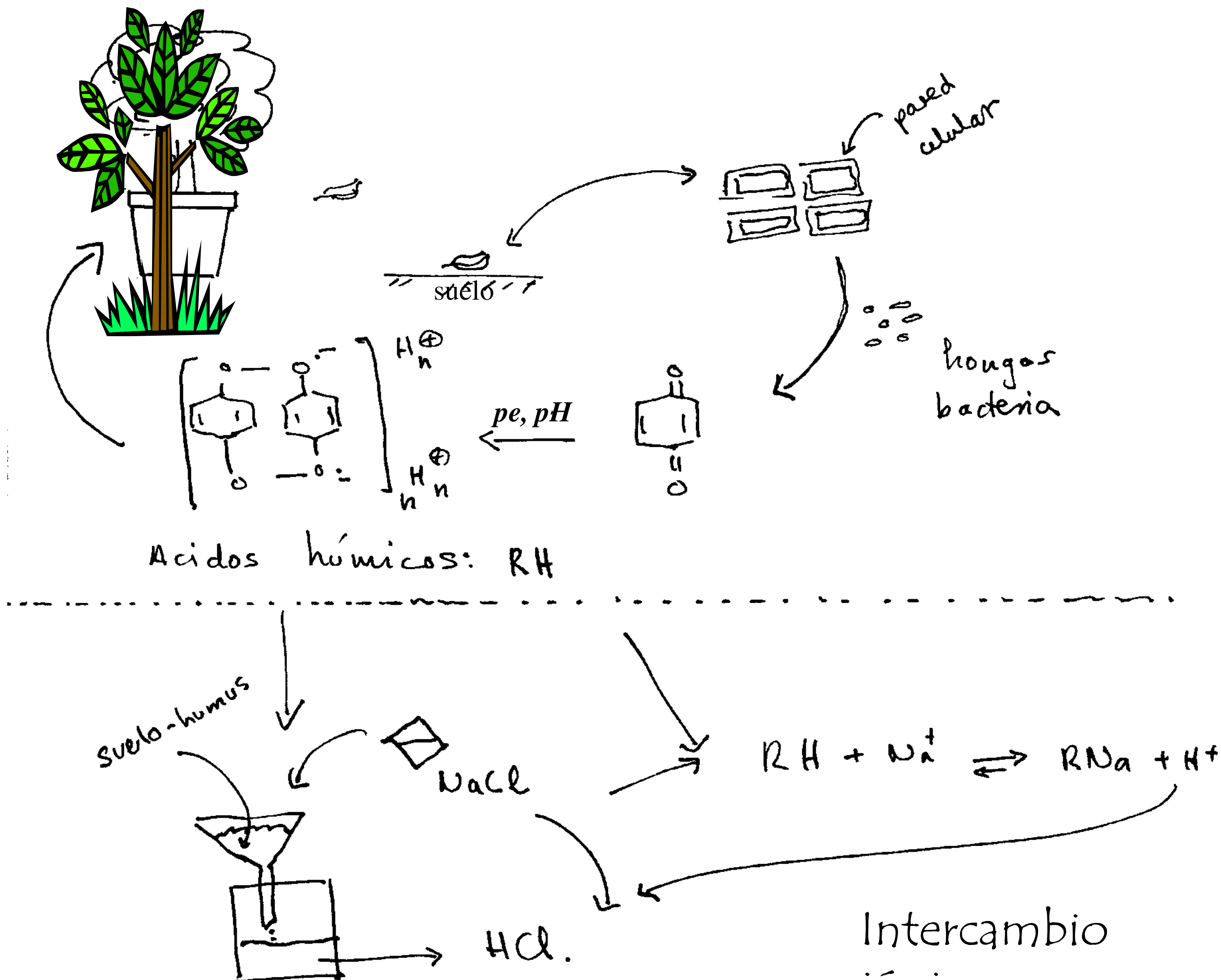
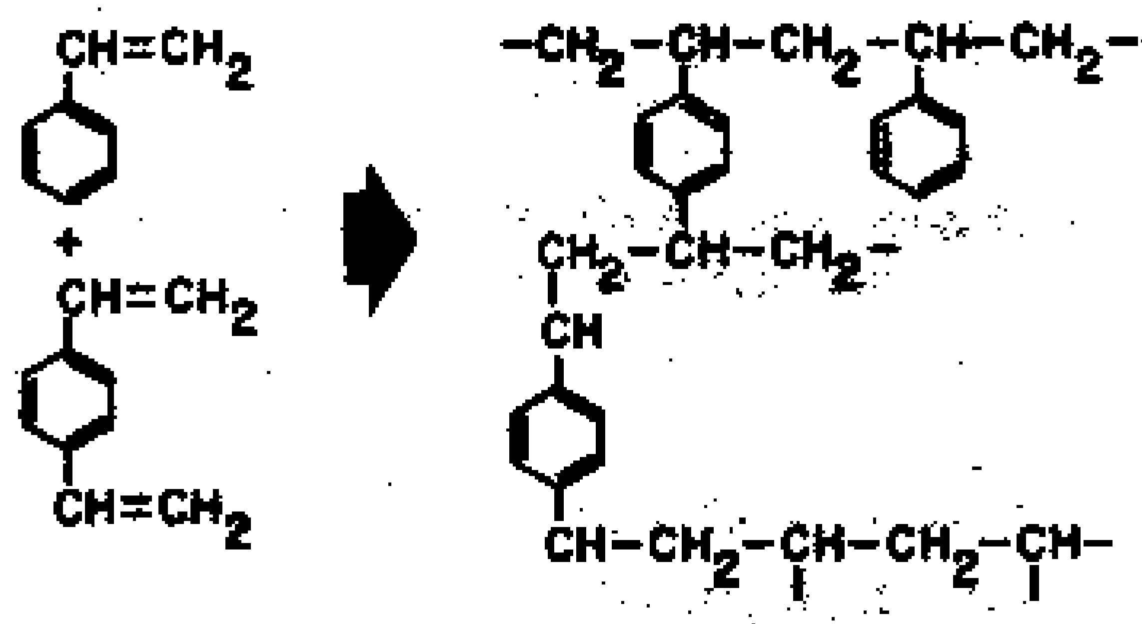
Química Analítica I (1402)

