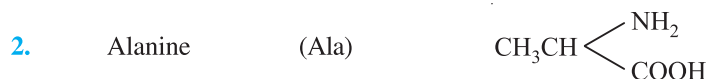
3. Neutral Amino acids : These contain only one amino and one carboxyl group. They are further classified according to the position of amino group in relation of carboxyl group into α -, β -, γ - and δ - amino acids.



Out of these α -amino acids are most important as they are the building blocks of 'bio-proteins'.

Types of α -Amino acids :

(i) **Amino acids with Non-polar side chain :** Examples are :



(ii) Amino acids with Polar but Neutral side chain : Examples are :

1. Serine (Ser) $\text{OH}-\text{CH}_2-\text{CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$
2. Tyrosine (Tyr) $\text{HO}-\text{C}_6\text{H}_4\text{CH}_2-\text{CH}_2-\text{CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$

(iii) Amino acids with Acidic side chains : Examples are :

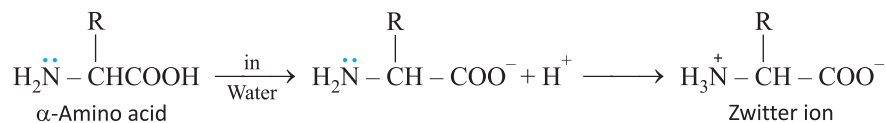
1. Aspartic acid (Asp) $\text{HOOC}-\text{CH}_2-\text{CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$
2. Glutamic acid (Glu) $\text{HOOC}-\text{CH}_2\text{CH}_2\text{CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$

(iv) Amino acids with Basic side chains : Examples are :

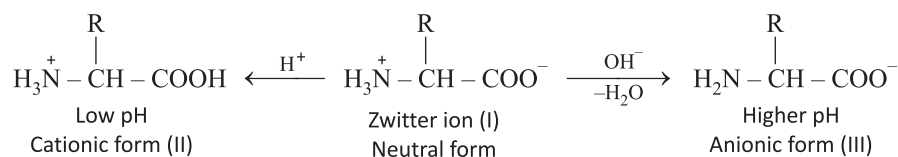
1. Lysine (Lys) $\text{H}_2\text{N}-(\text{CH}_2)_4\text{CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$
2. Arginine (Arg) $\begin{array}{c} \text{HN} \\ \parallel \\ \text{H}_2\text{N}-\text{C}-\text{NH}-(\text{CH}_2)_3\text{CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases} \end{array}$

Properties :

1. They are colourless, crystalline substances having sweet taste. They melt with decomposition at higher temperatures (more than 200°C). They are soluble in water but insoluble in organic solvents.
2. Except glycine, all the α -amino acids are **optically active** and have an **asymmetric** carbon atom (α -carbon atom).
3. Their aqueous solution is neutral and behaves like solutions of substance of high dipole moment.
4. **The Zwitter ion** : Since the $-\text{NH}_2$ group is basic and $-\text{COOH}$ group is acidic, in neutral solution, it exist in an internal ionic form called a Zwitter ion where the proton of $-\text{COOH}$ group is transferred to the $-\text{NH}_2$ group to form inner salt, also known as dipolar ion.



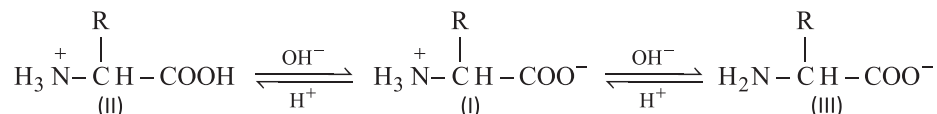
The zwitter ion is dipolar, charged but overall electrically neutral. Therefore, amino acids are amphoteric. Depending on the pH of the solution, the amino acid can donate or accept proton.



5. Iso-Electric point : When an ionized form of amino acid is placed in an electric field, it will migrate towards the opposite electrode. Depending on the pH of the medium, following three things may happen:

- (i) In acidic solution, the positive ion moves towards cathode.
- (ii) In basic solution, the negative ion moves towards anode.
- (iii) The zwitter ion does not move towards any of the electrodes.

The intermediate pH at which the amino acids show no tendency to migrate towards any of the electric field is known as **isoelectric point**.



In other words, the iso-electric point (pI) of the amino acid is the pH at which it has no net charge. It is the pH at which the amount of negative charge on an amino acid exactly balances the amount of positive charge.

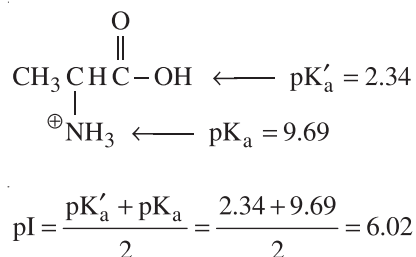
pI = pH at which there is no net charge (pH_i) on the amino acids.

