

# Química Analítica III

“Disolventes no acuosos”

Titulaciones ácido-base.

\*etanol

\*acetonitrilo

\*ácido-acético

Agua



otro disolvente

Reactividad

solubilidad

especiación

operatividad

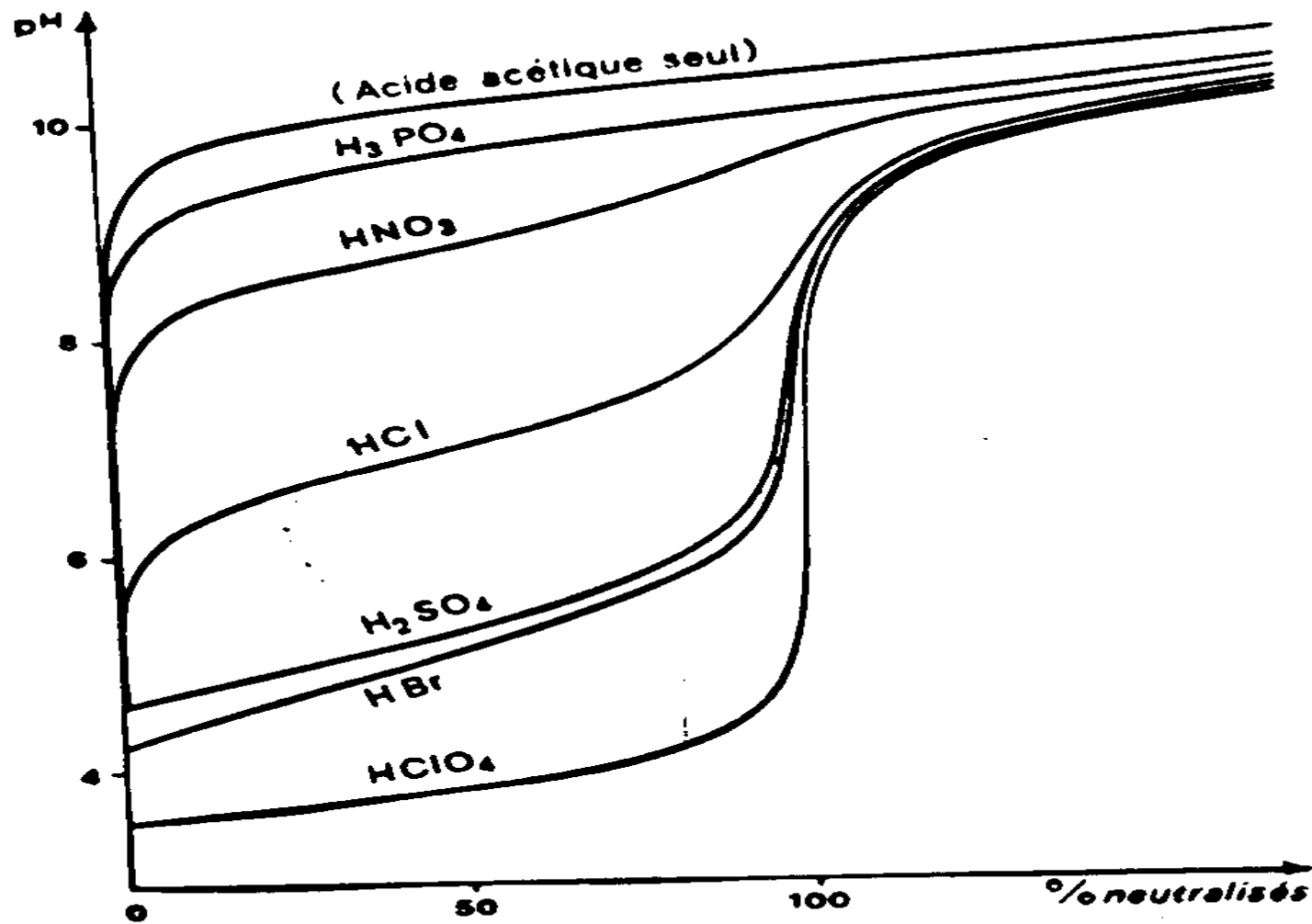
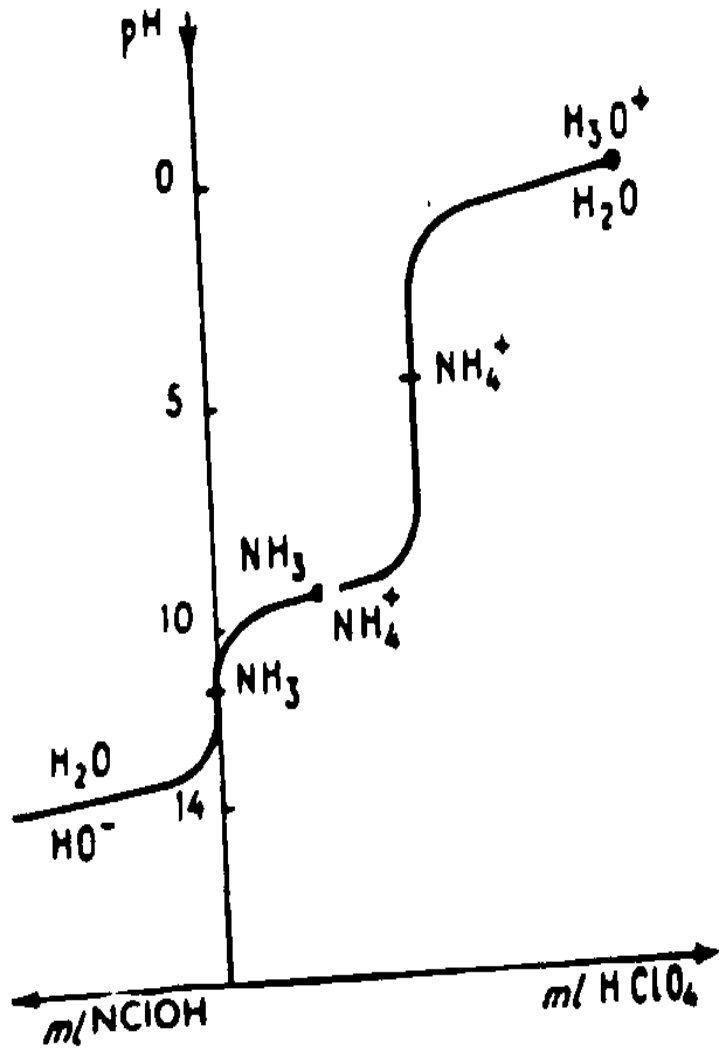
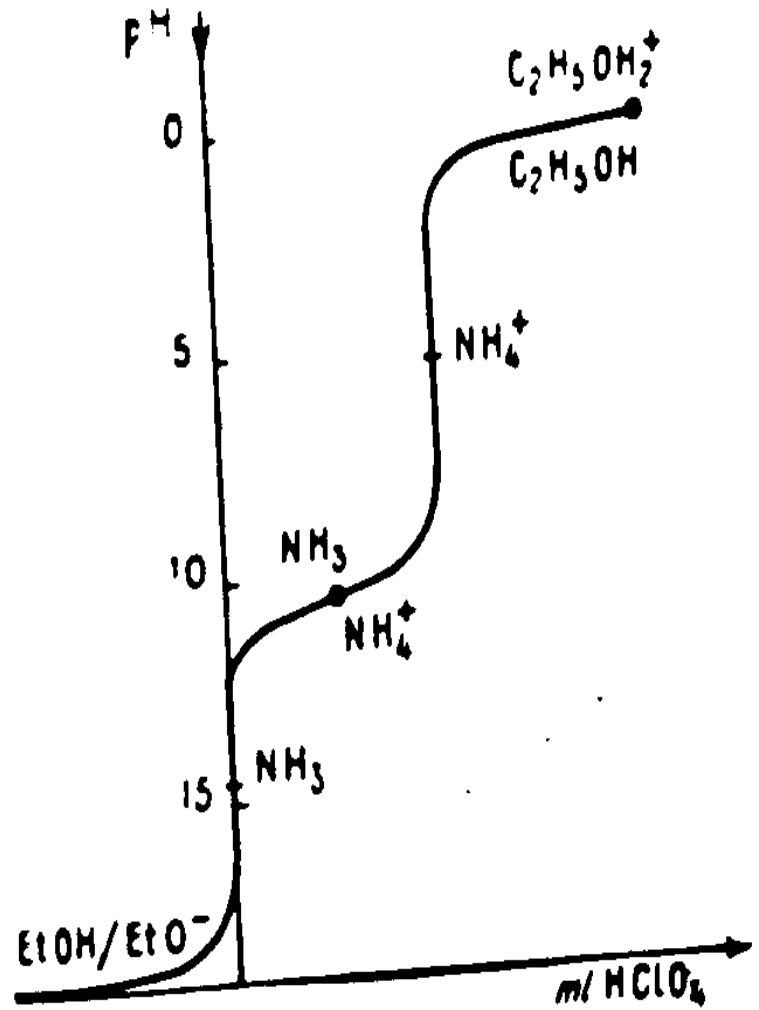


FIG. 3. — Variation du pH mesuré (électrode de verre) au cours de la neutralisation par l'acétate de pyridinium de 5 acides minéraux en solution 0,02 M dans l'acide acétique anhydre (d'après LE PORT, 1966).