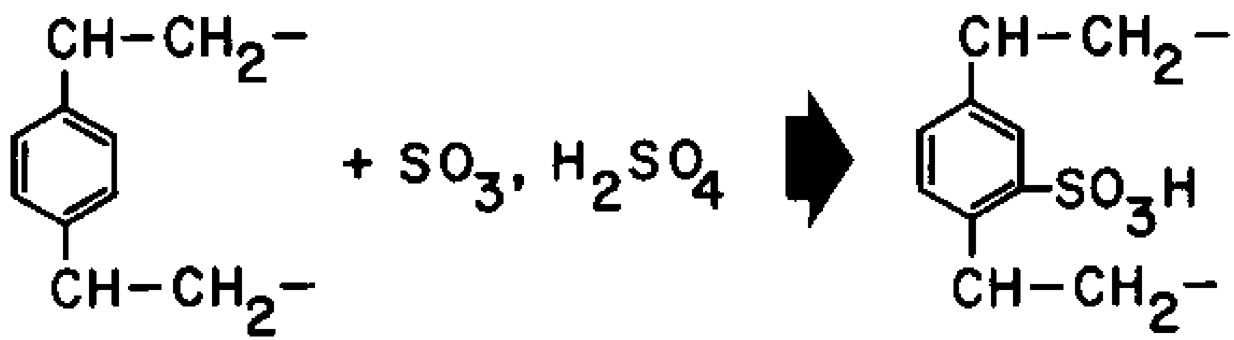
Resinas intercambiadoras de iones

(Aspectos generales)

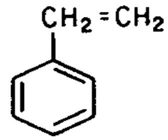


Intercambio iónico.

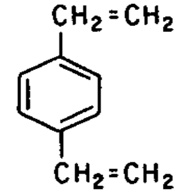

CH=CH2
+
CH=CH2
CH=CH2
-CH2-CH-CH2-CH-CH2-
CH2-CH-CH2-
CH
CH-CH2-CH-CH2-CH-


CH-CH2-
CH-CH2-
+ SO3, H2SO4
CH-CH2-
SO3H
CH-CH2-

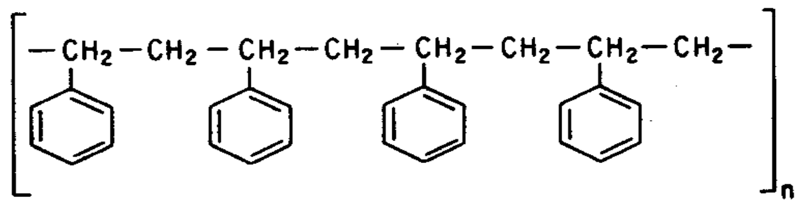
ESTIRENO
(VINIL BENCENO)
(VB)



DIVINIL BENCENO
(DVB)



(2) POLIMERIZACION DEL ESTIRENO EN POLIESTIRENO



(3) COPOLIMERIZACION DEL ESTIRENO Y DIVINIL BENCENO, MOSTRANDO LA FUNCION QUE DESEMPEÑA EL DVB EN EL ENTRECRUZAMIENTO DE LAS CADENAS DEL POLIESTIRENO.

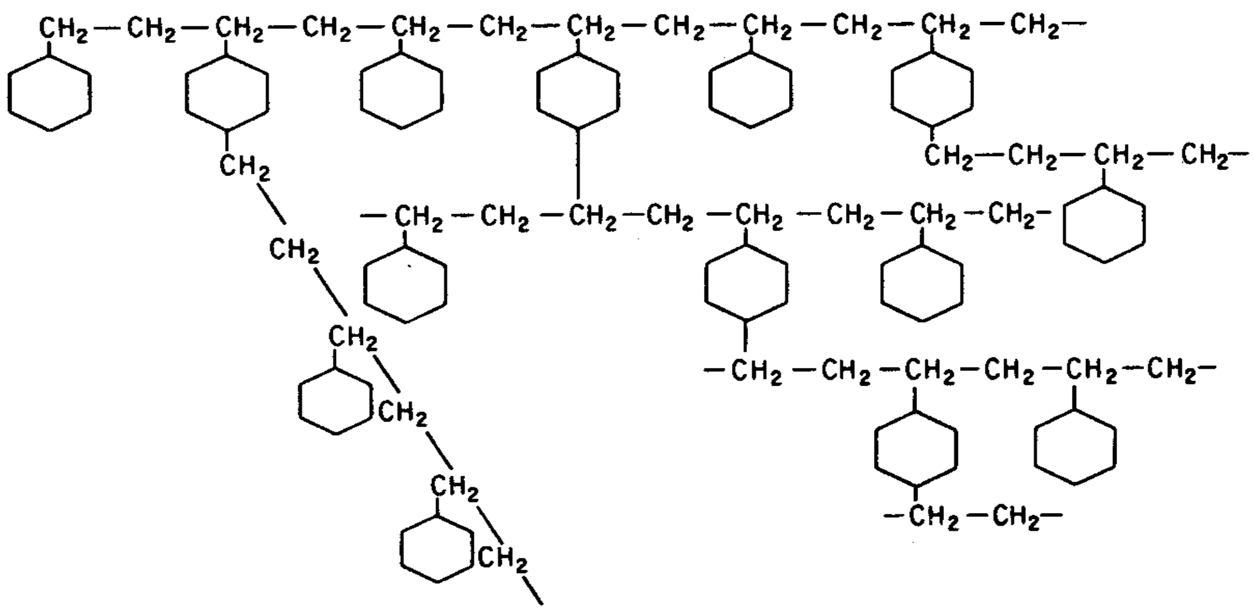


Figura 12.3 Producción de resinas intercambiadoras de iones estables mediante copoli merización.

