## Practical Work No. 1: <br> pH-metric dosage (Dosage of a weak acid with a strong base)

## 1-Reminder:

- The self-containment of water and pH : It results in the following equilibrium:

$$
2 \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}
$$

- The law of mass action: $\mathrm{K}_{\mathrm{c}}(\mathrm{T})=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{c}}\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}=\mathrm{K}_{\mathrm{e}} / \mathrm{K}_{\mathrm{e}}$ : The ionic product of water.
At $25^{\circ} \mathrm{C}:\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14} \mathrm{~mol} . \mathrm{l}^{-1}$
$>$ The medium is acidic: $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>10^{-7}$ mol. $\mathrm{l}^{-1}$
$>$ The medium is neutral: $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-7} \mathrm{~mol} . \mathrm{l}^{-1}$
$>$ The medium is basic: $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]<10^{-7}$ mol. $\mathrm{l}^{-1}$
The concentration limit between an acidic medium and a basic medium is anextremely small number $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-7}=0.0000001 \mathrm{mol}. \mathrm{l}^{-1}$

Generally speaking, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is expressed by negative powers of 10 , such numbers are notconvenient \& handle. They should be transformed using a mathematical operation that simplifies writing. Each concentration is characterized by its negative decimal logarithm (cologarithm $=1 / \log$ ).

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We pose: \(\quad \mathrm{pH}=\operatorname{colog}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\)
    \(\mathrm{pOH}=\operatorname{colog}\left[\mathrm{OH}^{-}\right]=-\log \left[\mathrm{OH}^{-}\right]\)
    \(\mathrm{pK}=\operatorname{cologt} \mathrm{K}=-\log \mathrm{K}\)
Example: \(\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{x}} \mathrm{mol} / \mathrm{l} \Rightarrow \log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\log 10^{-\mathrm{x}}=10^{-\mathrm{pH}} \Rightarrow \mathrm{pH}=\mathrm{x}(\mathrm{x}>0)\)
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## - pH of a strong monoacid:

A concentration $\mathrm{C}_{\mathrm{a}}$ of strong acid HA is introduced into the water.
The dissociation is total: $\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-}$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\log \mathrm{C}_{\mathrm{a}}
$$

## - pH of a weak monoacid:

This time the dissociation reactions are equilibrium: $\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}$
Three equations will allow us to calculate the pH :

- Law of mass action: $K=\frac{\left[\mathrm{H}_{2} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]\left[\mathrm{H}_{2} \mathrm{O}\right]} \quad \Rightarrow \quad \mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{2} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
- Electrical neutrality of the solution: In dissociation forms as many positive charges as charges negative. Neglecting the self-ionization of water, we have $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{A}^{-}\right]$
- Conservation of A during the dissociation: $\mathrm{C}_{\mathrm{a}}=[\mathrm{HA}]+\left[\mathrm{A}^{-}\right]$.

Equation (3) simplifies. In fact, the weak acid is very little dissociated. We neglect [ $\mathrm{A}^{-}$] in front of [HA].
We obtain the equation: $\mathrm{C}_{\mathrm{a}}=[\mathrm{HA}]$
We enter into equation (1) the results (2) and (4)
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{2} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{\mathrm{C}_{\mathrm{a}}} \Rightarrow\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left(\mathrm{K}_{\mathrm{a}} \mathrm{C}_{\mathrm{a}}\right)^{1 / 2} \Rightarrow-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 / 2\left(-\log \mathrm{K}_{\mathrm{a}}-\log \mathrm{C}_{\mathrm{a}}\right)$

And

$$
\mathrm{pH}=1 / 2\left(\mathrm{pK}_{\mathrm{a}}-\log \mathrm{C}_{\mathrm{a}}\right)
$$

- Colored indicators: A colored indicator is an acid-base pair whose acid form and basic form have different colors
Let $\mathrm{K}_{\mathrm{i}}$ be the mass action constant of the equilibrium between the two forms:
$\mathrm{HIn}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{In}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{i}}=\frac{\left[\mathrm{H}_{2} \mathrm{O}^{+}\right]\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]}$
$>$ The first color is observed when: $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \geq 10 \mathrm{~K}_{\mathrm{i}}$. either : $\mathrm{pH} \leq \mathrm{pK}_{\mathrm{i}}-1$
$>$ The second color is observed when: $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \leq \mathrm{K}_{\mathrm{i}} / 10$ either: $\mathrm{pH} \geq \mathrm{pK}_{\mathrm{i}}+1$
Example: Helianthin $\left(\mathrm{pK}_{\mathrm{i}}=3.4\right)$
$>$ First color:red when

$$
\begin{aligned}
& \mathrm{pH} \leq \mathrm{pK}_{\mathrm{i}}-1 \Rightarrow \mathrm{pH} \leq 2.4 \\
& \mathrm{pH} \geq \mathrm{pK}_{\mathrm{i}}+1 \Rightarrow \mathrm{pH} \geq 4.4
\end{aligned}
$$

> Second color:yellow when

## 2- Objectives:

- How to do the calibration?
- Determination of the concentration of ethanolic acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ by pH -metric assay.


## 3- Materials:

- pH -metric + electrode, stirrer, magnetic rod, graduated cylinder ( 150 ml ), beaker ( 250 ml ), graduated burette, funnel, volumetric pipette ( 10 ml ).


## 4- Products:

- Buffer solutions ( $\mathrm{pH}=7, \mathrm{pH}=4$ or $\mathrm{pH}=10$ ), Ethanol acid solution $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$, Sodium hydroxide solution $(\mathrm{NaOH}) 0.1 \mathrm{~mol} / 1$. colored indicator and distilled water.


## 5- Operating Mode:

- Prepare the pH meter (calibration) using the buffer solutions.
- Refill the burette with the basic solution $(\mathrm{NaOH})$.
- Using a pipette, take 10 ml of $\mathrm{CH}_{3} \mathrm{COOH}$ then add it to the graduated cylinder.
- Make up with distilled water to 150 ml .
- Pour this volume into a beaker $(250 \mathrm{ml})$.
- Immerse the electrode and the magnetic bar in the acid solution then start stirring.
- Note the $\mathrm{pH}_{0}$ value (initial pH ).
- Add 2 to 3 drops of the colored indicator.
- Add 1 ml each time and note the pH
$\checkmark$ Note: In the toning area (pour the basic solution drop by drop).
$\checkmark$ Data: Table of some colored indicators,

| Indicator | turning area | First color (color in acidic <br> environment) <br> (HA) | Second color (color in the <br> basic environment) (A)) |
| :--- | :--- | :--- | :--- |
| Helianthin (Methyl's orange) | $2.4-4.4$ | Red | Yellow |
| Methyl red | $4,1-6.1$ | Red | Yellow |
| Bromothymol blue | $6.6-7.6$ | Yellow | Red |
| Phenolphthalein | $8.2-10.2$ | colorless | Red |