Agua



Etanol



... en agua y en alcohol

Fisicoquímico: 1968. France-URSS

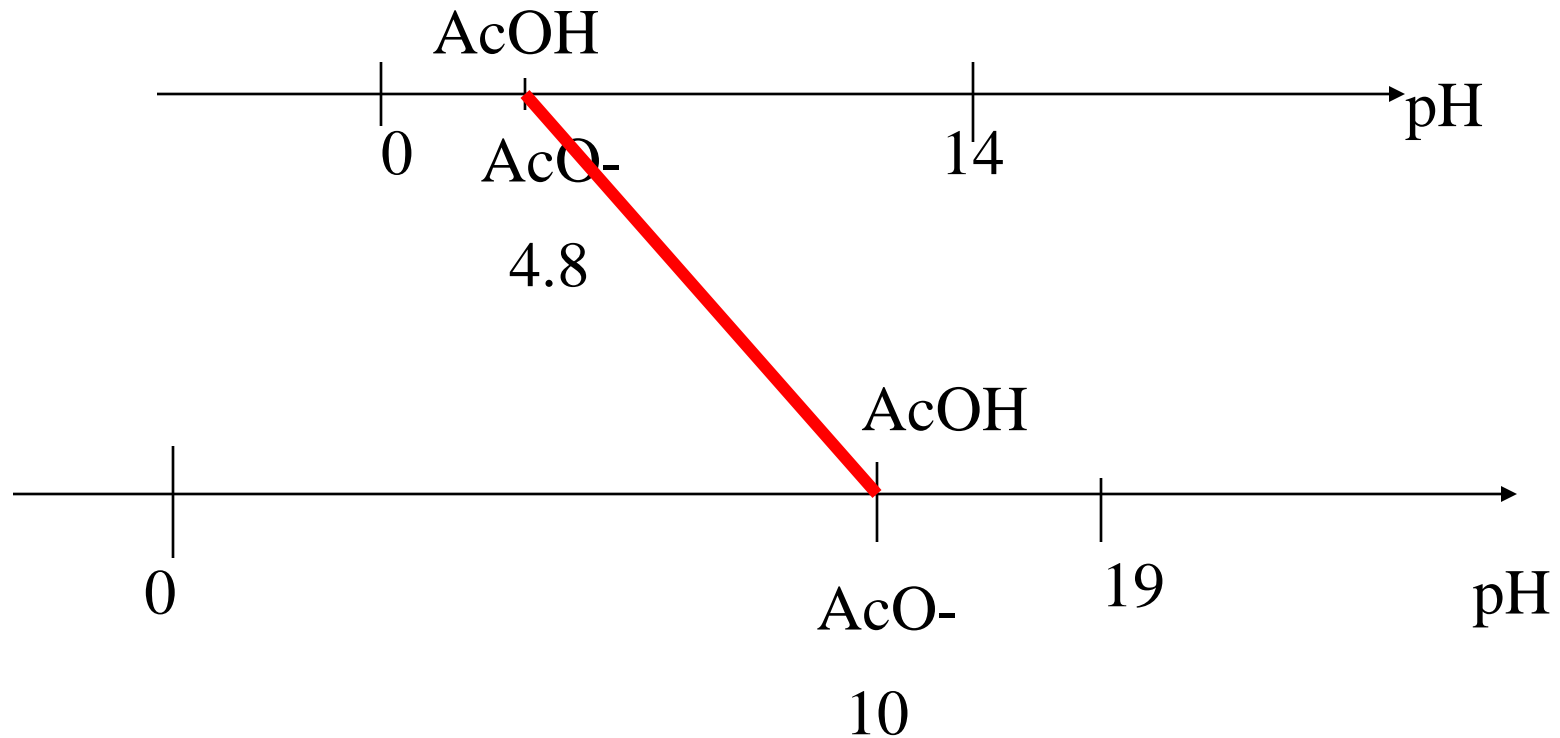
Termodinámica de disoluciones: propiedades de transferencia

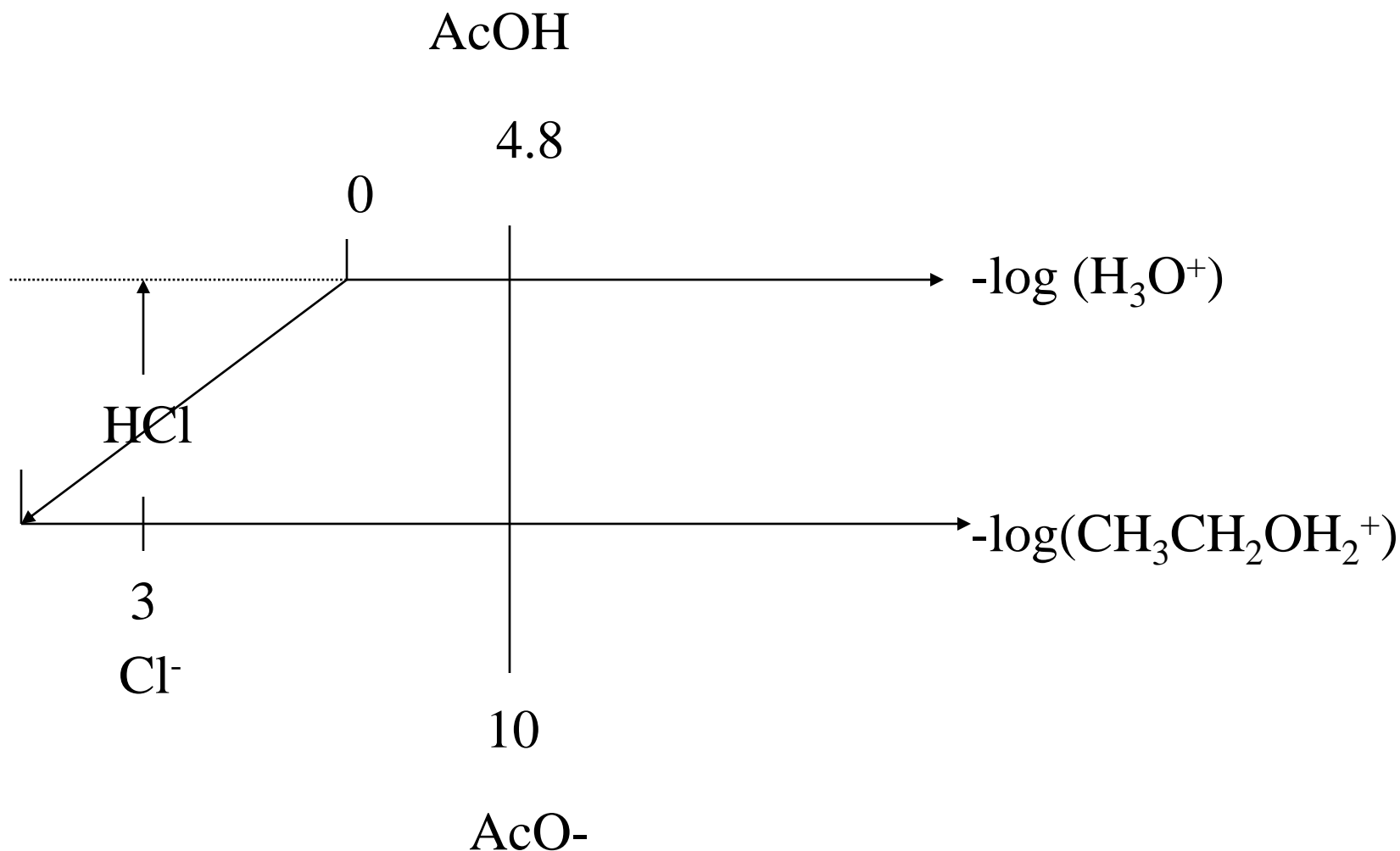
Determinación experimental:  $K_{eq}$ ,  $K$ , estructura.

