18.2 Amines, amides, amino acids and proteins

Answers to Exam practice questions

Pages 255–258

1 **a)** D **b)** C **c)** E **d)** B **e)** A **f)** D [1] for each

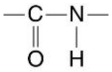
2 **a)** Proton acceptor [1] lone pair which can be donated. [1]

b) $(CH_3CH_2CH_2CH_2NH_3^+)_2\ SO_4^{2-}$ [1]

c) Bases are lone pair donors. [1] Inductive effect of alkyl group increases electron density on N in butylamine so better lone pair donor. [1] Lone pair is delocalised into aromatic ring in phenylamine so poorer lone pair donor. [1]

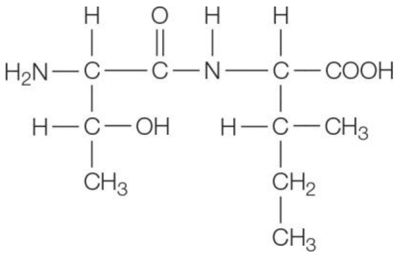
d) Deep blue solution [1]; acts as a ligand [1]; $[Cu(C_4H_9NH_2)_4(H_2O)_2]^{2+}$(aq). [1]

3 **a)** **i)** Insertion of



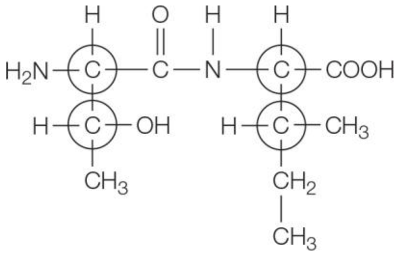
$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$

to give:



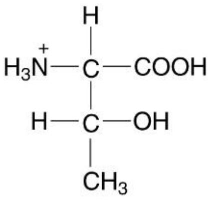
[2] (wrong way around gets [1])

ii) All four chiral centres circled [3]; three chiral centres circled [2]; two chiral centres circled [1].

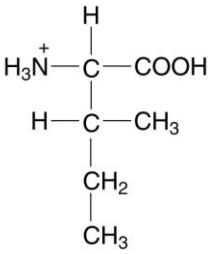


b) The compound has at least one carbon atom with four different atoms or groups attached to it. [1] Molecules of the compound are asymmetric. [1] The compound has optical isomers. [1]

c)



[1]



[1]

4 **a)** The $-NH_2$ group in amino acids can act as a base accepting H^+ ions and the $-COOH$ group can act as an acid, donating H^+ ions. [1] Therefore, in solution, amino acids, like glycine, can exist as zwitterions such as $H_3{}^+N{-}CH_2{-}COO^-(aq)$. [1]

At one particular pH, the glycine particles will form zwitterions with an overall net charge of zero and this pH is the isoelectric point of the amino acid. [1]

b) The isoelectric point of the amino acid will be dictated by the relative abilities of the $-COOH$ group to donate H^+ ions and the $-NH_2$ group to accept them. [1] These relative abilities are not equal, so the isoelectric point is not at pH = 7. [1]

As the isoelectric point of glycine is at pH = 6; this suggests that the $-COOH$ group loses H^+ ions to form $-COO^-$ ions more readily than the $-NH_2$ group accepts them to form $-NH_3{}^+$ ions. [1]

However, at pH = 6 (i.e. $[H^+] > [OH^-]$), the dissociation of $-COOH$ is suppressed and the acquisition of H^+ by $-NH_2$ is raised so that the two processes are equally likely. [1] At this pH, the zwitterions are most stable and the average net charge on glycine particles is zero. [1]

c) Glutamic acid has two $-COOH$ groups and only one $-NH_2$ group. This will mean that $-COO^-$ anions form more readily than $-NH_3{}^+$ cations. [1] In order to suppress the formation of $-COO^-$ groups and promote the formation of $-NH_3{}^+$ groups relative to the glycine situation, the pH must be more acidic. [1] Therefore, the isoelectric point of glutamic acid will be less than pH = 6. [1]

5 **a)** **i)** $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$ [1]

Note that the HBr formed will react with NH_3 to form the salt NH_4Br, so strictly the equation should be:

$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$

ii) Nucleophilic substitution [1]

iii) $(CH_3CH_2)_2NH$ and $(CH_3CH_2)_3N$ [2]

iv) The ethylamine which forms is a better nucleophile than ammonia [1] and may react with any unreacted bromoethane forming diethylamine. [1]

$CH_3CH_2Br + CH_3CH_2NH_2 \rightarrow \underset{\text{diethylamine}}{(CH_3CH_2)_2NH} + HBr$

The diethylamine can also react as a nucleophile [1] with any excess bromoethane to form triethylamine.

