LEBANESE UNIVERSITY
FACULTY OF ENGINEERING

الجامعة اللبنانية
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Entrance Exam 2006-2007 **CHEMISTRY** **Duration: 1 h**

First Exercise
Identification and Synthesis of an Ester

The hydrolysis of an ester (E) gives an acid (A) of formula R – COOH and an alcohol (B) of formula R´ - OH.

Given:

- R and R´ are two alkyl groups.
- Molar mass in $g.mol^{-1}$: $M_{(H)} = 1$; $M_{(C)} = 12$; $M_{(O)} = 16$; $M_{(R'-OH)} = 60$.

I- Determination of the formula of (E)

1- Write the formula of (E) in terms of R and R´.
2- Show that the formula of (E) is $C_xH_{2x}O_2$.
3- Determine the molecular formula of (E) knowing that the percentage by mass of oxygen, in this compound, is equal to 31.37 %.
4- Determine the molecular formula of (B), write the condensed structural formula and give the name of (B), knowing that it is a primary alcohol.
5- Deduce the molecular formula of (A).
6- Write the condensed structural formula of (E) and give its name.

II- A Synthesis Reaction of (E)

A mixture of 1 mol of (A) and 2 mol of (B) is carried out. A homogenous equilibrium is established when this mixture is maintained at a constant temperature of 100 ºC,

1- Write, using the condensed structural formulas, the equation of the esterification reaction.
2- Give two characteristics of this reaction.
3- Determine the composition, in moles, of the mixture at equilibrium knowing that the equilibrium constant is $K_c = 4$.

Second Exercise
Evolution of The pH during a Titration

Using a buret, a volume V_B of sodium hydroxide solution ($Na^+ + HO^-$) of concentration $C_B = 1 \times 10^{-2} mol.L^{-1}$ is progressively added into a volume V_A = 20 mL of ethanoic acid solution, CH_3COOH, of concentration $C_A = 1.2 \times 10^{-2}$ mol.L^{-1}.

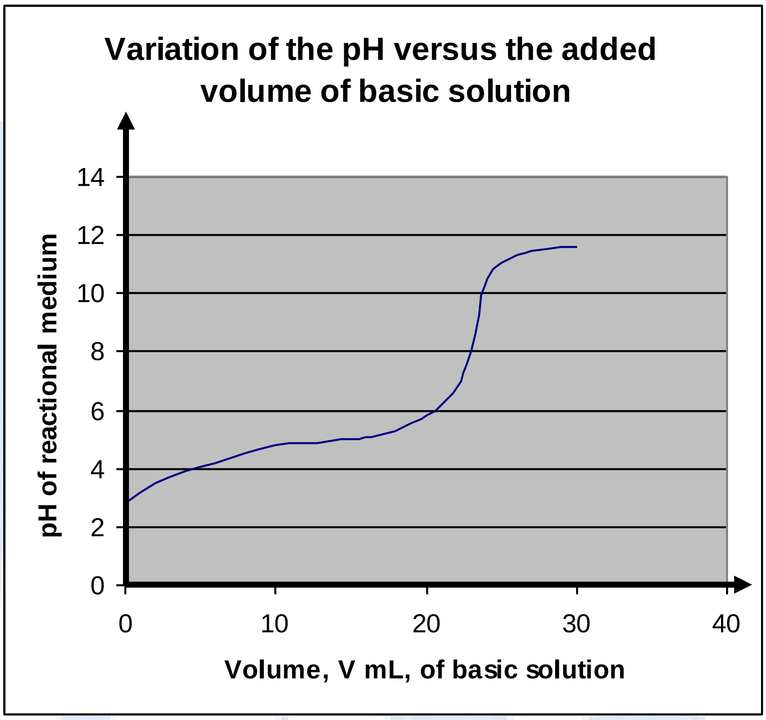
Given: $pK_A(CH_3COOH/CH_3COO^-) = 4.80$; $pK_A(H_2O/HO^-) = 14,0$

I- Study of the Equivalence

1- Write the equation of the titration reaction.
2- Determine the needed volume of sodium hydroxide solution to reach the equivalence point.
3- Specify the acid-base nature at the equivalence.

II- Evolution of pH during titration

1- Show that the pH, before the equivalence point, is given by the relation:
$pH = 4.8 + \log \frac{V_B}{V_{BE} - V_B}$ and after the equivalence it is given by the relation:
$pH = 14 + \log \frac{C_B(V_B - V_{BE})}{V_A + V_B}$.
2- The experimental results permit to plot the following curve:



By using the graph:

a) Determine the concentration of ethanoic acid solution and compare the obtained value with that indicated in the beginning of the exercise.

b) Verify the value of $pK_A(CH_3COOH/CH_3COO^-)$.