CORRELACION DE ESCALAS/AGUA.

1980'S : FITTING.

Disolventes: anfiprotico, disociante ( $\epsilon$ ), polar, moleculares





Para disolventes no disociantes u otros: **MODELO EXTRATERMODINAMICO.**

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**DISOLVENTES NO ACUOSOS**  
**RESOLUCION DE UNA MEZCLA DE ACIDOS**

**OBJETIVO:** Estudiar el efecto del cambio de disolvente en la valoración de una mezcla de ácidos.

Lograr la resolución de dicha mezcla en medio etanólico.



## FUNDAMENTO TEORICO:

\* **Acción del Disolvente:**



\* **La disociación se favorece entre mayor sea la constante dieléctrica del disolvente.**

$$\epsilon_{\text{agua}} = 78.5$$

$$\epsilon_{\text{etanol}} = 24.3$$

**El etanol es un disolvente menos disociante que el agua.**

\* **El etanol presenta comportamientos básico y ácido: es un disolvente anfiprótico:**

Como base:



Como ácido:



\* La curva de valoración de una mezcla de ácidos clorhídrico y benzoico 0.01 M (cada uno) en medio acuoso se obtiene según la ecuación:

$$V = \frac{n_0 \Phi_{Bz} + n_0 + V_0 (10^{pH-14}) - V_0 (10^{-pH})}{10^{-pH} + C_t - 10^{pH-14}}$$

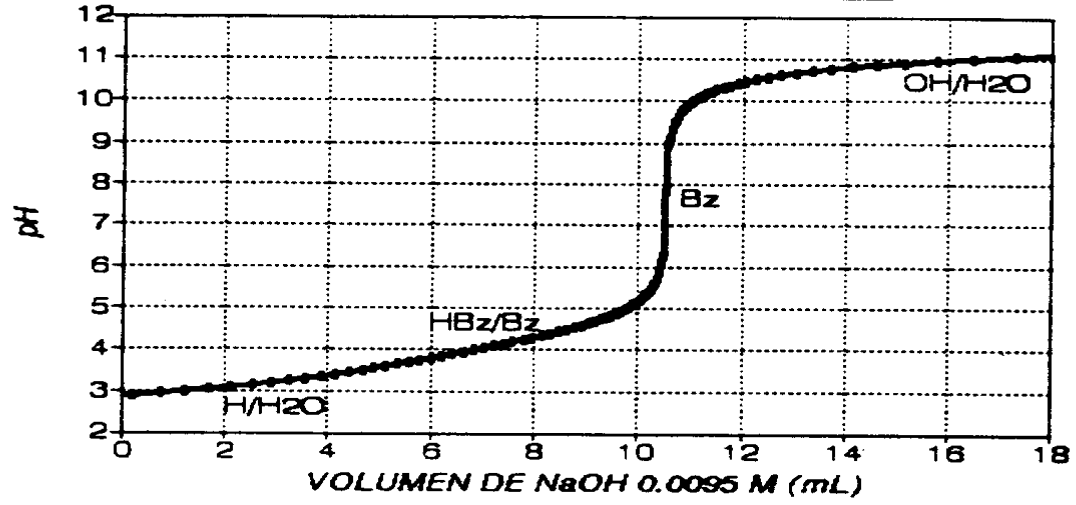
donde:  $\Phi_{Bz} = [1 + 10^{4.19-pH}]^{-1}$        $C_t = 9.5 \text{ mM}$   
 $n_0 = 0.05 \text{ mmol}$        $V_0 = 0.04 \text{ L}$

\* Mientras que la curva de valoración en etanol sigue la ecuación:

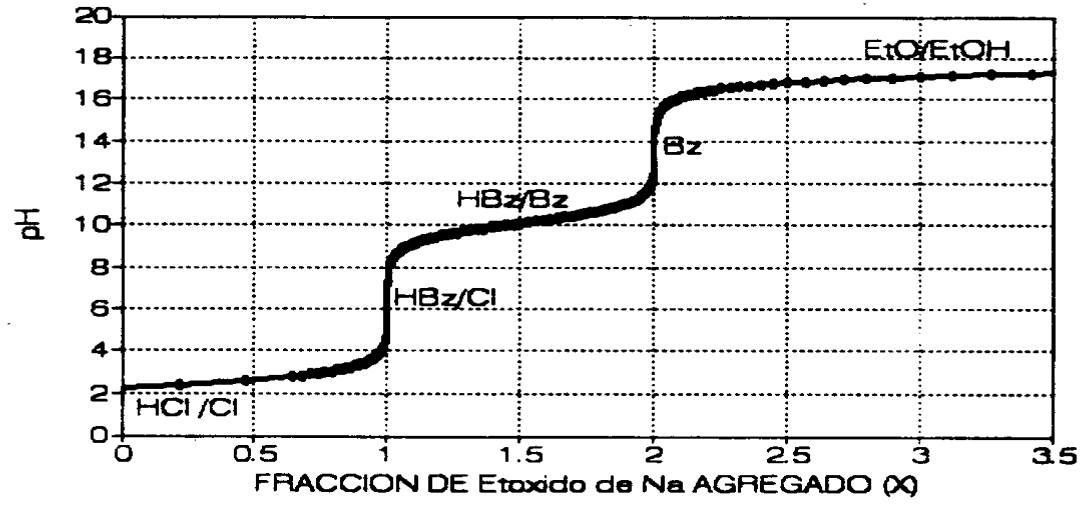
$$X = \Phi_{Bz} + \Phi_{Cl} + 10^{pH-17.1} - 10^{2-pH}$$

donde  $\Phi_{Bz} = [1 + 10^{10.1-pH}]^{-1}$       y       $\Phi_{Cl} = [1 + 10^{2.2-pH}]^{-1}$

CURVA TEORICA DE VALORACION DE UNA MEZCLA DE ACIDOS EN MEDIO ACUOSO



CURVA TEORICA DE VALORACION DE UNA MEZCLA DE ACIDOS EN ETANOL



## **ESTRATEGIA EXPERIMENTAL:**

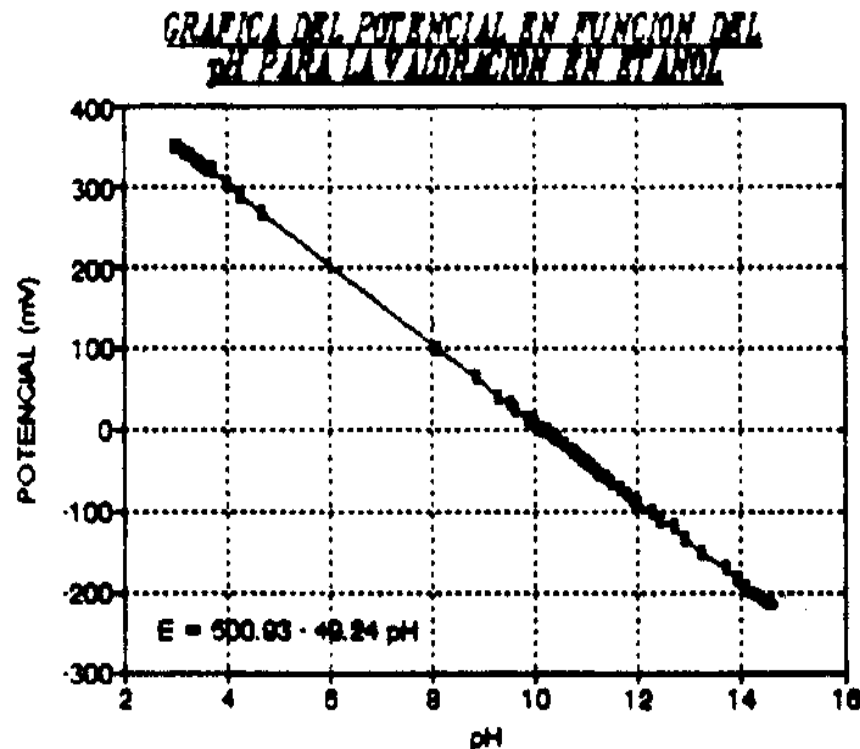
**Valoración de una mezcla de ácidos clorhídrico y benzoico 0.01 M  
(cada uno) en medios acuoso y etanólico.**