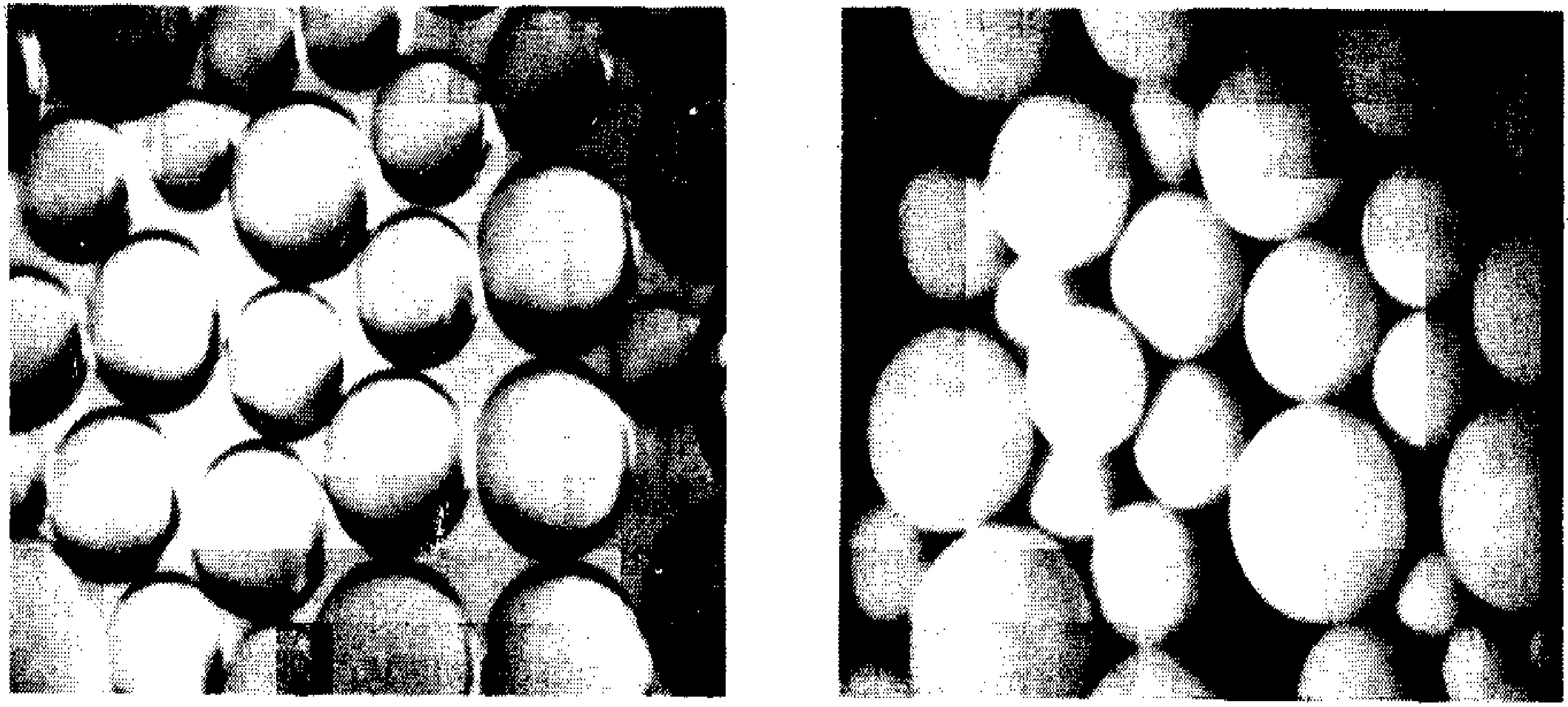


Figura 12.2 Los intercambiadores comerciales típicos pertenecen a dos estructuras generales, del tipo de gel (izquierda) y del tipo de macroporo (derecha). Estas son amplificaciones.