Entrance Exam 2006-2007 **Solution of Chemistry** **Duration: 1 h**

First Exercise
Identification and Synthesis of an Ester

I- Determination of the formula of (E)

1- R – COOH acid ; R´– OH alcohol

R – COOR´ This is the formula of the resulting ester (E)

2- R et R´ are two alkyl groups
Formula of R : C_nH_{2n+1} Formula of R´ : $C_{n'}H_{2n'+1}$
The formula of (E) is $C_nH_{2n+1}COOC_{n'}H_{2n'+1}$
x= n+ n´+1 and 2x = 2n+1+2 n´+1 = 2(n+ n´+1) then the formula is : $C_xH_{2x}O_2$

3- M_E (12x+2x+32) g.mol^{-1}
According to the law of defined proportions we can write;
$\frac{12x}{m_C} = \frac{2x}{m_H} = \frac{2\times16}{31{,}37} = \frac{12x+2x+32}{100}$, $x=5$ the molecular formula of (E) is $C_5H_{10}O_2$

4- M(B) = 60 g.mol^{-1}
M´=14 n´+18= 60 $\Rightarrow$ n´=3 . The molecular formula of (B) is C_3H_7OH
– CH_2OH characterizes any primary alcohol:
The formula $CH_3 – CH_2 – CH_2OH$: 1-propan *ol*

5- Ester (E) $C_5H_{10}O_2$
$C_nH_{2n+1}–\underset{\underset{O}{\|}}{C}– O – C_{n'}H_{2n'+1}$ $\Rightarrow$ from alcohol (B)
$CH_3–CH_2–CH_2OH$
from acid (A)

$C_xH_{2x}O_2$: x = 5 = n+ n´+1 , according to the formula of alcohol (B)
n´= 3
x = 5 = n+3 + 1 give n = 1
The molecular formula of (A) is CH_3COOH

6- n = 1 and n´= 3, the condensed structural formula of (E) in 5
by replacing n by 1 and n´ by 3

(E) : $CH_3 – \underset{\underset{O}{\|}}{C} – O – CH_2–CH_2–CH_3$ is name: propyl ethanoate

II- A Synthesis Reaction of (E)

$$CH_3-\underset{\underset{O}{\|}}{C}-OH + CH_3-CH_2-CH_2OH \Leftrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-CH_3 + H_2O$$

1- * Partial
   * Athermic

2- Let x be the number of mole of (A) that has reacted.

	(A): CH_3COOH	(B): C_3H_7OH	(E): $C_5H_{10}O_2$	(A): H_2O
initial state (mol)	1	2	0	0
final state (mol)	1-x	2-x	x	x
[ ]	1-x / v	2-x / v	x / V	x / V

V_L mixture of volume reaction

Or, $K_c = \dfrac{[H_2O]\times[C_5H_{10}O_2]}{[CH_3COOH]\times[C_3H_7OH]}$

$$K_c = \frac{\frac{x}{V}\times\frac{x}{V}}{\frac{1-x}{V}\times\frac{2-x}{V}} = \frac{x^2}{(1-x)(2-x)} = 4$$

$x^2 = 4(1-x)(2-x) = 4(x^2 - 3x + 2)$, or $3x^2 - 12x + 8 = 0$

$\Delta' = 36 - 24 = 12$,

$x = \dfrac{6+\sqrt{2}}{3} = 3{,}5 > 1$ then this is to be rejected because the number of moles (A) will be negative or $x = \dfrac{6-\sqrt{2}}{3} = 0{,}85$

The composition of he mixture at equilibrium is
(A) : $1-x = 0{,}15$ mol, (B) : $2-x = 1{,}15$ mol and (E) : $x = 0{,}85$ mol
and water $x = 0{,}85$ mol

Second Exercise
Evolution of The pH during a Titration

I- Study of the Equivalence

1- pK_A (CH_3COOH / CH_3COO^-) = 4,8 and pK_A (H_2O / HO^-) = 14
Due to the difference between the pK_A values, the reaction that will be produced between the strongest acid in the (CH_3COOH) and the strongest base (HO^-) is almost complete.
$CH_3COOH + OH^- \Rightarrow CH_3COO^- + H_2O$

2- At equivalence : we have $C_AV_A = C_BV_B$

$$V_{BE} = \frac{C_AV_A}{C_B} = \frac{1{,}2\times10^{-2}\times20.10^{-3}}{10^{-2}} = 24.10^{-3}L$$, then V_{BE} = 24mL

3- At the equivalence point of (E), the reactants HO^- and CH_3COOH have disappeared because the reaction is almost complete. The solution contains CH_3COONa in the ionic state
$CH_3COO^- + Na^+$
CH_3COO^- is a weak base.
Na^+ neutral ion, the solution at equivalence has a basic nature.