**Titulantes: Disoluciones acuosa y etanólica de NaOH 0.01 M.  
Normalizadas con biftalato de potasio como patrón  
primario y fenolftaleína como indicador.**

**Técnica: Potenciométrica, con electrodo de vidrio (monitoreo del  
pH y potencial de la disolución). Nota: Para realizar la  
valoración en etanol, el potenciómetro debe ser calibrado**

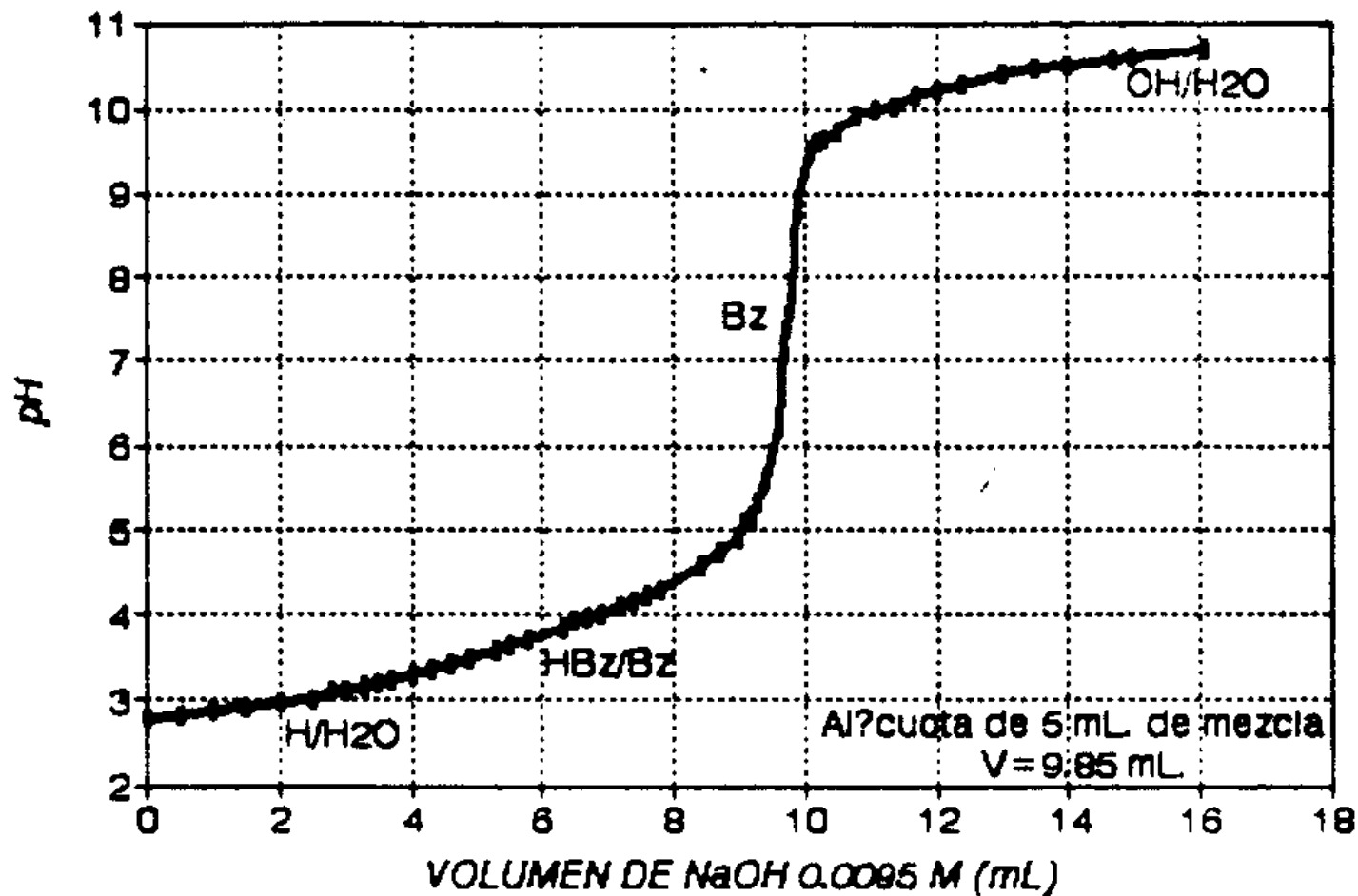
## RESULTADOS Y PROCESAMIENTO DE DATOS:

- \* Con la ayuda del gráfico  $E = f(\text{pH})$  se obtuvieron los valores de pH mayores de 14 para la valoración en medio etanólico.

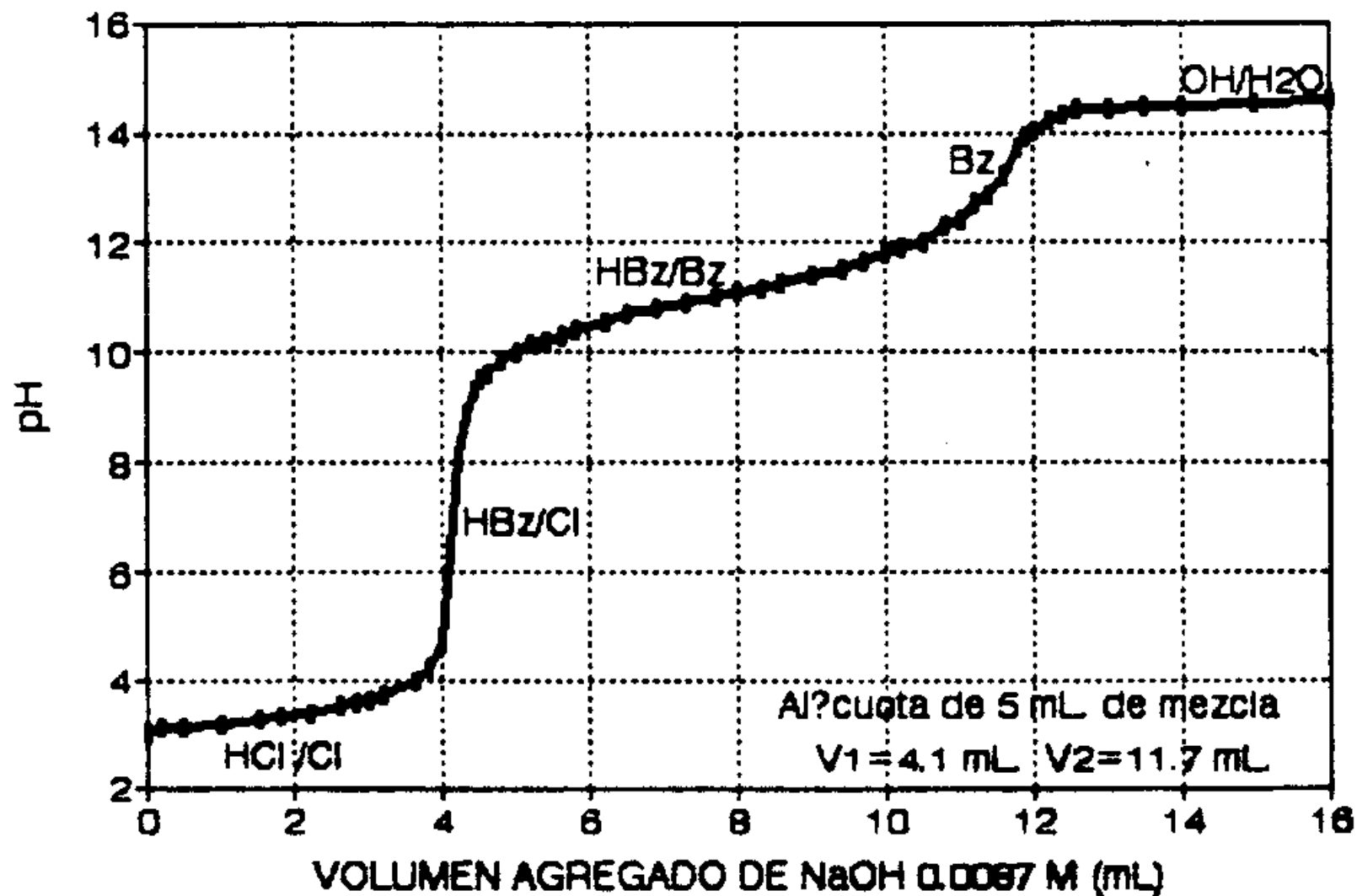


Las curvas de valoración experimentales son:

VALORACION DE UNA MEZCLA DE ACIDOS  
CLORHIDRICO Y BENZOICO EN MEDIO ACUOSO



# VALORACION DE UNA MEZCLA DE ACIDOS CLORHIDRICO Y BENZOICO EN ETANOL



\* Las constantes de acidez asociadas a los pares  $\text{HCl} / \text{Cl}^-$  y  $\text{HBz} / \text{Bz}^-$  en medio etanólico, se calcularon de acuerdo a las siguientes consideraciones:

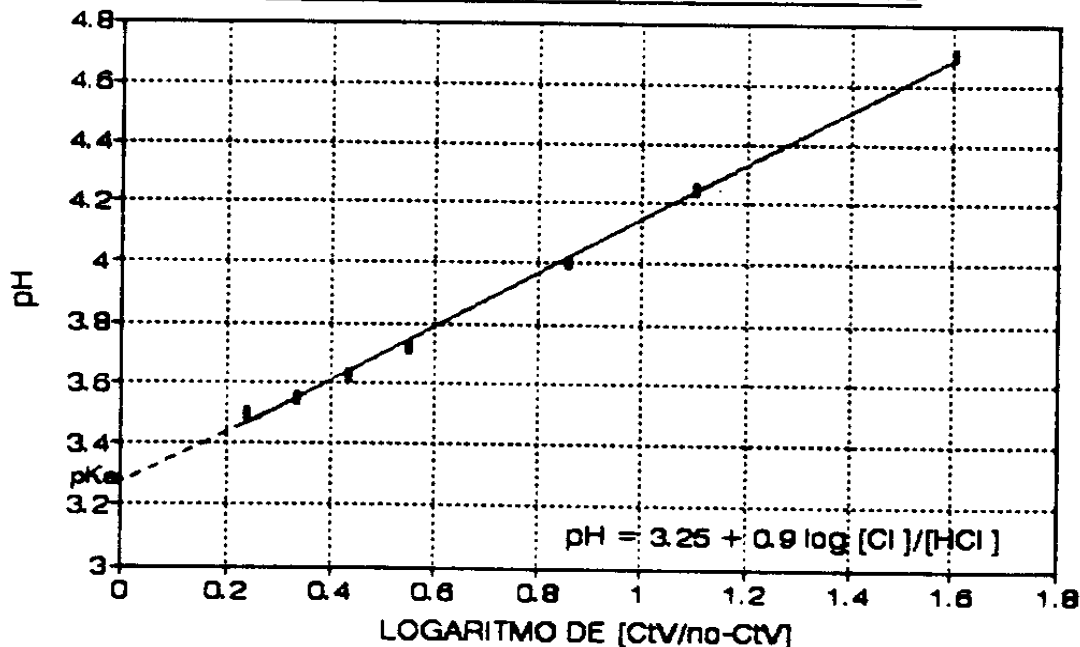
1. Antes del primer punto a la equivalencia el pH está impuesto por el par  $\text{HCl} / \text{Cl}^-$ , cuyas concentraciones están dadas por

$$[\text{HCl}] = (n_0 - CtV) / (V_0 + V) \quad \text{y} \quad [\text{Cl}^-] = CtV / (V_0 + V)$$

por lo que

$$\text{pH} = \text{pk}_{\text{H}^+}^{\text{HCl}} + \log (CtV / (n_0 - CtV))$$

DETERMINACION DE LA CONSTANTE DE ACIDEZ  
DEL ACIDO CLORHIDRICO EN ETANOL





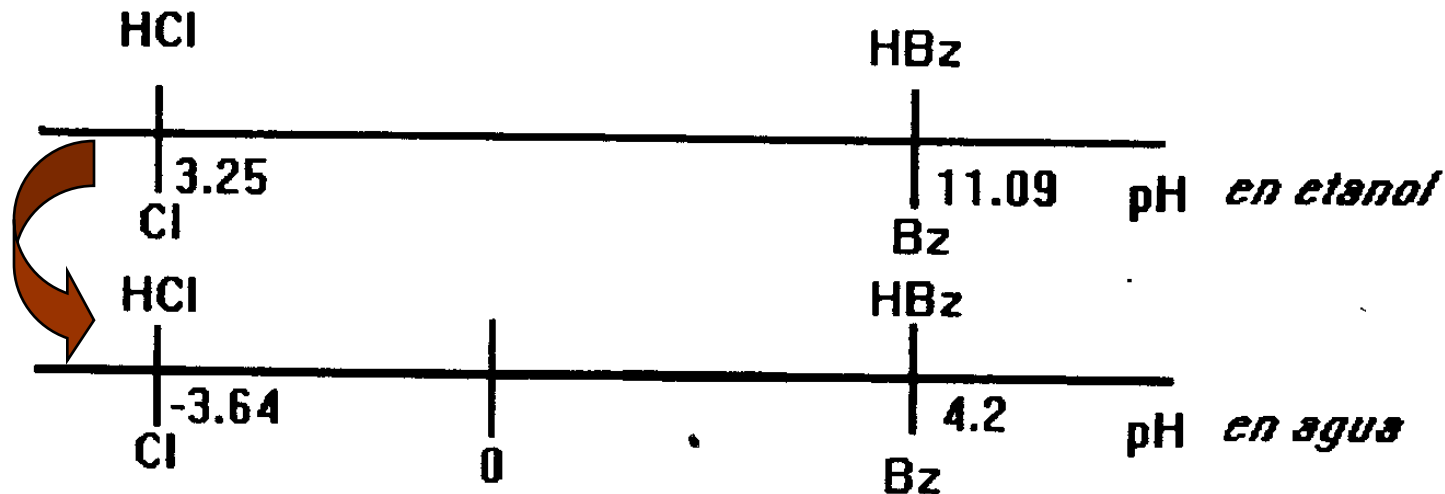
2. Entre el primer y segundo puntos de equivalencia el pH está impuesto por el par HBz/Bz<sup>-</sup>, cuyas concentraciones son:

$$[\text{HBz}] = [n_0 - Ct(V - V_1)] / (V_0 + V) \quad \text{y} \quad [\text{Bz}^-] = Ct(V - V_1) / (V_0 + V)$$

por lo que:

$$\text{pH} = \text{pka} + \log [Ct(V - V_1) / n_0 - Ct(V - V_1)]$$

- \* Se correlacionaron las escalas de pH en ambos disolventes, para estimar por extrapolación el pKa del ácido clorhídrico en agua:



## CONCLUSIONES:

\* Comparando los sistemas HCl/Cl<sup>-</sup> y HBz/Bz<sup>-</sup> en agua y en etanol:

### AGUA

El HCl es un ácido nivelado:



El HBz es un ácido no nivelado:



### ETANOL

Tanto el HCl como el HBz son ácidos no nivelados:



concluimos que el etanol es un disolvente menos disociante que el agua.

- \* Sin embargo, es posible correlacionar las escalas de pH en medios acuoso y etanólico, para extrapolar valores de pKa de ácidos nivelados en agua, como el HCl:

$$pK_{H^+}^{HCl} = -3.64 \quad (-3.7)$$

$$pK_{H^+}^{HCl} = 3.25 \quad (2.2)$$

$$pK_{H^+}^{HBz} = 4.2$$

$$pK_{H^+}^{HBz} = 11.09 \quad (10.1)$$

- \* La mezcla de ácidos en cuestión fué resoluble al utilizar etanol como disolvente: las concentraciones de la mezcla resultaron ser:

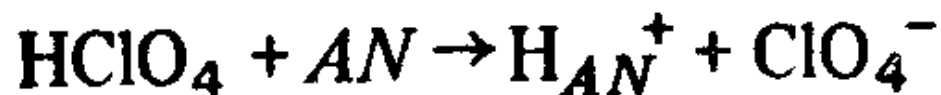
$$[HCl] = 7.13 \text{ mM} \quad \text{y} \quad [HBz] = 13.22 \text{ mM}$$

- \* El electrodo de vidrio respondió adecuadamente al potencial de la disolución en medio etanólico.