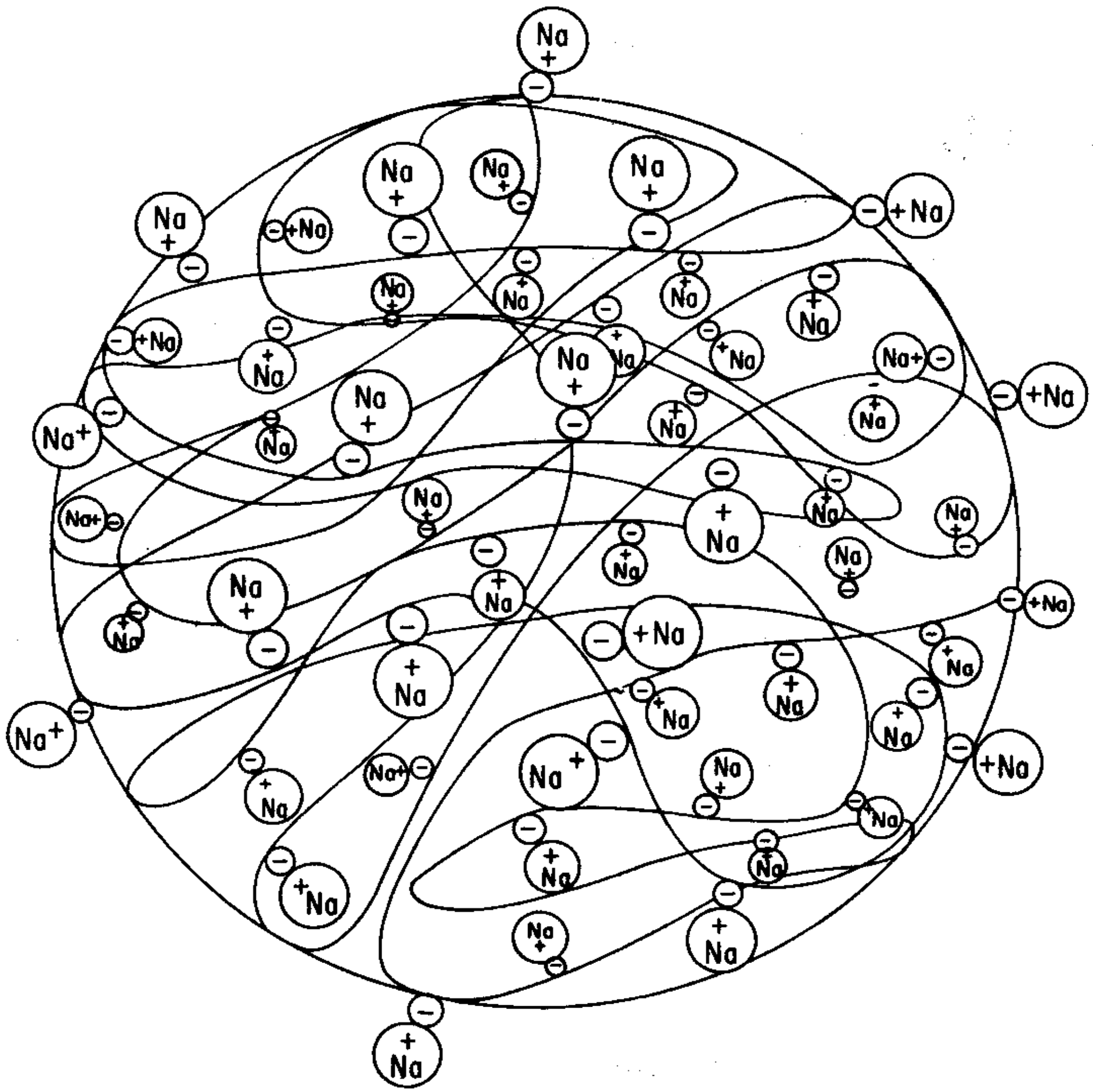
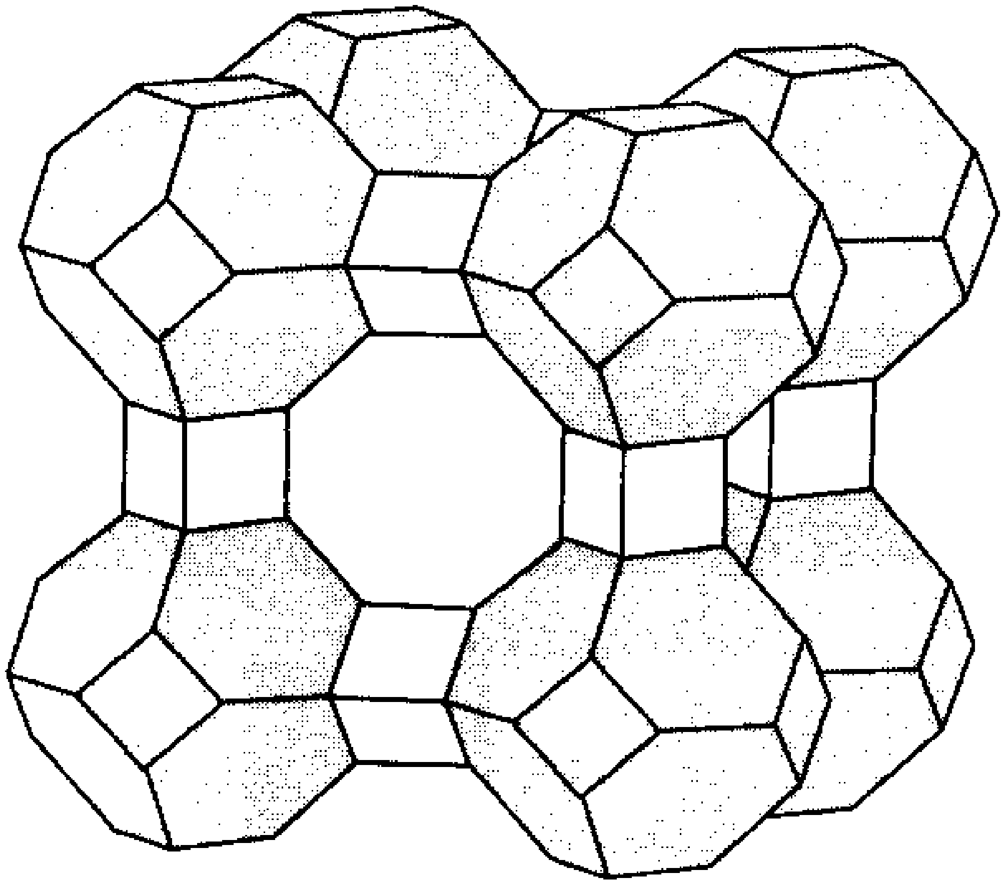
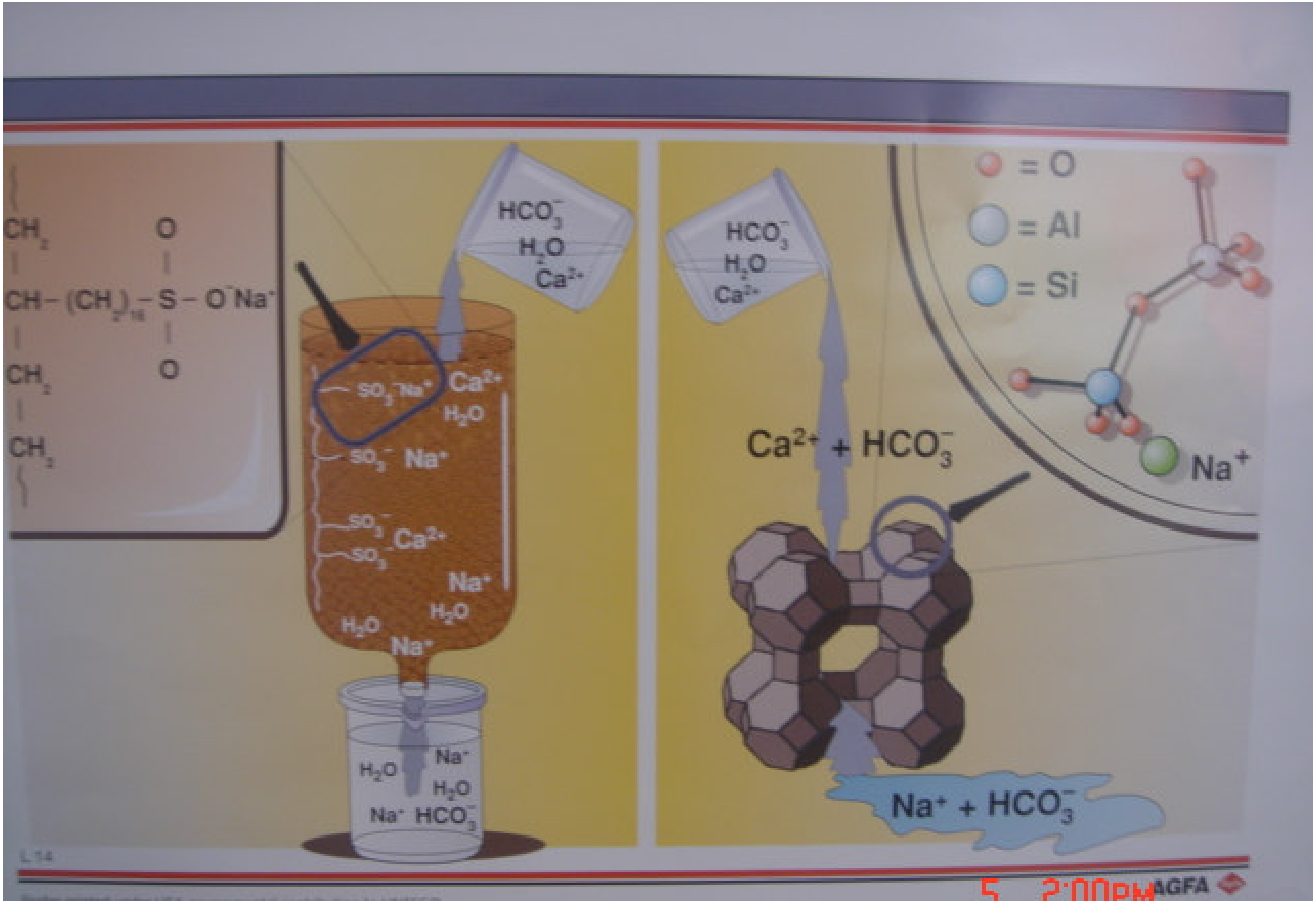


