Chem Factsheet

www.curriculum-press.co.uk Number 171

Zwitterions

First try deciding whether the following statements are true or false.

Statement	True	False
1 Zwitterions are amino acids with one extra hydrogen atom.		
2 Zwitterions are formed by an amino acid gaining a hydrogen ion when dissolved in an acid solution.		
3 Zwitterions have become charged as they have lost a hydrogen ion when an alkali was added to their solution.		
4 Zwitterions can only exist in solution.		
5 A zwitterion has both a positive and a negative charge.		
6 The molecular formula of a zwitterion is the same as that of its amino acid.		

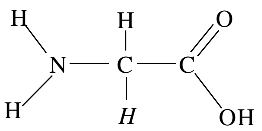
The first four statements are false and are common misconceptions; the last two are true. If you were correct in all your answers you might like to skip to the practice questions at the end and test yourself further.

In order to understand zwitterions, you will first need to know and understand the general formula and some of the chemistry of amino acids.

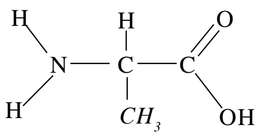
Amino acids are compounds which contain an amino group $–NH_2$ and a carboxylic acid –COOH group. The amino acids which you study are found in biological systems and are the 'building blocks' of proteins. They have the amino group attached to the carbon atom which is next to the –COOH group and so they are called 2-amino acids or α-amino acids.

The terms 2-amino acid and α-amino acid are equivalent and which is used depends on your examining board.

Examples



glycine or 2-aminoethanoic acid (the first in the α-amino acid series)



alanine or 2-aminopropanoic acid (the second in the α-amino acid series)

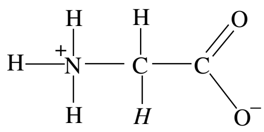
The group shown in *italics* changes as you go along the 2-amino acid series, and in general they are represented by *R*.

*The formation of zwitterions is due to the presence of **$–NH_2$** and **–COOH** groups in the same amino acid compound.*

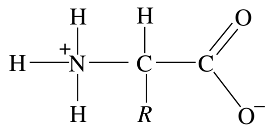
The Formation of Zwitterions

One of the hydrogen atoms of the carboxyl group transfers as a hydrogen ion and attaches itself to the amine group (via its N lone pair), forming $–NH_3^+$ and leaving $–COO^–$. No atoms or ions are lost or gained by the amino acid, the positive hydrogen ion is just transferred from one part of the amino acid to the other, taking with it a positive charge and leaving behind a negative charge.

Zwitterions have no overall charge.



Zwitterion of glycine



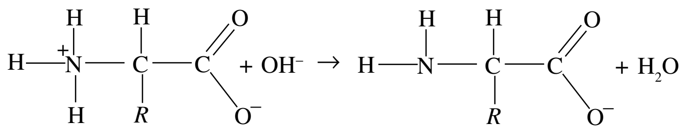
A general Zwitterion

Zwitterions are a form in which amino acids can exist in the solid state and in solution. They have no overall charge. A part of them is always positively charged and a part negatively charged, so that the two opposite charges cancel out. Only the *R* group changes from one amino acid zwitterion to another.

Amino acids crystallise as zwitterions and so they form solids which have high melting points.

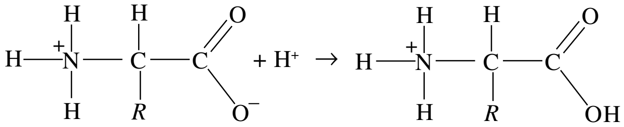
Depending on the pH of their solution, amino acids can also exist as positive or negative ions. They become positive or negative ions by gaining or losing a hydrogen ion.

Beginning with a solution containing zwitterions, if the pH of the solution is increased by adding hydroxide ions, then the hydrogen ion will be removed from the $–NH_3^+$ group and this can be shown by the equation



The ion formed is not a zwitterion, but a negative ion.

If the pH of the solution is decreased by adding an acid to an amino acid solution, the hydrogen ions are taken up by the $–COO^–$ of the zwitterion.



The ion formed is not a zwitterion, but a positive ion.

The positive ion formed has two acidic hydrogens, one of which is in the –COOH group and one of which is in the $-NH_3^+$ group. The hydrogen of the –COOH is more easily lost as it is more acidic and so if an alkali is added this hydrogen is lost first, and the zwitterion is formed again.

> In acidic solution the $-NH_2$ group *ionises* as $-NH_3^+$.
> In alkaline solution the –COOH group *ionises* as $-COO^-$.
> At some intermediate pH value, the zwitterion $H_3N^+CH(R)CO_2^-$ exists.

Electrophoresis can be used to study this. A filter paper which has been moistened with water is placed on a microscope slide and each end of the filter paper attached to the opposite terminals of a battery. A drop of the amino acid solution is then placed in the centre of the filter paper. The zwitterion will *not* move as the forces due to the positive and negative parts cancel out. However, positive ions will move towards the negative electrode and the negative ions towards the positive electrode.

The position of the amino acid can be found by detaching the electrodes, spraying the filter paper with a solution of ninhydrin, allowing it to dry and then heating it. The amino acid then appears as a blue/purple coloured spot on the filter paper.

The pH at which there is no movement during electrophoresis is known as the *isoelectric point* of the amino acid. It is slightly different for each amino acid, due to the different effects of the R group.

