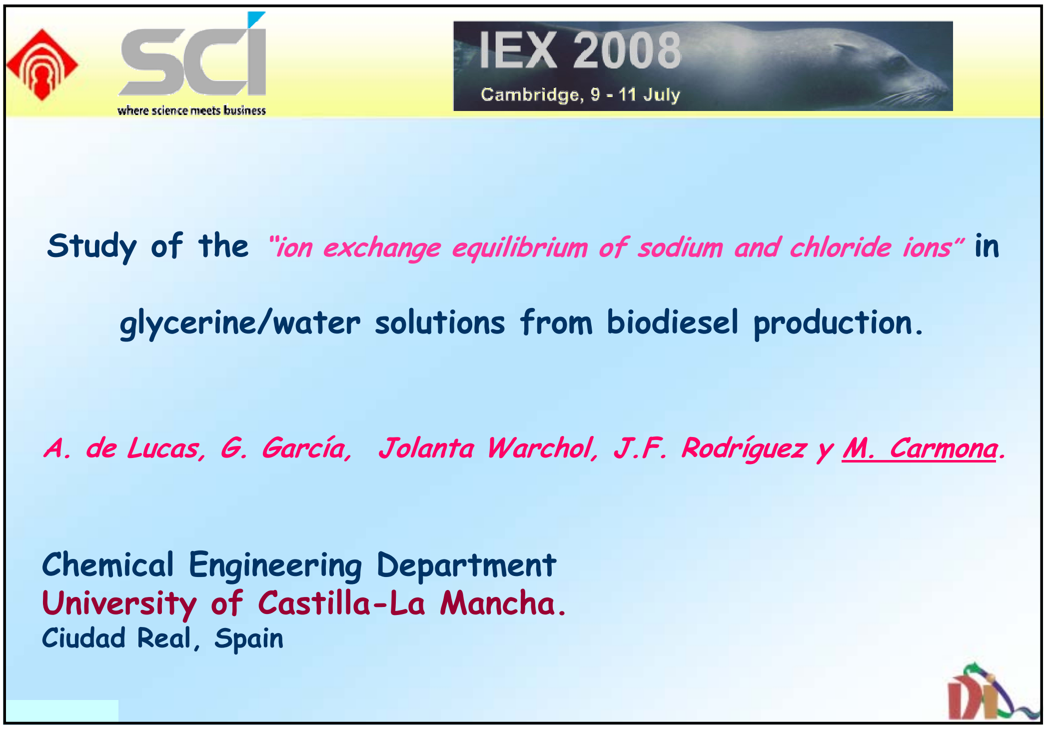

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IEX 2008
Cambridge, 9 - 11 July

Study of the *"ion exchange equilibrium of sodium and chloride ions"* in glycerine/water solutions from biodiesel production.

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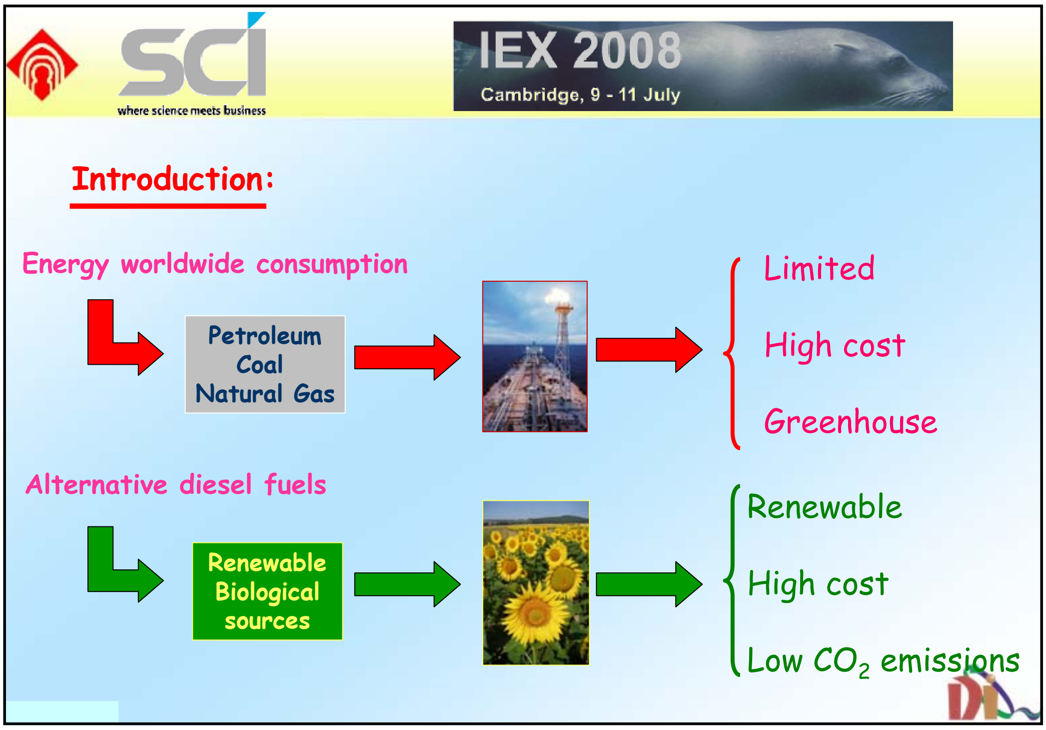