Figura 12.1 Modelo de un intercambiador de cationes, mostrando los sitios de intercambio negativamente cargados sobre el esqueleto que sostiene los iones de sodio como uvas en un racimo.



$\{Na_{12}(Al_{12}Si_{12}O_{48})\cdot 27H_2O\}$.



CH₂
CH – (CH₂)₁₆ – S – O⁻Na⁺
O
O
CH₂
CH₃
HCO₃⁻
H₂O
Ca²⁺
SO₃⁻Na⁺
Ca²⁺
H₂O
SO₃⁻ Na⁺
SO₃⁻
Ca²⁺
SO₃⁻
Na⁺
H₂O
H₂O
Na⁺
Na⁺
H₂O
H₂O
Na⁺ HCO₃⁻
= O
= Al
= Si
Ca²⁺ + HCO₃⁻
Na⁺
Na⁺ + HCO₃⁻
L 14
AGFA
5 2:00PM

* Aplicaciones analíticas del intercambio iónico.

valoraciones titulométricas bifásicas
(*desarrollo analítico farmacéutico*)

separaciones analíticas
(*aminoacidos, cationes*)

Aplicaciones sintéticas del intercambio iónico

*

separaciones preparativas
(*productos naturales, Plutonio)*

desmineralización de agua

síntesis inorgánica

Vehículo de medicamentos

TABLE XIX
Anion Exchange Determination of Alkaloidal Salts

Compounds analyzed	Sample size	Resin, (OH^-) form	Charge	Sample solvent	Eluent	Titrant	Indicator
Salts of Czech. Pharm. 2	100 mg.	Amberlite IR-4B	1 × 10 cm.	Hot 80% ethanol (10 ml.)	Hot 80% ethanol (50 ml.)	0.1*N* HCl	Methyl red–methylene blue
Various alkaloidal salts	100–200 mg.	Amberlite IR-4B	0.5 × 5 cm.	95% Ethanol (20 ml.)	Hot 95% ethanol (50 ml.)[b]	0.1*N* HCl	Methyl red–methylene blue
	10–30 mg.	Amberlite IR-4B	0.8 × 3.5 cm. (2.5 gm.)	Hot 90% ethanol (10 ml.)	Hot 90% ethanol (20 ml.)	0.01*N* HCl	Potentiometrically
	0.5–1.0 meq.	Amberlite IRA-400	0.8 × 7.5 cm.	50% Ethanol	50% Ethanol (50 ml.)	0.1*N* HCl	Bromophenol blue
		Dowex 2	1 × 13.5 cm.	70% Ethanol	70% Ethanol	0.1*N* HCl	Bromophenol blue
Antihistamine salts	0.25 meq.	Amberlite IRA-410[a]	1 × 10 cm.	60% Ethanol (15 ml.)	60% Ethanol (50 ml.)	0.1*N* HCl	Bromocresol green
Local anesthetic salts	20–50 mg.	Amberlite IRA-400	8–10 gm.	75% Ethanol (20 ml.)	Hot 95% ethanol (30 ml.)	0.1*N* HCl	Methyl red
Narcotic salts	75 mg.	Amberlite IR-4B					
Sympathomimetic amine salts		Amberlite IR-45		50% Ethanol	75% Ethanol	0.1*N* HCl	Methyl red
	25 mg.	Amberlite IR-45[d]		Water	75% ethanol (200 ml.)[e]	0.1*N* HCl	Methyl red

[a] Weaker bases are titrated potentiometrically.
[b] Methanol is used for morphine and quinine salts, and 75% ethanol for strychnine nitrate.
[c] A 1 × 20 cm. charge of Amberlite IR-4B may be
[d] Nonphenolic compounds are also determined with
[e] A large volume of eluent is required to remove the

TABLE XX
Cation Exchange Determination of Alkaloidal Bases

Sample	Resin	Solvent	Wash	Eluent	Determination	Refs.
Total alkaloids[a]						
A. Belladonna	IMAC-C22 (H⁺)	70% Alcohol acidulated with HCl	(1) 70% Alcohol, (2) 50% alcohol, (3) water, (4) basic NH_4OH–NH_4Cl buffer, (5) water	1N NH_4OH	A. Titration, 0.1N HCl[b,c]	(394)
B. Cinchona					B. Titration, 0.1N HCl[b]	
C. Hydrastis					C. Gravimetric	
D. Hyoscyamus					D. Titration, 0.1N HCl[b,c]	
E. Ipecac					E. Titration, 0.1N HCl[b]	
F. Lobelia					F. Titration, 0.1N HCl[b]	
G. Nux vomica					G. Titration, 0.1N HCl[b,d]	
Brucine	Duolite CS-101 (NH_4^+)			0.1M NH_4Cl		(830)
Caffeine	Amberlite IRC-50 (H^+)			6N HCl		(829)
Cinchona bark[e]	Zeo-Karb[f] (H^+) Duolite C-10	0.1N H_2SO_4	Dilute NaOH	Alcohol		(24,25) (121)
Cinchona extract	Duolite C-10 (NH_4^+)	46% Alcohol	(1) 46% alcohol, (2) water, (3) basic NH_4OH-NH_4Cl buffer	5% NH_4OH in 95% alcohol	Titration, 0.1N HCl[d]	(120)