If an amino acid has amino group and one carboxyl group, it has two pK_a values. The isoelectric point (pI) of this amino acid has the average value of both the pK_a value, i.e.,

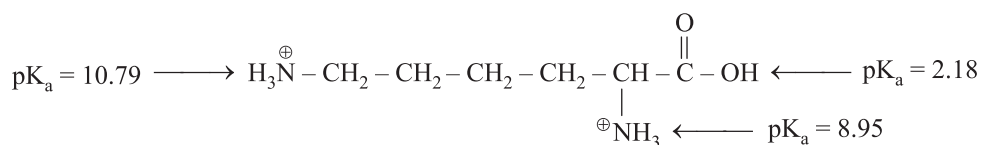
$$\text{pI} = \text{pH}_i = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2}$$

For Example :

If an amino acid does not have an ionisable side chain, its pI value is average of pK_a values of the carboxyl group and the protonated amino group, e.g., *In alanine*,



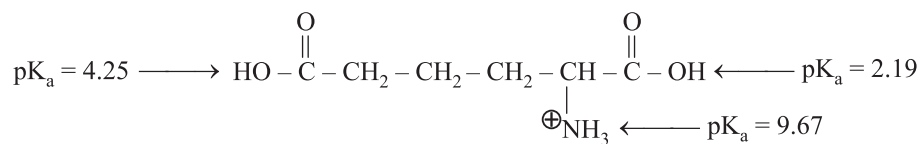
If an amino acid has an ionisable side chain, its pI is the average of the pK_a values of the similarly ionising groups, i.e., positive ionising to neutral and neutral ionising to negative, e.g., *In lysine*,



Ionisable side chain is $-\text{NH}_2$, hence, pI is the average of pK_a value of both $-\text{NH}_3^+$ that change to $-\text{NH}_2$ (by loss of proton).

$$\text{pI} = \frac{8.95 + 10.79}{2} = 9.87$$

In glutamic acid,



Ionisable side chain is $-\text{COOH}$, hence, pI is the average of pK_a of $-\text{COOH}$ group (that remains neutral) and pK_a of other $-\text{COOH}$ group that changes to $-\text{COO}^-$ (by the loss of proton).

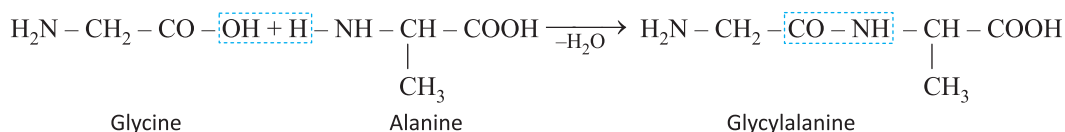
$$\text{pI} = \frac{2.19 + 4.25}{2} = 3.22$$

Note : At iso-electric point, an amino acid has the least solubility in water and hence this property has been used in the separation of different amino acids obtained from the hydrolysis of proteins.

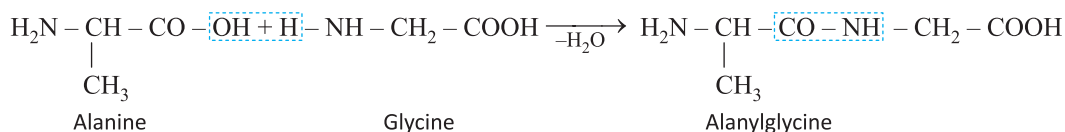
Peptide Bonds :

Peptides are amides formed by the condensation of amino group of one α -amino acid with the carboxyl group of another molecule of same or different α -amino acid with the elimination of a water molecule.

The $\overset{\text{O}}{\parallel}{\text{C}} - \text{NH} -$ bond formed is called the **peptide bond** or the **peptide linkage**. The peptide bond is simply another name for amide bond. Depending upon the number of amino acid residues per molecule, they are known as dipeptides, tripeptides and so on and finally polypeptides, e.g., when $-\text{COOH}$ group of glycine combines with the $-\text{NH}_2$ group of alanine, we get dipeptide, glycylalanine.



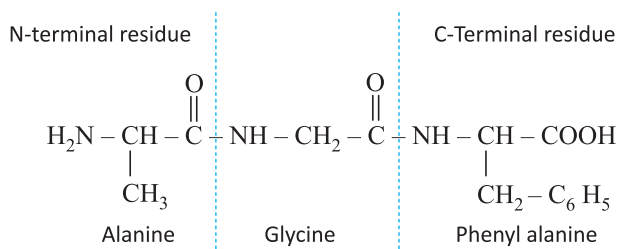
Also, the $-\text{NH}_2$ group of glycine may react with $-\text{COOH}$ group of alanine resulting in the formation of different dipeptide, alanylglycine.



Note : Since the resulting molecule still has a free amino and a carboxyl group, it may react with other amino acids at either ends to give a higher molecular weight linear or condensation product.