$CH_3CH_2Br + (CH_3CH_2)_2NH \rightarrow \underset{\text{triethylamine}}{(CH_3CH_2)_3N} + HBr$

Note that the HBr formed in each of these reactions will react with the amines in the reaction mixture to form substituted ammonium salts.

b) Ethylamine vapour and hydrogen chloride gas will diffuse away from the cotton wool plugs along the tube [1]. The relative molecular mass of HCl (M_r = 36.5) is marginally less than that of ethylamine (M_r = 45.0) so it will diffuse slightly faster along the tube. [1]

When the vapours meet (approximately midway along the tube, but slightly closer to the ethylamine end [1]), a white smoke will form, eventually settling on the bottom of the tube as a white powder [1]. This is ethylammonium chloride.

$CH_3CH_2NH_2(g) + HCl(g) \rightarrow CH_3CH_2NH_3^+Cl^-(s)$ [1]

6 **a)** **i)** Fishy smell [1]

ii) 1,5-Diaminopentane [1]

iii) $Cl^- \, ^+H_3N{-}CH_2CH_2CH_2CH_2CH_2NH_3^+Cl^-$ [1]

iv) $NH_4^+Cl^-$ [1]; ammonium chloride [1]

v) NaCl [1]; H_2O [1]

b) **i)** Primary amines have one alkyl or aryl group attached to an NH_2 group. [1]

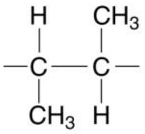
Secondary amines have two alkyl or aryl groups attached to an N–H group. [1]

Tertiary amines have three alkyl or aryl groups attached to a nitrogen atom. [1]

ii) Cadaverine is a primary amine [1]; piperidine is a secondary amine. [1]

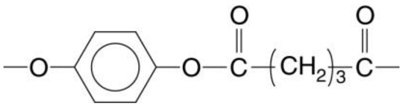
c) Their infrared spectra will be very similar [1]; because they have exactly the same types of bonds. [1]

7 **a)**



$-\mathrm{CH(CH_3)}-\mathrm{CH(CH_3)}-$

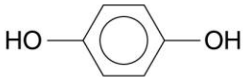
[1]



[1]

b) $CH_3CH{=}CHCH_3$ [1]; but-2-ene [1]

c) **i)**

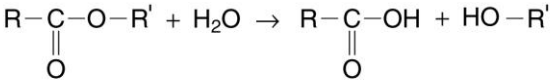


and $HOOC(CH_2)_3COOH$

[1] [1]

ii) 1,4-Dihydroxybenzene (4-hydroxyphenol) or pentanedioic acid [1]

d) Ester links in the condensation polymer can be hydrolysed by water [1]; and this process will be catalysed if the conditions are acidic or alkaline. [1]



$$R-\underset{\underset{O}{\|}}{C}-O-R' + H_2O \rightarrow R-\underset{\underset{O}{\|}}{C}-OH + HO-R'$$ [1]

The C–C and C–H bonds in polymer A are strong and non-polar, so are not degraded by sunlight, water, acids, alkalis or microorganisms. [1]

8 a) i) Mass C : H : N = 61.0 : 15.3 : 23.7 [1]

$$\text{Moles C : H : N} = \frac{61.0}{12.0} : \frac{15.3}{1.0} : \frac{23.7}{14.0}$$

= 5.08 : 15.30 : 1.69 [1]

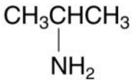
= 3 : 9 : 1 [1]

Empirical formula = C_3H_9N

ii) Its relative molecular mass (or molar mass). [1]

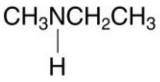
iii) $CH_3CH_2CH_2NH_2$

propylamine



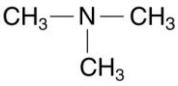
$$CH_3\underset{\underset{NH_2}{|}}{C}HCH_3$$

2-aminopropane



$$CH_3\underset{\underset{H}{|}}{N}CH_2CH_3$$

ethylmethylamine



$$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$$

trimethylamine

[1] for each.

b) The alkyl groups provide an inductive effect towards the nitrogen atom. This increases the electron density on the nitrogen atom and also its basic character. [1]

Therefore, the predicted order of basic strength from the strongest to the weakest should be: trimethylamine (3 alkyl groups) > ethylmethylamine and 2-aminopropane (2 alkyl groups) > propylamine (1 alkyl group). [1]

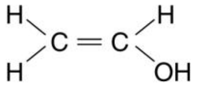
c) In water, the amines are protonated by the water:

$R_2NH + H_2O \rightleftharpoons R_2NH_2^+ + OH^-$

$R_3N + H_2O \rightleftharpoons R_3NH^+ + OH^-$ (Both equations needed for [1].)

