Session #31: Homework Solution

Problem #1

Rank the following amino acids in decreasing order of migration towards the cathode (negative electrode) when separated by electrophoresis in a solution of pH = 7.3.

I. Lysine: pI = 9.87
II. Alanine: pI = 6.02
III. Aspartate: pI = 5.95

Solution

I > II > III

Problem #2

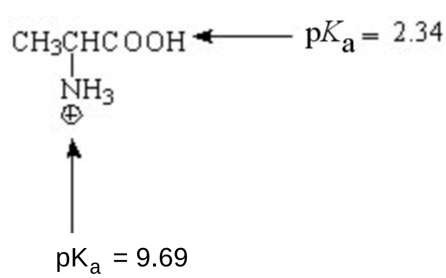
Define what is meant by isoelectric point (pI) and give an example.

Solution

Isoelectric point is the pH of an amino acid at which it has no net electric charge. For amino acids that have no ionizable side chain, the pI value is the average of its two pK_a's. If the amino acid has an ionizable side chain, the pI value is the average of the pK_a's of similarly ionizable groups.

Ex:

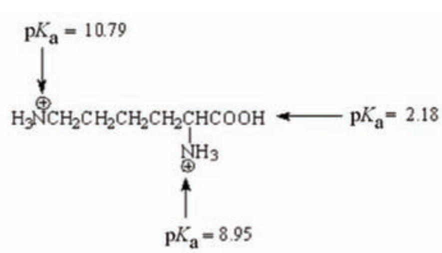
Alanine:



$$pI = \frac{2.34 + 9.69}{2} = 6.02$$

Ex.

Lysine:



Lysine:

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

Problem #3

You are given a mixture that contains glutamic acid (pI = 3.2), arginine (pI = 10.8), and valine (pI = 6.0), and you subject the mixture to electrophoresis.

(a) Which amino acids migrate towards the cathode when the electrophoresis is carried out at a pH of 7.1?

(b) Which amino acids migrate toward the anode when the electrophoresis is carried out at a pH of 7.1?

(c) Which amino acid migrates farthest toward the anode at a pH of 7.1?

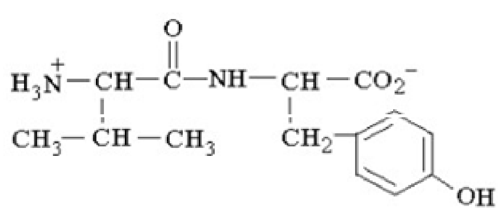
Solution

a) arginine
b) valine and glutamic acid
c) glutamic acid

Problem #4

Draw the dipeptide Val-Tyr at pH 7.0.

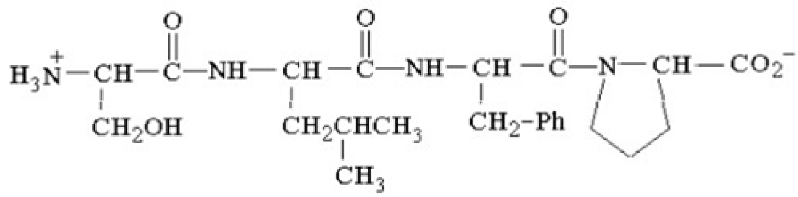
Solution



Problem #5

Draw the structure of the tetrapeptide Ser-Leu-Phe-Pro at pH 7.0.

Solution



Problem #6

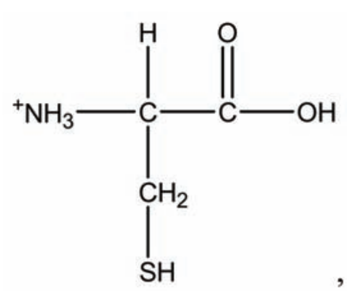
The pKa values for the α-carboxylic acid and the α-amino acid groups is cysteine are 1.092 and 10.78, respectively. The pKa for the titratable −SH side chain in the amino acid is 8.33. Calculate the pI of cysteine.

Solution

The structure of **cysteine** at $pH = 7$ shows that the side group is protonated. So we must conclude that even though the pKa is 8.33, the **sulfhydryl** (−SH) is acting as an acid.

The **isoelectric point**, pI, is the pH at which the **zwitterion** is the dominant species.

Let's start with extreme acid conditions, $pH < 1.96$. Under these circumstances according to the **LeChatelier Principle** the amino acid will be fully protonated in an effort to try to consumer the proton excess in solution. The resulting structure of the amino acid is



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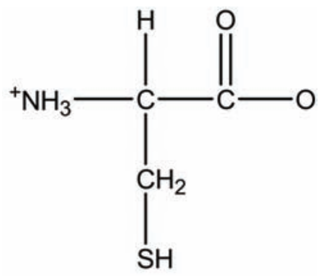
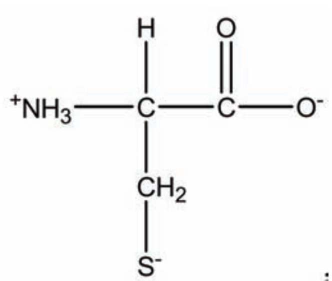
, which is net positive (**cationic**).

In slightly more alkaline solutions, $1.96 < pH < 8.33$, the carboxylic acid sheds its proton in order to neutralize OH^-. The resulting structure of the amino acid is



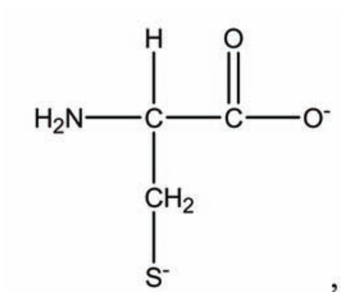
, which is the **zwitterion**. Hence we calculate the value of *pI* to be the average of 1.06 and 8.33 = 5.14.

Just to complete the analysis, consider still greater basicity, 8.33 < *pH* < 10.78. Over this range of composition the resulting structure of the amino acid is



, which is net negative (**anionic**).

Finally, at extreme alkaline conditions, *pH* > 10.78, everything is deprotonated in an effort to neutralize the rising OH^- population. Over this range of composition the resulting structure of the amino acid is



, which is net negative and doubly charged (**anionic**). Also worth mentioning, at neutral *pH*, reduced **sulfhydryls** on two different **cysteine** side groups can be **oxidized** to form **disulfide linkages**.