II- Evolution of pH during titration

1) pH= 4,8+log $\frac{V_B}{V_{BE}-V_B}$

	CH_3COOH	OH^-	CH_3COO^-	H_2O
The Mixture quantities	C_AV_A	C_BV_B	0	0
The remaining quantities	C_AV_A - C_BV_B	0	C_BV_B	C_BV_B

V_B is the volume of soud poured < V_{BE} , The number of mole of HO^- introduced will be C_BV_B

$$pH = pK_A + \log\frac{CH3COO-}{CH3COOH} = pK_A + \log\frac{C_BV_B}{C_AV_A - C_BV_B}$$

$$pH = pK_A + \log\frac{C_BV_B}{C_BV_{BE} - C_BV_B} = 4{,}8 + \log\frac{V_B}{V_{BE}-V_B}$$

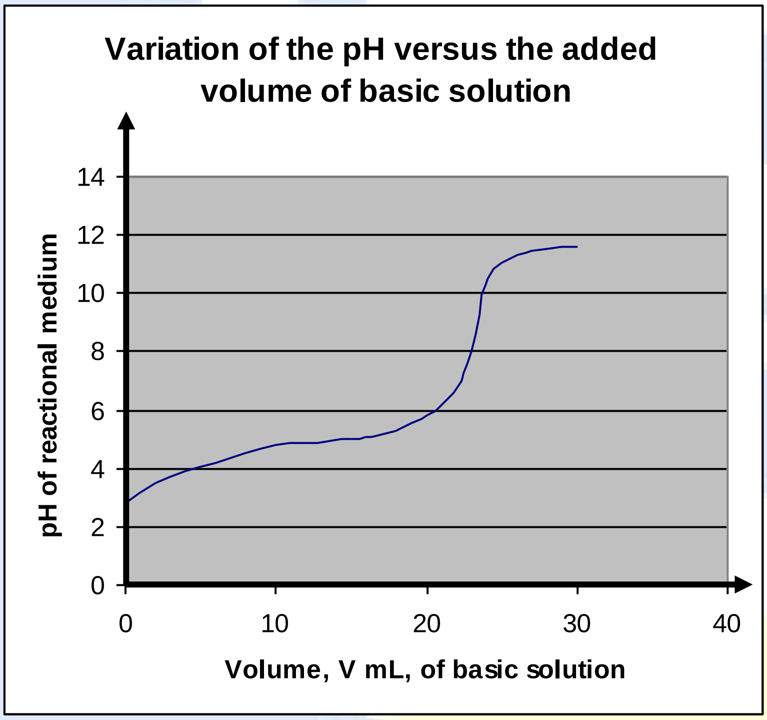
- After equivalence : pH= 14+log $\frac{C_B(C_B - C_{BE})}{V_A+V_B}$

- After equivalence, there remains only CH_3COO^- and as a result, the acid / base couple will be (H_2O / HO^-) of water. The number of mole HO^- which remains, will be
  $C_BV_B - C_AV_A = C_BV_B - C_BV_{BE} = C_B(V_B - V_{BE})$
  The total volume is then $V_A + V_B$

$[HO^-] = \dfrac{C_B(V_B - V_{BE})}{V_A + V_B}$ and $[H_3O+] = \dfrac{K_e}{[HO^-]}$

$pH = -\log [H_3O+] = -\log K_e + \log [HO^-] = 14 + \log \dfrac{C_B(V_B - V_{BE})}{V_A + V_B}$

2)



a- The equivalence point is determined graphically by the parallel tangents method.

$C_A = \dfrac{C_BV_{BE}}{V_A} = \dfrac{10^{-2} \times 24}{20} = 1.2\ 10^{-2}$ mol.L^{-1}

b- The value of pKA is indeed the value of pH at half-equivalence, when the volume poured is 12 mL. According to the graph $pK_A = 4,8$