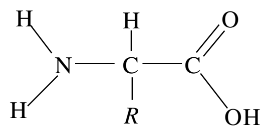
> *An amino acid exists as a zwitterion at a pH value called the isoelectric point. Different R groups in α-amino acids result in different isoelectric points. It can be used to identify particular amino acids.*

The R group of an amino acid may contain either a –COOH group or an $-NH_2$ group, and then the isoelectric point will be very different from the isoelectric points of the other amino acids (of about pH=6 to pH=7). For example glutamic acid (isoelectric point at pH = 3.2) has the R group $(CH_2)_2COOH$ and so can form a doubly negatively charged ion, whereas lysine (isoelectric point at pH = 9.7) has the R group $(CH_2)_4NH_2$ and so can form a doubly positively charged ion. For questions involving isoelectric points all the values will be given to you (so you do not need to learn them).

Practice Questions

1. (a) Explain why the solid form of the amino acid glycine is crystalline. (3 marks)
   (b) Why is glycine soluble in water? (2 marks)

2. The general structure of a 2-aminocarboxylic acids is shown below (where R represents different possible side chains). Re-draw the structure to show the main form in which this general amino acid would exist when in solution at pH7 (given that R is non-polar).



(3 marks)

3. An amino acid is in aqueous solution at pH7 and R is non-polar. What is the overall charge of this amino acid? (1 mark)

4. What feature of an amine group results in it being able to accept an H^+ ion under certain conditions? (1 mark)

5. An amino acid is in zwitterionic form in a neutral solution. State and explain the effect on the zwitterions of adding hydroxide ions (alkali) to this solution. (2 marks)

6. State and explain the effect of decreasing the pH of an amino acid solution which consists of zwitterions. (2 marks)
   Give the general structural formula of the resulting species. (2 marks)

7. Amino acids may be described as having an amphoteric character. Explain this. (2 marks)

8. Amino acids are organic compounds which are in general less soluble in organic solvents than in water. Explain this. (2 marks)

9. Given that the R group for the α-amino acid alanine is CH_3 and its isoelectric point is pH = 6, draw and explain the structure of the ion formed at pH = 6.0 (2 marks)

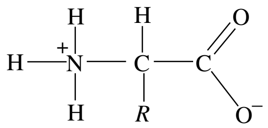
10. The isoelectric point for glutamic acid is pH = 3.2 and it has the R group $(CH_2)_2COOH$, draw the structure of the ion formed at pH = 9.0 (2 marks)

11. The isoelectric point for lysine is pH = 9.7, explain and draw the structure of the ion formed at pH = 1.5. [R group is $(CH_2)_4NH_2$] (3 marks)

Answers

1. (a) In the solid form glycine exists as zwitterions. (1 mark)
This results in it being like an ionic solid. (1 mark)
It has a high melting point due to the strong electrostaticforces holding the lattice together. (1 mark)
(b) The amine group and carboxylic acid group are polar. (1 mark)
This means that the amino acid molecules can interact with the water molecules through hydrogen bonding. (1 mark)

2.



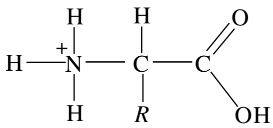
1 mark for correct structure
1 mark for correct charge on correct oxygen
1 mark for correct charge on nitrogen

3. Zero (– it will exist as the zwitterion).

4. The amine group has a lone pair of electrons on the nitrogen atom. (1 mark)

5. A negative ion is formed. (1 mark)
A hydrogen ion is removed from the $–NH_3^+$ group of the zwitterions by the hydroxide ions to form water. (The COO^- group remains.) (1 mark)

6. The zwitterions become positive ions (1 mark)
because the $–COO^-$ part of the zwitterion gains a hydrogen ion from the acidic solution. (the NH_3^+ group remains.) (1 mark)

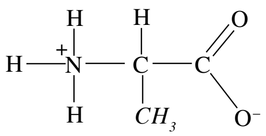


1 mark for correct structure
1 mark for correct charge

7. They react with both acid and alkali. In acid solution both the amine and carboxyl functional groups are mainly protonated (1 mark) whereas in alkaline solution the reverse occurs and they exist as $–NH_2$ and $–COO^-$. (1 mark)

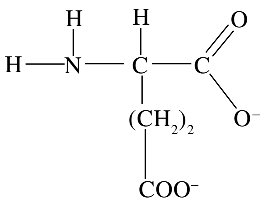
8. Their zwitterionic structure (1 mark) means that they can form hydrogen bonds with water molecules and with themselves. Organic solvents in general will not form hydrogen bonds. (1 mark)

9. Alanine is in solution at its isoelectric point and so will exist in the zwitterionic form.



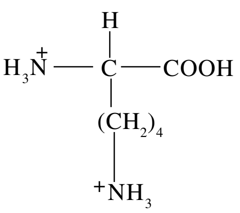
(1 mark for structure ; 1 mark for correct charges)

10. Glutamic acid is in solution at a higher pH than its isoelectric point and so will exist as a negative ion. It has two –COOH groups so both will form $–COO^-$.



Glutamic acid pH =9
Isoelectric point pH =3.2
1 mark for structure ; 1 mark for charges

11. Lysine is in solution at a lower pH that its isoelectric point and so will exist as a positive ion. It has two $–NH_2$ groups and so both will become $–^+NH_3$. (1mark)



Lysine at pH = 1.5
Isoelectric point pH = 9.7
1 mark for correct charges ; 1 mark for correct structure

Acknowledgements: *This Factsheet was researched and written by Christine Collier.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ISSN 1351-5136***