Ephedrine	Amberlite IRC-50 (H^+)			6N HCl		(829)
Morphine sulfate	Amberlite IRC-50	Alcohol[a]		0.1N HCl		(361)
	Dowex 50 (H^+)	Water	Water	Aqueous NaOH	Colorimetric, Radulescu reaction	(768)
Morphine	Amberlite IRC-50			0.1N HCl	Spectrophotometric	(1)
	Amberlite IRC-50 (H^+)	Methanol		1N HCl or 4N NH_4OH in methanol		(321)
Morphine sulfate	Amberlite IR-120	Water		4N NH_4OH in methanol		(321)
Nicotine	Duolite CS-101 (NH_4^+)			0.1M NH_4Cl		(830)
Quinine	Amberlite IRC-50			6N HCl		(829)
	Amberlite IRC-50	Absolute alcohol		Ammonia saturated alcohol	Polarimetric	(648)
Quinine hydrochloride	Duolite C-10	30% Alcohol		10% NH_4OH in 95% alcohol		(120)
Quinine sulfate	Zeo-Karb[f] (H^+)	0.1N H_2SO_4	Water	Alcoholic NaOH		(512)
Strychnine	Duolite CS-101 (NH_4^+)			0.1M NH_4Cl		(830)
Sympathomimetic amine salts	Amberlite IRC-50	Water	Water	75% Alcohol	Titration, 0.1N HCl[d]	(779)

[a] In extracts, fluidextracts, tinctures, etc.
[b] Potentiometrically.
[c] To bromophenol blue indicator end point.
[d] To methyl red indicator end point.
[e] Method of preparation of totaquine.
[f] Sulfonated coal.

Table 27

Summary of the application of ion exchangers in medicine with the example of Amberlite exchangers (CE = cation exchanger, AE = anion exchanger)

Stage of application	*Field of application*	*Exchanger type*
Introduced applications	ulcers, hyperacidity	weak base AE; Amberlite IRP-58
	adsorption of toxins, infantile diarrhea	weak base AE; Amberlite IRP-58 plus kaolin
	elimination of sodium, hypertension, and cardiac edema	weak acid CA; Amberlite IRP-64 and Amberlite IRP-88
	elimination of potassium, kidney problems	weak acid CA; Amberlite IRP-64
	tuberculosis; PAS-carrier	weak base AE; Amberlite IRP-58 as carrier for p-aminosalicylic acid
	diagnostic indicator of gastric acid	weak acid CE: Amberlite IRP-64 salt of Azure Blue
	dietary control, allergy, cough suppression	strong acid EC; Amberlite IR-120 as salt with alkaloids, antihistimine, amphetamine
	tablet disintegrator	K-form of weak acid CE; Amberlite IRP-88
	vaginitis	weak acid CE: Amberlite IRP-64
	vitamin B-12 stabilization	weak acid CE: Amberlite IRP-64
	pruritis	strong base AE: Amberlite XE-235
	ointment additive	mixture of all exchangers; Amberlite XE-87
Clinical investigations	against obesity	weak base exchangers with little cross-linking, which swell in the stomach
	as laxative	weak acid exchangers with little cross-linking, which swell in the intestine
	as sustained-release hypertensive agents	nitrate and nitrate forms of AE

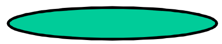
Blood therapy	decalcifying of blood	Amberlite 200
	normalization of blood and transfusion of preserved blood	mixture of all exchanger types
	extracorporeal elimination of K+ and NH_4^+ in hepatic coma	Amberlite 200
	removal of toxins: for example, elimination of aspirin and barbiturates in extracorporeal transfusion	Amberlite IRA-900
	artificial kindneys	
Planned applications	elimination of common salt	Amberlite IR-120
	all-purpose antitoxin	types will low degree of cross-linking
	aspiring stabilization and buffering	aspirin salt of Amberlite IRP-58
	redox control	Amberlite XE-239
	tablet drying	dry Amberlite types as drying agents
	surgical dressings, gauze	ion exchange fibers for pH control and as drug substitutes

Cuadro 2–1. Intercambiadores celulósicos de iones†

Intercambiadores de aniones	Grupo ionizable	mEq/g*
Celulosa AE	Aminoetilo $-O-CH_2-CH_2-NH_2$	0.3–1.0
Celulosa DEAE	Dietilaminoetilo $-O-CH_2-CH_2N(C_2H_5)_2$	0.1–1.1
Celulosa TEAE	Trietilaminoetilo $-O-CH_2-CH_2-N(C_2H_5)_3$ (X)	0.5–1.0
Celulosa GE	Guanidoetilo $-O-CH_2-CH_2-NH-C(=NH)-NH_2$	0.2–0.5
Celulosa PAB	*p*-Aminobencilo $-O-CH_2-C_6H_4-NH_2$	0.2–0.5
Celulosa ECTEOLA	Trietanolamina acoplada con celulosa mediante cadenas de glicerilo y poliglicerilo. Grupos mixtos	0.1–0.5
Celulosa BD	Celulosa DEAE benzoilada	0.8
Celulosa BND	Celulosa DEAE benzoilada y naftoilizada	0.8
Celulosa PEI	Polietilenimina adsorbida a la celulosa o celulosa débil fosforilada	0.1

Intercambiadores de cationes	Grupo ionizable	mEq/g*
Celulosa CM	Carboximetilo $-O-CH_2-COOH$	0.5–1.0
Celulosa P	Fosfato $-O-P(=O)(OH)-OH$	0.7–7.4
Célula SE	Sulfoetilo $-O-CH_2CH_2-S(=O)_2-OH$	0.2–0.3

* La capacidad acidobásica está indicada por el fabricante.