Writing Formula and Nomenclature of Polypeptide :

According to conventions, the structures of polypeptides are written in such a way that amino acid with the free amino ($-\text{NH}_2$) group is written on the left hand side of the polypeptide chain while the amino acid with the free carboxyl ($-\text{COOH}$) group is written on the right hand side of the chain. e.g., the tripeptide, alanylglycylphenylalanine is represented as :



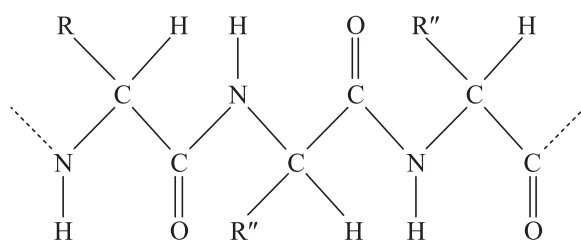
The name of any polypeptide is written from the N-terminal residue. While writing the name, the suffix ine in the name of the amino acid is replaced by yl for all constituent except the C-terminal residue.

Properties :

1. These are amphoteric in nature due to the presence of terminal ammonium and carboxylate ions as well as the ionized side chains of amino acid residues.
2. Like, amino acids, they also neutralise both acids as well as bases and also possess iso-electric point.
3. At isoelectric point, polypeptides have least solubility and hence can be separated.

Structure of Peptides (Proteins) :

Proteins may have one or more polypeptide chains. The **primary structure** of a protein refers to the covalent structure including disulphide bridges of each polypeptide chain. It simply refers to the sequence in which the various amino acids present in a protein are linked to one another.



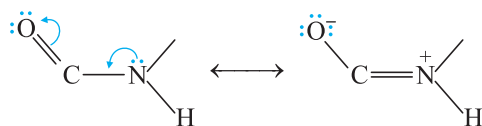
Primary structure of a Protein

The first ever primary structure of a protein i.e. insulin was determined by the British chemist, Frederic Sanger. The different chemical and biological properties of various proteins are primarily due to the differences in their primary structures. A protein containing 100 amino acids is a very small protein, yet 20 different amino acids can be combined at one time in $(20)^{100}$ different ways to give an equal number of proteins each having its own characteristic properties.

The importance of the primary structure of a protein in determining its biological activity is shown by the fact that replacement of just one amino acid in the sequence of a protein destroys its biological activity.

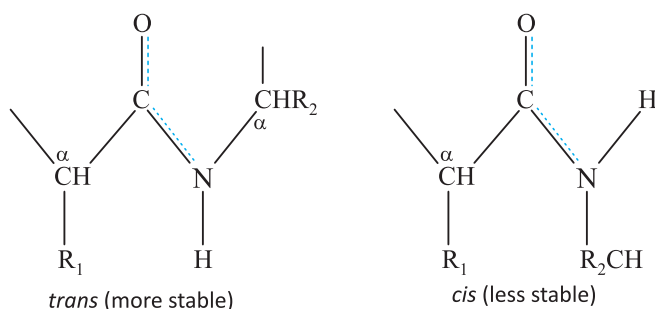
Configuration and conformation of the peptide bond in polypeptides :

The lone pair of electrons on the N-atom in the peptide bond is delocalised over the $>C=O$ group. As a result, carbon-nitrogen bond acquires some double bond character. In other words, the rotation about the $C-N$ bond is hindered and as a result of this hindered rotation, the peptide bond can show **geometrical isomerism**. Further because of much larger steric repulsions between R_1 and R_2 groups, in the cis-isomer, the trans-isomer is more stable.



Resonance Structure of Peptide Bond

Thus, the atoms forming the peptide bond, i.e., CONH group lie in a plane with the O and H atoms in trans-orientation.



POLYMERS

Section - 3

Introduction :

Polymers form the backbone of the modern civilization and are the chief products of the modern chemical industries. Polymers, (Greek poly means many and mer means unit or part), are very high molecular mass compounds, each molecule of which consists a very large number of simple structural units joined together through covalent bonds in regular fashion. The simple molecules from which the repeating structural units are derived are called **monomers** and the process by which these simple molecules, i.e., monomers are converted into polymers is called polymerisation.

Classification of Polymers :

1. Classification of Polymers on the basis of Origin :

(A) Natural Polymers :

They are available in nature (animals or plants). Examples of such polymers are: natural rubber (1,4-cis-polyisoprene), natural silk, cellulose, starch, proteins, etc. Polymers such as polysaccharides (starch, cellulose), proteins and nucleic acids etc., which control various life processes in plants and animals are called **biopolymers**.

(B) Semisynthetic Polymers :

They are chemically modified natural polymers such as hydrogenated, halogenated or hydro-halogenated natural rubber, cellulotics, i.e., esters and ethers of cellulose such as cellulose nitrate, methyl cellulose, etc.