## 2.3 Acetonitrile



Assuming the  $K_s$  for *AN* is  $10^{-28.6}$ , the pH scale in acetonitrile ranges from 0 to 28.6, with a pH of 14.3 being neutral.



$$K_{\text{HCl}} = \frac{[\text{H}_{\text{AN}}^+][\text{Cl}^-]}{[\text{HCl}]}$$

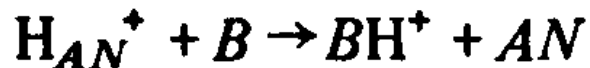
TABLE 2.1

Dissociation Constants for Acids and Conjugate Acids of Bases in Acetonitrile\*

Acid	$pK_{HA}$	Base	$pK_{BH^+}(AN)$	$pK_{BH^+}(H_2O)$	$\Delta pK$
Hydrobromic	5.5	Ammonia	16.5	9.2	7.3
Sulfuric	7.25	Methylamine	18.4	10.6	7.8
Hydrochloric	8.9	Dimethylamine	18.7	10.6	8.1
Nitric	8.9	Trimethylamine	17.6	9.8	7.8
2,4,6-Trinitrophenol	11.0	Ethylamine	18.4	10.6	7.8
2,4-Dinitrophenol	16.0	Triethylamine	18.7		
3,5-Dinitrobenzoic	17.2	<i>n</i> -Propylamine	18.2	10.5	7.7
4-Nitrobenzoic	18.7	Pyrrolidine	19.6	11.3	8.3
3-Bromobenzoic	19.5	1,3-Diphenylguanidine	17.9	10.0	7.9
Benzoic	20.7	Pyridine	12.3	5.2	7.1
4-Nitrophenol	20.7	<i>p</i> -Toluidin	11.3	5.1	6.2
4-Hydroxybenzoic	20.8	Aniline	10.7	4.6	6.1
2-Nitrophenol	22.0	Urea	7.7		
Phenol	26.6	Dimethylformamide	6.1	—	—
		Dimethylsulfoxide	5.8	—	—
		Anthraquinone	3.5	—	—

\* Data from J. E. Coetzee and G. R. Padmanabian, *J. Phys. Chem.*, **69** (1965), 3193; *J. Am. Chem. Soc.*, **87** (1965), 5005; also, from I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhomik, *Anal. Chem.*, **39** (1967), 1627.

may be illustrated for the titration of a base,  $B$ , with a strong acid in acetonitrile.



Neglecting the anion of the titrant acid, the formation constant for this titration is

$$K = \frac{[BH^+]}{[H_{AN}^+][B]} = \frac{1}{K_{BH^+}}$$

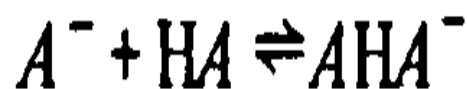
If the titrant anion forms an ion pair with  $BH^+$ , the dissociation constant of the ion pair must be used to calculate the  $BH^+$  concentration that is substituted into the titration formation constant expression for equilibrium calculations.

$$K_{BHA} = \frac{[BH^+][A^-]}{[BHA]} = \frac{[BH^+]^2}{[BHA]}$$

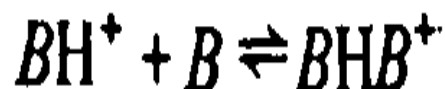
$$[BH^+] = \sqrt{K_{BHA}[BHA]}$$

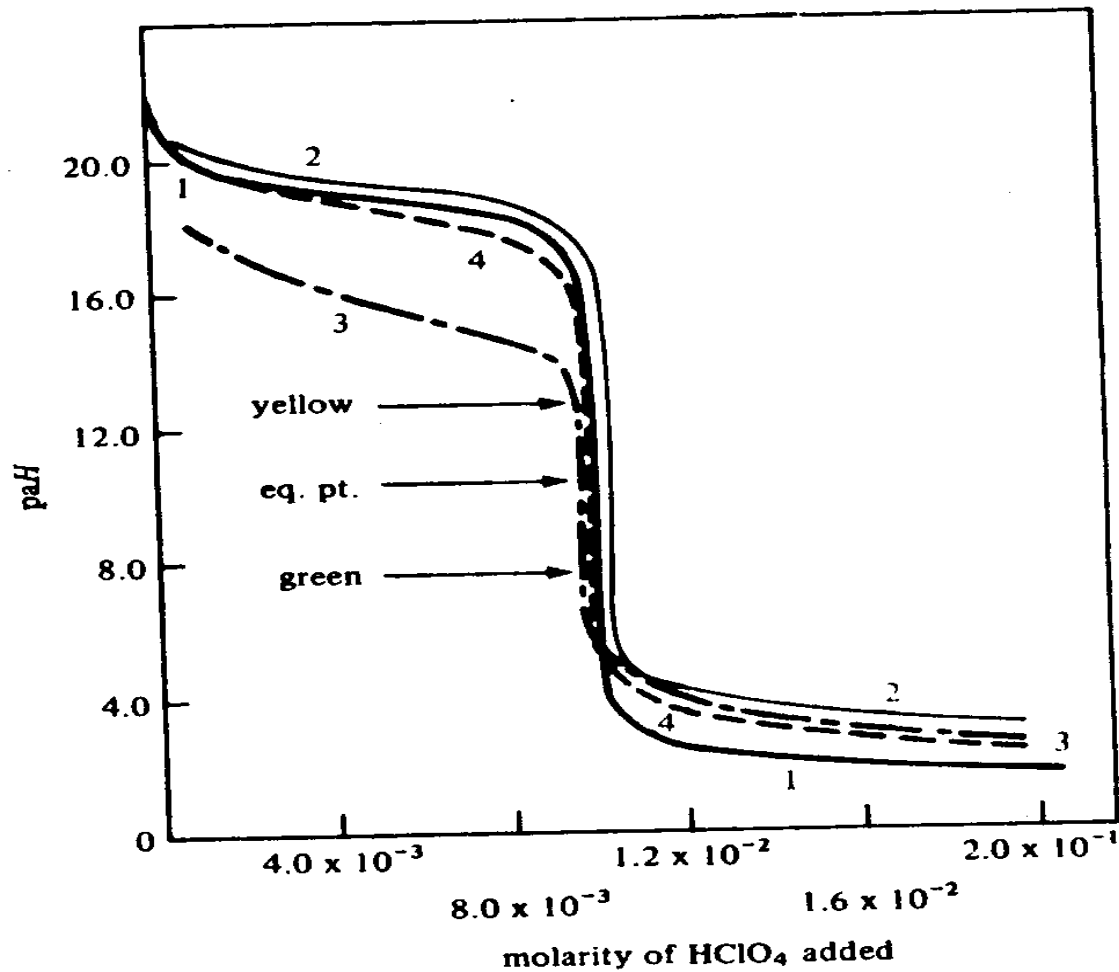
Ion pair dissociation constants for  $\text{NH}_4\text{HSO}_4$  and  $\text{LiNO}_3$  have been found to be  $1.4 \times 10^{-3}$  and  $4.1 \times 10^{-4}$ , respectively.

Another factor has been observed which complicates acid-base equilibria in acetonitrile. Because of its poor solvating properties and moderately low dielectric constant, the anion of a weak acid is stabilized by association with the free acid.



The salt of a base may also associate with the free base,





**Figure 2.1** Potentiometric titration of 0.01 M triethylamine in acetonitrile with perchloric acid: (1) calculated curve, (2) curve with  $\text{HClO}_4 \cdot 1.4\text{H}_2\text{O}$  (in nitromethane), (3) curve with  $\text{HClO}_4$  (in anhydrous acetic acid), (4) curve with  $\text{HClO}_4$  (in nitromethane, 0.84 M in acetic acid). The indicator is *p*-naphtholbenzein. [Reprinted from I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhomik, *Anal. Chem.*, **39**, (1967): 315. Copyright 1967 by the American Chemical Society. Reprinted by permission of the copyright owner.]



## 2.4 Acetic Acid

Glacial acetic acid is another amphiprotic solvent with an autoprotolysis constant only slightly different from that of water.

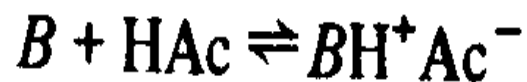


$$K_s = [\text{H}_{\text{HAc}}^+][\text{Ac}^-] = 10^{-14.45}$$

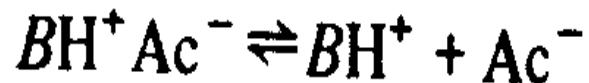
$$K_{\text{HClO}_4} = \frac{[\text{H}_{\text{HAc}}^+][\text{ClO}_4^-]}{[\text{HClO}_4]} = 10^{-4.87}$$

$\text{HClO}_4$  1 M (nivelado), pH=2.0

The acidic properties of acetic acid solvent are sufficient to cause bases of medium strength to react more or less completely with the solvent.