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Introduction:

Energy worldwide consumption

Petroleum
Coal
Natural Gas

- Limited
- High cost
- Greenhouse

Alternative diesel fuels

Renewable
Biological
sources

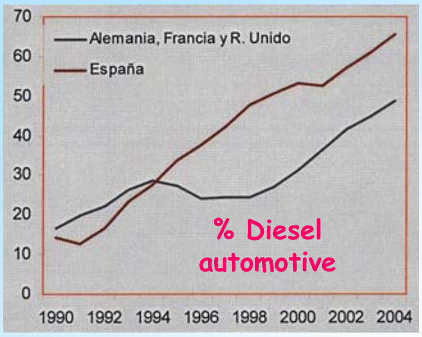
- Renewable
- High cost
- Low CO_2 emissions

Introduction: Securing the Energy Future

Directive 2003/30/EC: Promotion of the use of biofuels or other renewable fuels for transport

2005	2010	2015	2020
2	5.75	7	8 %

Fuel replaced by biofuel



% Diesel automotive

Europe

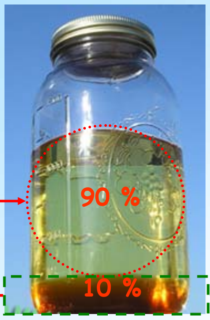
✓ Biodiesel

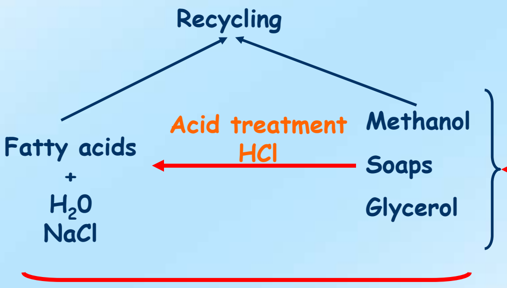
✗ Bioethanol

Introduction: Biodiesel Production

Transesterification:

Vegetable Oil (Triglyceride) + Alcohol $(3\ CH_3OH)$ $\xrightarrow{\text{Catalyst}}$ 60 °C Methyl Ester + Glycerol