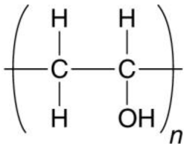
Because of the extra N–H bonds in the protonated secondary amines there is more hydrogen bonding possible. [1] This stabilises these ions more than the equivalent R_3NH^+. [1]

9 a) i)



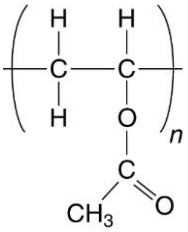
ethenol [1]

,



repeat unit [1]

ii)



[1]

iii) Relative mass of one poly(ethenol) unit = 44.0 [1]

Relative mass of one poly(ethenyl ethanoate) unit = 86.0 [1]

Relative molecular mass of polymer

= relative mass of 1800 poly(ethenol) units

+ relative mass of 200 poly(ethenyl ethanoate) units

$= (1800 \times 44.0) + (200 \times 86.0)$ [1]

$= 79\,200 + 17\,200 = 96\,400$ [1]

iv) Almost every monomer unit contains an –OH group which can hydrogen bond with water. [1] The extensive hydration of the –OH groups by water molecules results in a soluble polymer. [1]

b) i) Because there are fewer –OH groups on the polymer which can form hydrogen bonds with water molecules. [1] (Water molecules can, of course, still form hydrogen bonds with the O atoms in the C=O bonds of the ethanoate groups, but the larger size of the ethanoate group relative to the –OH group will reduce its solubility.)

ii) Because the –OH groups on the poly(ethenol) molecules will form hydrogen bonds with each other rather than with water molecules. [1]

iii) The poly(ethenol) forms a crystalline solid in which extensive hydrogen bonding between –OH groups along the polymer chain holds the molecule firmly together. [1] Few, if any, –OH bonds are available for hydrogen bonding with water and the poly(ethenol) is insoluble. [1]

(Allow credit for any sensible suggestions.)

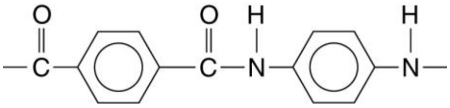
10 a) i) Induced dipole attractions [1]

ii) Low density polythene has short side chains attached to the main C–C chain. [1] This means that its molecules cannot pack as closely as those in high density polythene. [1]

iii) High density polythene has the higher melting temperature. [1] Molecules in high density polythene can pack closer than those in low density polythene. [1] This results in more and stronger induced dipole attractions. More energy is therefore needed to overcome the stronger forces in high density polythene, [1] so its melting temperature is higher.

b) i) A polyamide is a polymer with amide links between monomer units. [1]

ii)



[1]

iii) Hydrogen bonds [1]

iv) Hydrogen bonds between the H atom of an N–H group on one chain and the N atom on another chain. [1]

Hydrogen bonds between the H atom of an N–H group and the O atom of a C=O group on another chain. [1]

c) i) In the crystalline regions, the chains of different molecules are packed in a regular, parallel fashion, but in the non-crystalline regions, the molecules are more randomly placed. [1]

ii) In the crystalline regions, more hydrogen bonds can form between the parallel chains making the total intermolecular forces stronger. [1]

11 a) To prevent loss of nitrobenzene if the flask gets hot. [1]

b) The reaction is too slow if the temperature is too low. [1]

c) To allow unreacted nitrobenzene to evaporate. [1]

d) To neutralise the HCl so oily phenylamine forms from the water-soluble salt. [1]

To convert the tin compounds into soluble hydroxy complex ions. [1]

e) To saturate the aqueous layer and reduce the solubility of phenylamine in the water. [1]

f) Although the densities are similar, the salt increases the density of water so the phenylamine floats [1]; it is the upper layer. [1]

g) To absorb water. [1] (Other drying agents react with the phenylamine.)

h) 4.2 cm^3 nitrobenzene have mass 4.2 × 1.20 = 5.04 g [1]

Amount nitrobenzene = $\frac{5.04}{123.0}$ mol = amount phenylamine [1]

Max. mass phenylamine expected = $\frac{5.04}{123.0} \times 93.0 = 3.81$ g [1]

i) $C_6H_5NO_2(aq) + 7H^+(aq) + 6e^- \rightarrow C_6H_5NH_3^+(aq) + 2H_2O(l)$ [1]

$Sn(s) + 6Cl^-(aq) \rightarrow [SnCl_6]^{2-}(aq) + 4e^-$ [1]

$2C_6H_5NO_2(aq) + 14H^+(aq) + 3Sn(s) + 18Cl^-(aq) \rightarrow 2C_6H_5NH_3^+(aq) + 3[SnCl_6]^{2-}(aq) + 4H_2O(l)$ [1]

12 This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully sustained line of reasoning. Assess the quality of the answer taking into account both the key points made (*up to 4 marks*) and the logic and coherence of the discussion (*up to 2 marks*).

Points to make in the answer:

- C=O bond in ethanamide.
- Lone pair on N in propylamine accepts protons, so is basic.
- C=O withdraws electrons from lone pair on N, therefore ethanamide is not basic.
- Hydrogen bonding in propylamine, therefore liquid at room temperature.
- Delocalisation of lone pair from N onto C=O …
- … leads to a separation of charge and therefore stronger electrostatic forces in ethanamide.