The ion pair is only partially dissociated because of the low dielectric constant of acetic acid.



$\text{HClO}_4$  1 M (nivelado), pH=2.0

TABLE 2.3

Overall Dissociation Constants of Acids, Bases, and Salts in Glacial Acetic Acid ( $-\log$  Autoproyolysis Constant of Glacial Acetic Acid,  $pK_s = 14.45$ )\*

		<u><math>pK_{HX}</math></u>
Acids	Perchloric acid	4.87
	Sulfuric acid	7.24
	<i>p</i> -Toluenesulfonic acid	8.46
	Hydrochloric acid	8.55
		<u><math>pK_B</math></u>
Bases	Tribenzylamine	5.36
	Diethylaniline	5.78
	Pyridine	6.10
	Potassium acetate	6.10
	Sodium acetate	6.58
	Lithium acetate	6.79
	2,5-Dichloroaniline	9.48
	Urea	10.24
	Water	12.53
		<u><math>pK_{BHX}</math></u>
Salts	Sodium perchlorate	5.48
	Diethylaniline perchlorate	5.79
	Tribenzylamine hydrochloride	6.71
	Potassium chloride	6.88
	Urea hydrochloride	6.96
	Lithium chloride	7.08
	Dodecylamine hydrochloride	7.45

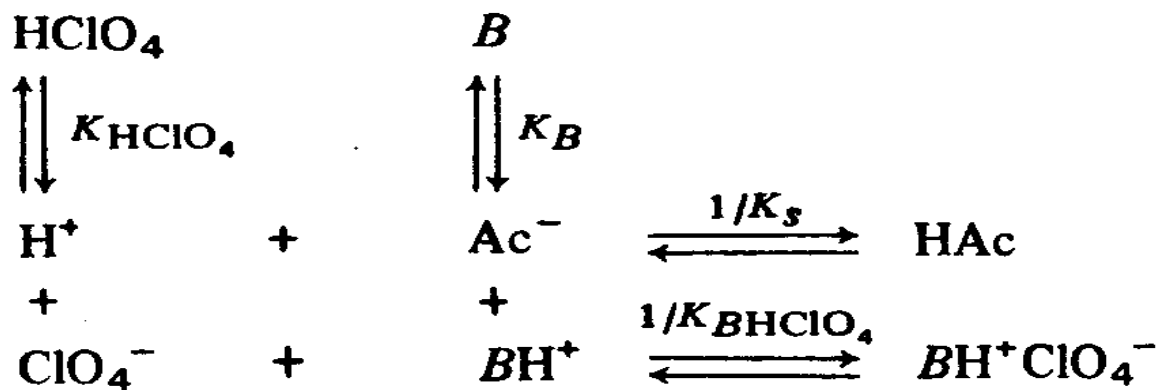
\* Data from *Treatise on Analytical Chemistry*, part 1, vol. 1, chap. 13.

In acetic acid the product of titration of a base,  $B$ , with a strong acid is a salt such as  $BHClO_4$ . Owing to the low dielectric constant, these salts are only slightly dissociated:



$$K_{BHClO_4} = \frac{[BH^+][ClO_4^-]}{[BHClO_4]}$$


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The over-all reaction then is



and the equilibrium constant for this reaction is:

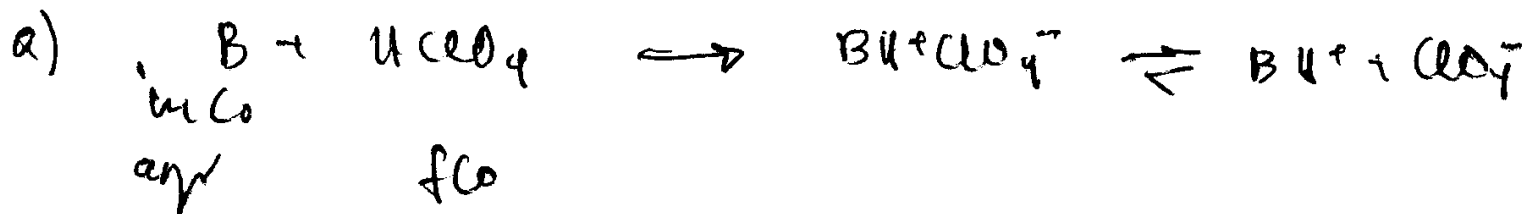
$$K = \frac{[BHClO_4]}{[HClO_4][B]} = \frac{K_{HClO_4} K_B}{K_{BHClO_4} K_s}$$

# Química Analítica en medios no acuosos.

①

## Equación General

$$|H^+| = \left[ \frac{k_s \left[ 1 + \frac{k_{BH} c_{O_4}}{k_s} |HBO_4| \right]}{1 + \frac{k_{BC} c_2}{k_s}} \right]^{1/2}$$



$0 < f < 1$

$c_0(1-f) \quad \epsilon_0$

$f=1 \quad \epsilon_1 \quad \epsilon_1$

$f > 1 \quad \epsilon_2 \quad \epsilon_2$

$f c_0$

$c_0$

$c_0$

$\epsilon_0 \quad \epsilon_0$

$\epsilon_1 \quad \epsilon_1$

$\epsilon_2 \quad \epsilon_2$

$$1) pK_B = 5 \quad pK_{H_2CO_3} = 5 \quad pK_{HCO_3^-} = 4.87$$

$$f = 0$$

$$1 \ll \frac{k_{BCB}}{k_s}$$

$$|H^+| = \left[ \frac{k_s + [1 + k_{B_1CO_3} |H_2CO_3|]}{\frac{k_{BCB}}{k_s}} \right]^{1/2}$$

$$|H^+| = \left[ \frac{k_s^2 + k_s^2 k_{B_1CO_3} |H_2CO_3|}{k_{BCB}} \right]^{1/2}$$

$$|H^+| = \left[ \frac{k_s^2}{k_{BCB}} \left( 1 + \frac{k_{B_1CO_3} |H_2CO_3|}{k_{BCB}} \right) \right]^{1/2}$$

$$|H^+| = \frac{k_s}{k_{BCB}} \left[ k_{BCB} + k_{B_1CO_3} |H_2CO_3| \right]^{1/2}$$

Since  $f = 0$   $|H_2CO_3| = 0$

$$|H^+| = \frac{k_s}{k_{BCB}} (k_{BCB})^{1/2}$$

$$pH = pK_s - \frac{1}{2} pK_s + \frac{1}{2} \log C_B$$

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$$0 < f < 1 \quad k_{BHDV} = k_B ; |HBDV| = f C_0$$

$$|W| = \frac{k_S}{k_B C_B} (k_B C_B + k_B f C_0)^{1/2}$$

$$|W| = \frac{k_S}{k_B C_B} (k_B (C_B + f C_0))^{1/2}$$

$$|W| = \frac{k_S k_B^{1/2}}{k_B C_B} (C_B + f C_0)^{1/2}$$

$$|W| = \frac{k_S}{k_B^{1/2} C_B} (C_B + f C_0)^{1/2}$$

para  $f = 0.5$  (50% titulada)

$$C_B = C_0 (1 - f) ; |HBDV| = f C_0$$

$$|W| = \frac{k_S}{k_B C_B} (k_B (C_0 (1 - f) + f C_0))^{1/2}$$

$$|W| = \frac{k_S}{k_B C_B} (k_B C_0)^{1/2}$$

$$|W| = \frac{k_S}{C_B} \left( \frac{C_0}{k_B} \right)^{1/2}$$

$$f = 1 \quad |B_H^+ClO_4^-| = C_S$$

$$K_{B_H^+ClO_4^-} = \frac{|B_H^+| |ClO_4^-|}{|B_H^+ClO_4^-|}$$

$$K_{HClO_4} = \frac{|H^+| |ClO_4^-|}{|H^+ClO_4^-|}$$

$$K_{B_H^+ClO_4^-} \frac{|B_H^+ClO_4^-|}{|B_H^+|} = \frac{K_{HClO_4} |H^+ClO_4^-|}{|H^+|}$$

$$|B_H^+| = \frac{K_B C_B |H^+|}{K_S}$$

$$\frac{K_{B_H^+ClO_4^-} |B_H^+ClO_4^-| K_S}{K_B C_B |H^+|} = \frac{K_{HClO_4} |H^+ClO_4^-|}{|H^+|}$$