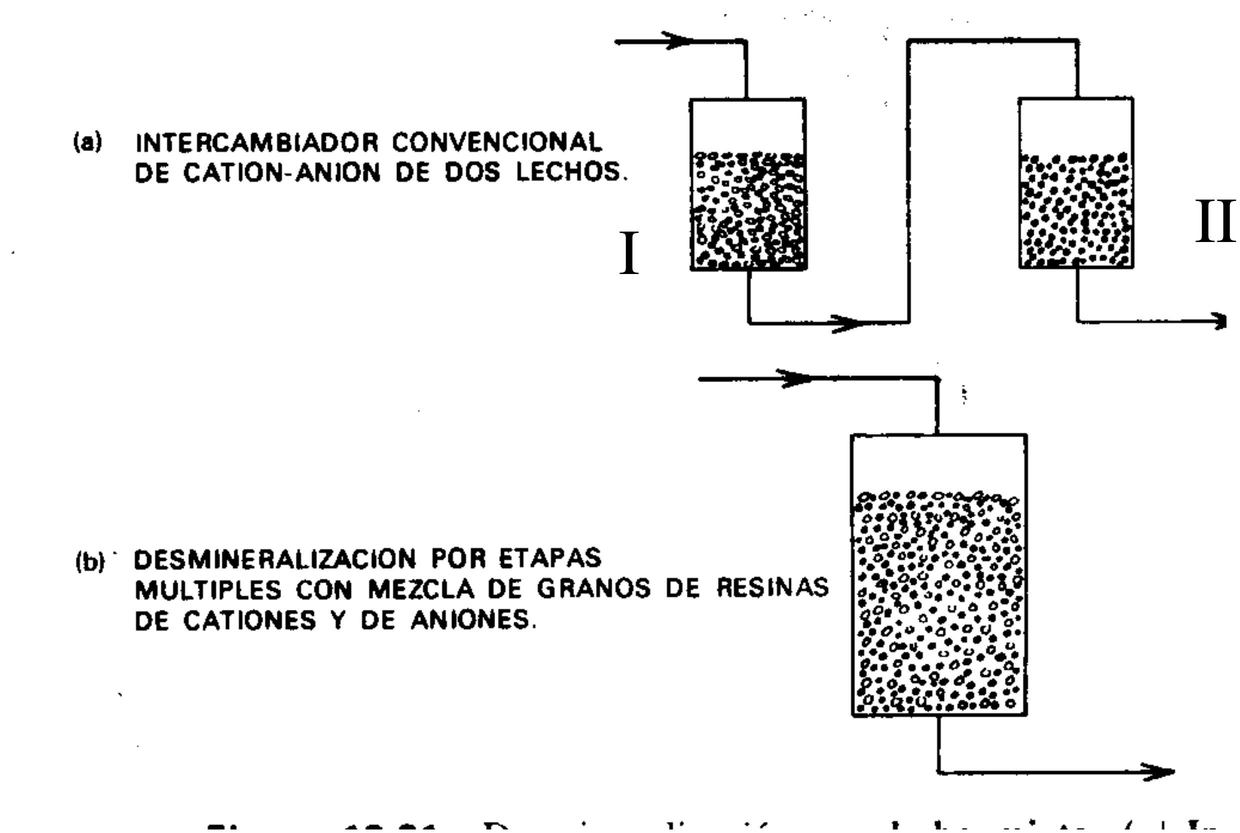
Bacilo Gram (+)
Leuconostoc sp.

Lactosa: disacárido (gluc-galact.)

ATP, gluconatos-Ca↓

Leuconstoc mesenteroides

Azucarantos de Ca.



I $RH + Na^+ \longrightarrow RNa + H^+$

II $ROH + Cl^- \longrightarrow RCl + OH^-$

$\longrightarrow H_2O$

microS/cm

< 1

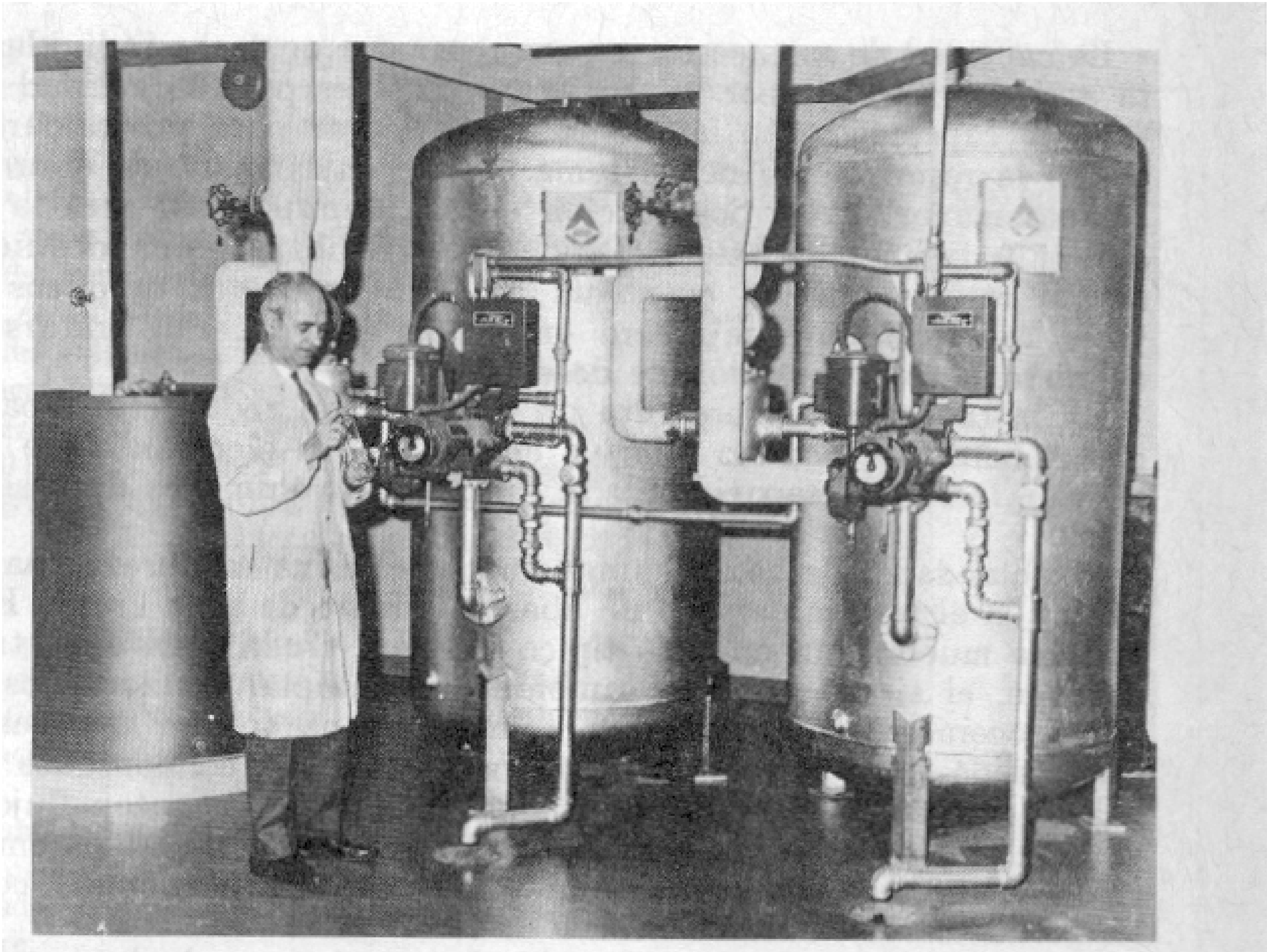


Tabla de variación de especies en intercambio iónico

	zRH	+	M(z+)	=	RzM	+	zH+
Inc	mCi		CoVo=no				
Equil	≈mCi		CoVo(1-f)		fCoVo		10^{-pH}