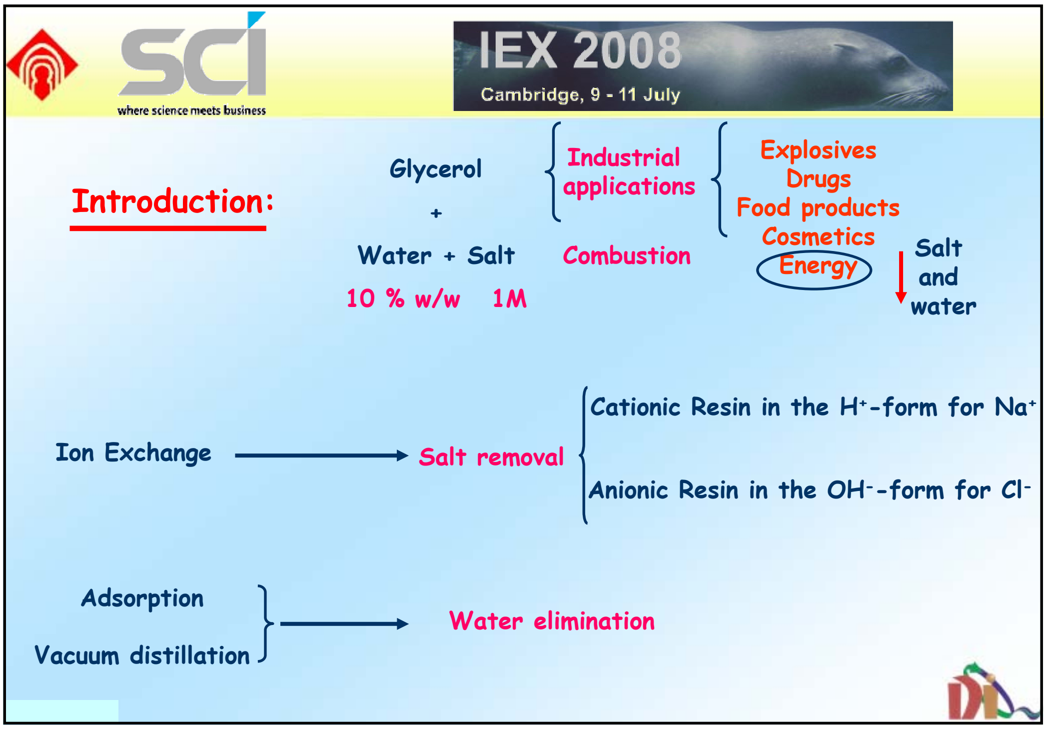


Fatty acids + H_20 NaCl

Acid treatment HCl

Methanol
Soaps
Glycerol

Glycerol+ Water + Salt



Introduction:

Glycerol
+
Water + Salt
10 % w/w 1M

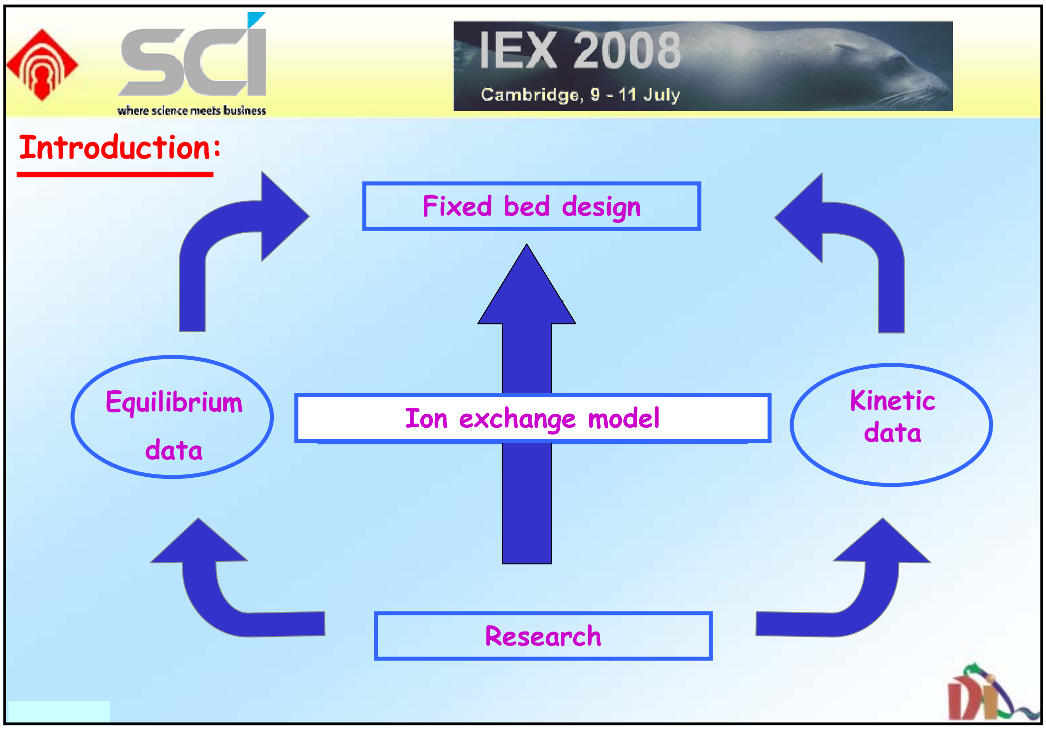
Industrial applications
- Explosives
- Drugs
- Food products
- Cosmetics
- Energy