According to Kotteloff:

$$|H^+| = \frac{k_s}{k_B C_B} \left[ k_{BH} C_{OH} |BH^+ C_{OH}^-| + k_B C_B \right]^{1/2}$$

$$|H^+| = \frac{k_s}{k_B C_B} \left[ k_{BH} C_{OH} |BH^+ C_{OH}^-| \right]^{1/2}$$

$$|H^+| = \left[ \frac{k_s^2 k_{BH} C_{OH} |BH^+ C_{OH}^-|}{k_B^2 C_B^2} \right]^{1/2}$$

$$\frac{k_{BH} C_{OH} |BH^+ C_{OH}^-|}{k_B C_B} = k_{HC} C_{OH} |H^+ C_{OH}^-|$$

$$\frac{k_{BH} C_{OH} |BH^+ C_{OH}^-|}{k_{HC} C_{OH} k_B} = |H^+ C_{OH}^-| C_B = C_B^2 \text{ ?}$$

$$|H^+| = \left[ \frac{k_s^2 k_{BH} C_{OH} |BH^+ C_{OH}^-| k_B k_{HC} C_{OH}}{k_B^2 k_{HC} C_{OH} |BH^+ C_{OH}^-| k_s} \right]^{1/2}$$

$$|H^+| = \left[ \frac{k_s k_{HC} C_{OH}}{k_B} \right]^{1/2}$$

$f > 1$

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(2)

(7)  $\phi$

$$K_{ВНс\omega\gamma} = \frac{|ВН\omega| |с\omega\gamma|}{|ВНс\omega\gamma|}$$

$$|ВН\omega| = \frac{K_{ВНс\omega\gamma} |ВНс\omega\gamma|}{|с\omega\gamma|};$$

$$K_{Нс\omega\gamma} = \frac{|Н\omega| |с\omega\gamma|}{|Н\omega\gamma|}; \quad K_{Нс\omega\gamma} \frac{|Н\omega\gamma|}{|Н\omega|} = |с\omega\gamma|$$

$$|ВН\omega| = \frac{K_{ВНс\omega\gamma} |ВНс\omega\gamma| |Н\omega|}{K_{Нс\omega\gamma} |Н\omega\gamma|} = \frac{K_B C_B |Н\omega|}{K_S}$$

$$\frac{K_S K_{ВНс\omega\gamma} |ВНс\omega\gamma|}{K_B K_{Нс\omega\gamma} |Н\omega\gamma|} = C_B$$

from 
$$|W+1| = \left[ \frac{k_s \left[ 1 + \frac{k_{vsc0y} |v_{sc0y}|}{k_a c_b} \right]}{1 + \frac{k_{0y}}{k_s}} \right]^{1/2}$$

$$|W+1| = \left[ \frac{k_s + k_{vsc0y} |v_{sc0y}|}{1 + \frac{k_{vsc0y} |v_{sc0y}|}{k_{vsc0y} |v_{sc0y}|}} \right]^{1/2} \quad 1/2$$

if excess  $v_{sc0y}$   $k_{vsc0y} |v_{sc0y}| > k_s$

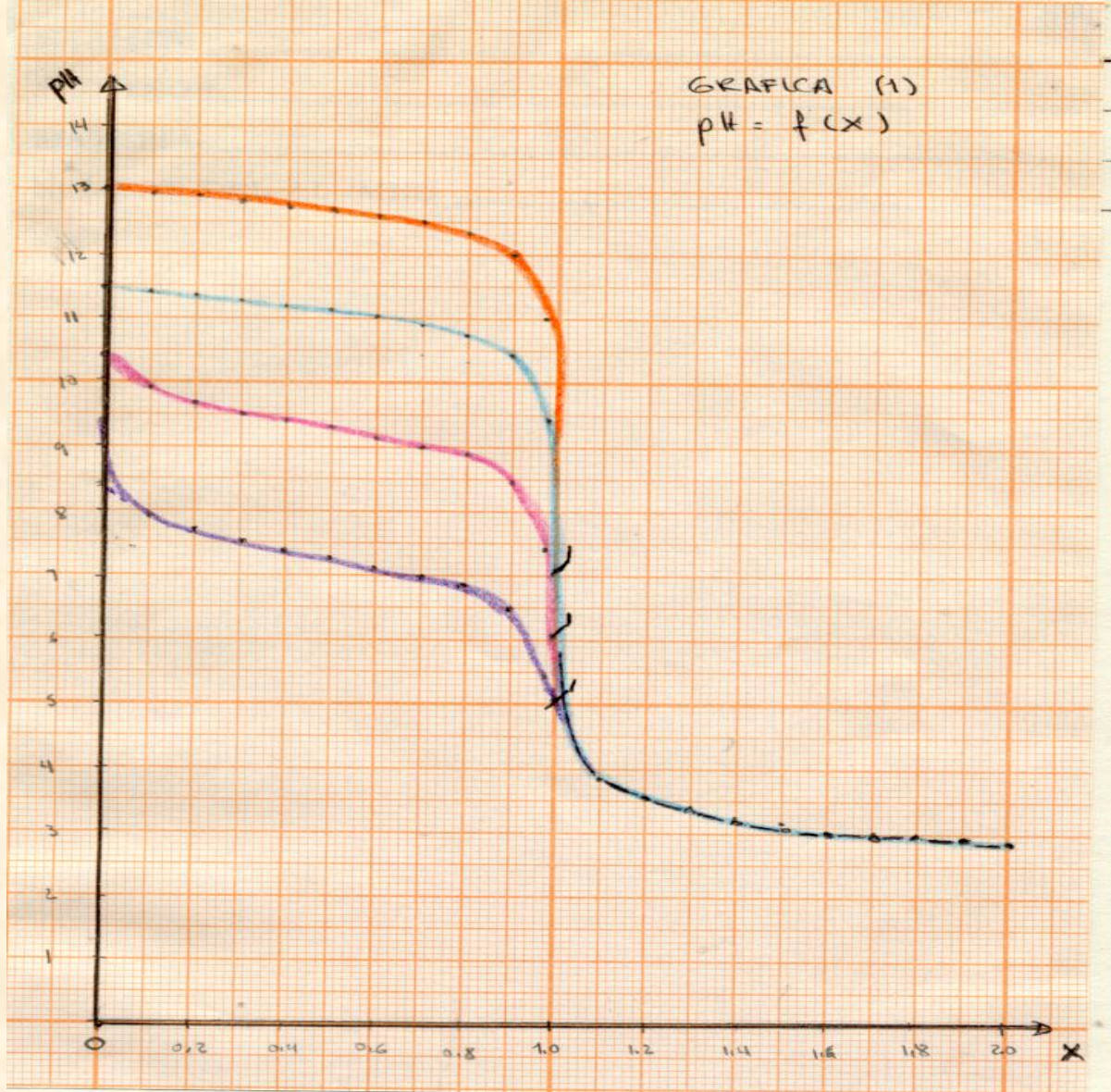
$$|W+1| = \left[ \frac{k_{vsc0y} |v_{sc0y}|}{1 + \frac{k_{vsc0y} |v_{sc0y}|}{k_{vsc0y} |v_{sc0y}|}} \right]^{1/2}$$

$$|W+1| = k_{vsc0y} |v_{sc0y}| \left[ k_{vsc0y} |v_{sc0y}| + k_{vsc0y} c_{vsc0y} \right]^{-1/2}$$

$$\Rightarrow |W+1| = \frac{k_{vsc0y} c_{vsc0y}}{[k_{vsc0y} |v_{sc0y}|]^{1/2}}$$

$$|W+1| = k_{vsc0y} |v_{sc0y}| \left[ k_{vsc0y} |v_{sc0y}| + k_{vsc0y} c_{vsc0y} \right]^{-1/2}$$

$$\Rightarrow |W+1| = \frac{k_{vsc0y} c_{vsc0y}}{[k_{vsc0y} |v_{sc0y}|]^{1/2}}$$



GRAFICA ①: Titulación de bases fuertes de  $pK_B = 5.0$  ■;  $pK_B = 7.0$  ■; y  $pK_B = 9.0$  ■, por el  $HCO_4$  en ácido acético. La grafica muestra también la curva de titulación de base fuerte por ácido fuerte en  $H_2O$  ■.