Log (f/1-f) = f (pH)

$$K_I = \frac{(fCoVo/m)\,(10^{-zpH})}{(Ci)^z\,(Co(1-f))}$$

Log (f/1-f) = log K + zlogCi +log(m/Vo) +zpH

f=fracciòn intercambiada= (n_{int}/n_0)

Ci = capacidad científica de la resina mmolH/g

Condición operatoria= ***mCi >> CoVo; pH impuesto.***

Trazar las graficas log (f/1-f) para el sodio y el calcio y plantear Una posible separacion a pH controlado con resina cationica fuerte Amberlita IR-120 o Dowex 50 (ambas sulfònicas fuertes tipo RH):

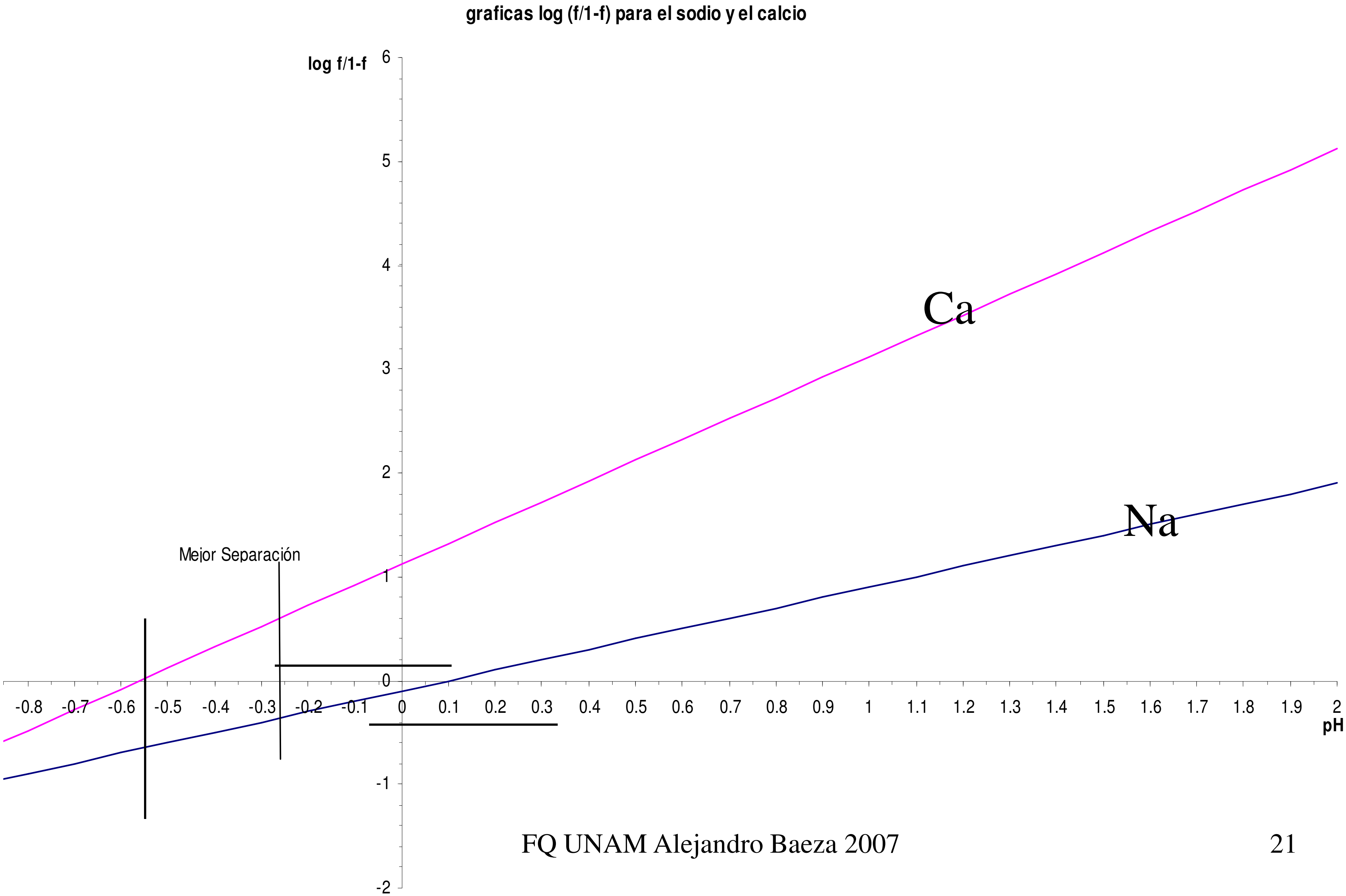
Datos:

$K_{Na,H} = 1.61$ $K_{Ca,H} = (2.28)^2$

Ci = 5 mmol/g; Co = 0.01 M; Vo =25 mL; m=2.5 g.

Tabla 6.1 A. Ringbom
"Formación de complejos en Química Analítica"
Editorial Alhambra. 1979. Pág. 234

$$Log\ (f/1\text{-}f) = log\ K + zlogCi + log(m/Vo) + zpH$$



graficas log (f/1-f) para el sodio y el calcio
log f/1-f
6
5
4
3
2
1
0
-1
-2
-0.8
-0.7
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
pH
Ca
Na
Mejor Separación

Ci = 5 mmol/g; Co = 0.01 M; Co =25 mL; m=2.5 g,

Log (f/1-f) = log K + zlogCi +log(m/Vo) +zpH

Para Na

$$\log (f/1-f) = 0.2 + 0.7 \ -1 + pH = -0.1 + pH$$

Para Ca

$$\log (f/1-f) = 0.72 + 1.4 \ -1 \ +2pH= 1.12+2pH$$

Na(I) + Ca (II)

pH = -0.25; p(m/V) = -1

Fase sólida
80% Ca
30% Na

fase líquida
70% Na
20%Ca