Combustion

Salt and water

Ion Exchange → Salt removal
- Cationic Resin in the H^+-form for Na^+
- Anionic Resin in the OH^--form for Cl^-

Adsorption
Vacuum distillation
→ Water elimination

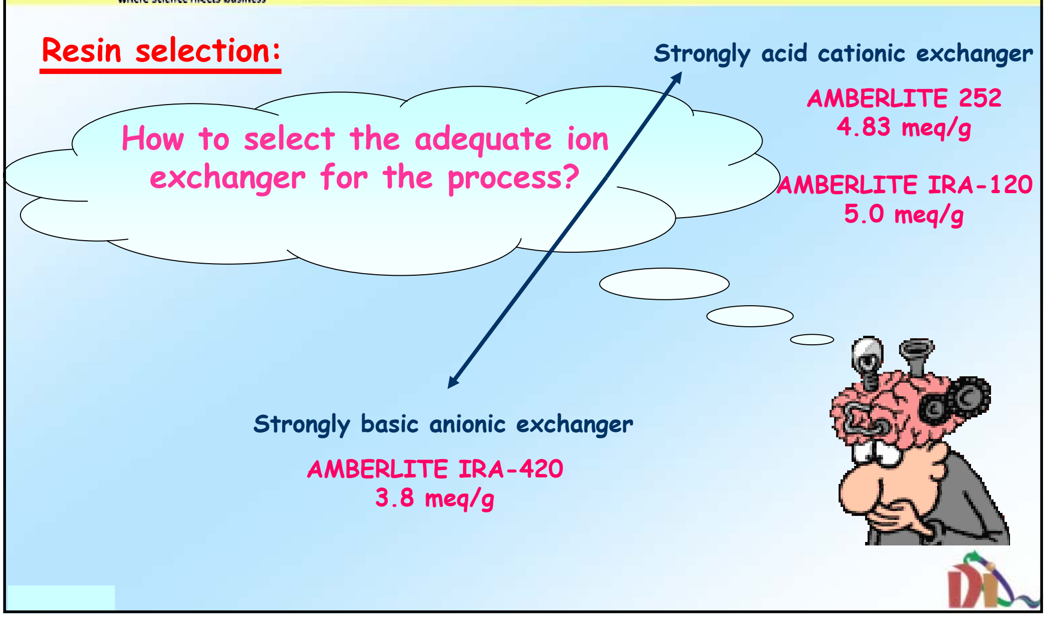


Introduction:

Scope of this Work:

- To determine the equilibrium of ion exchange of sodium ions between a synthetic mixture of glycerine/water 90/10 by weight and a strongly acid cationic exchanger at three different temperatures.
- To determine the equilibrium of ion exchange of chloride ions between a synthetic mixture of glycerine/water 90/10 by weight and a strongly basic anionic exchanger at three different temperatures.
- To evaluate two different models an empirical and another theoretical to reproduce the equilibrium of ion exchange.
- To know the effect of the temperature on effective diffusion coefficients using the cationic exchanger.

Resin selection:



How to select the adequate ion exchanger for the process?

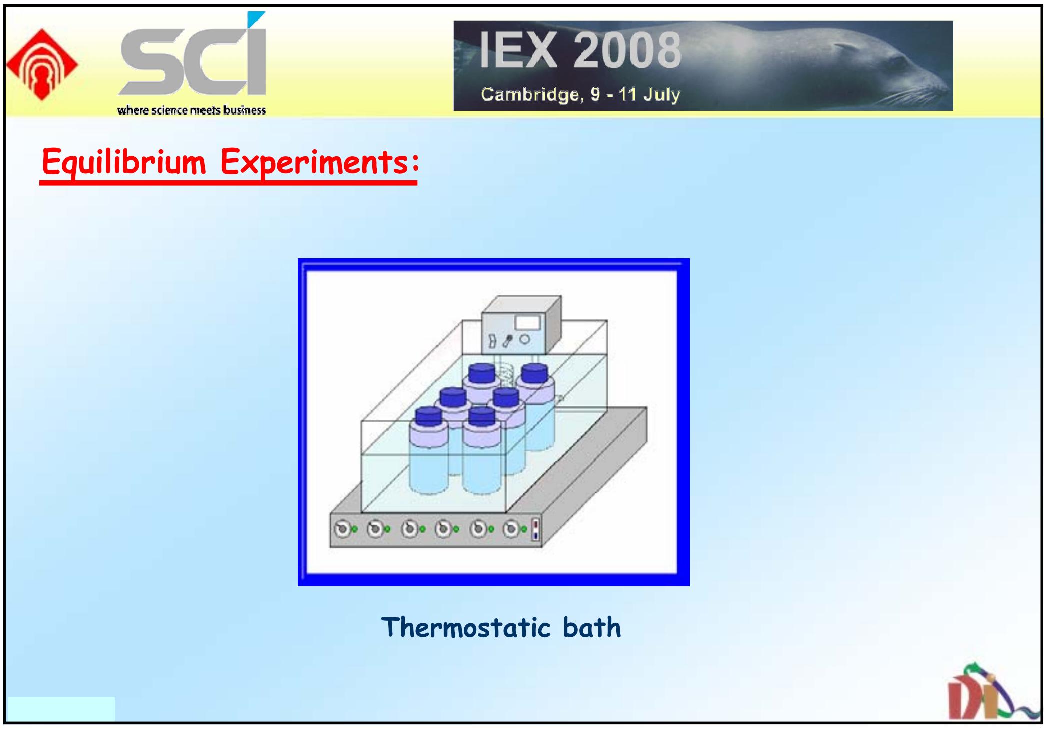
Strongly acid cationic exchanger

AMBERLITE 252
4.83 meq/g

AMBERLITE IRA-120
5.0 meq/g

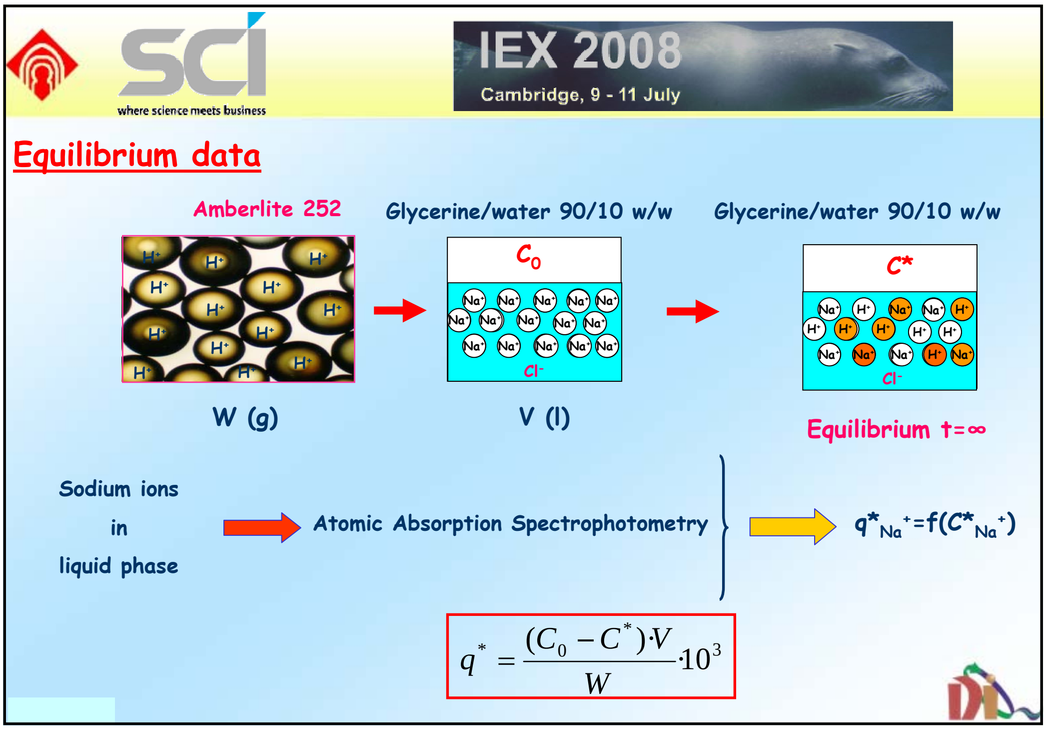
Strongly basic anionic exchanger

AMBERLITE IRA-420
3.8 meq/g



Equilibrium Experiments:

Thermostatic bath



Equilibrium data

Amberlite 252

Glycerine/water 90/10 w/w

Glycerine/water 90/10 w/w

W (g)

V (l)

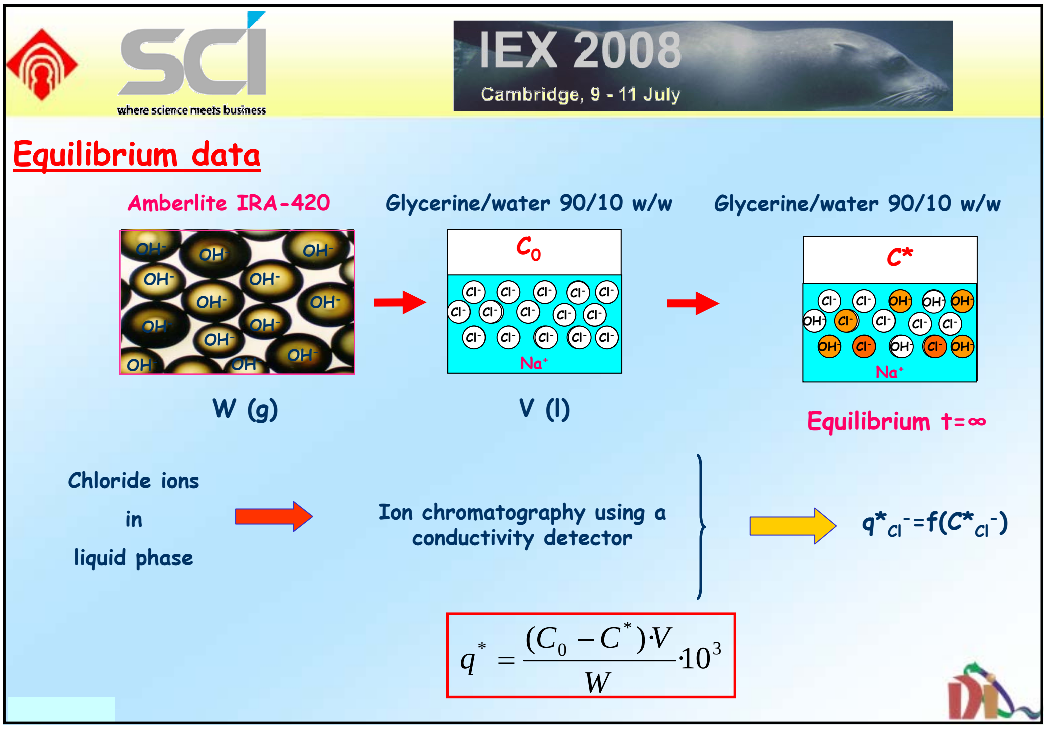
Equilibrium t=∞

Sodium ions
in
liquid phase

Atomic Absorption Spectrophotometry

$q^*_{Na^+} = f(C^*_{Na^+})$

$$\boxed{q^* = \frac{(C_0 - C^*)\cdot V}{W}\cdot 10^3}$$



Equilibrium data

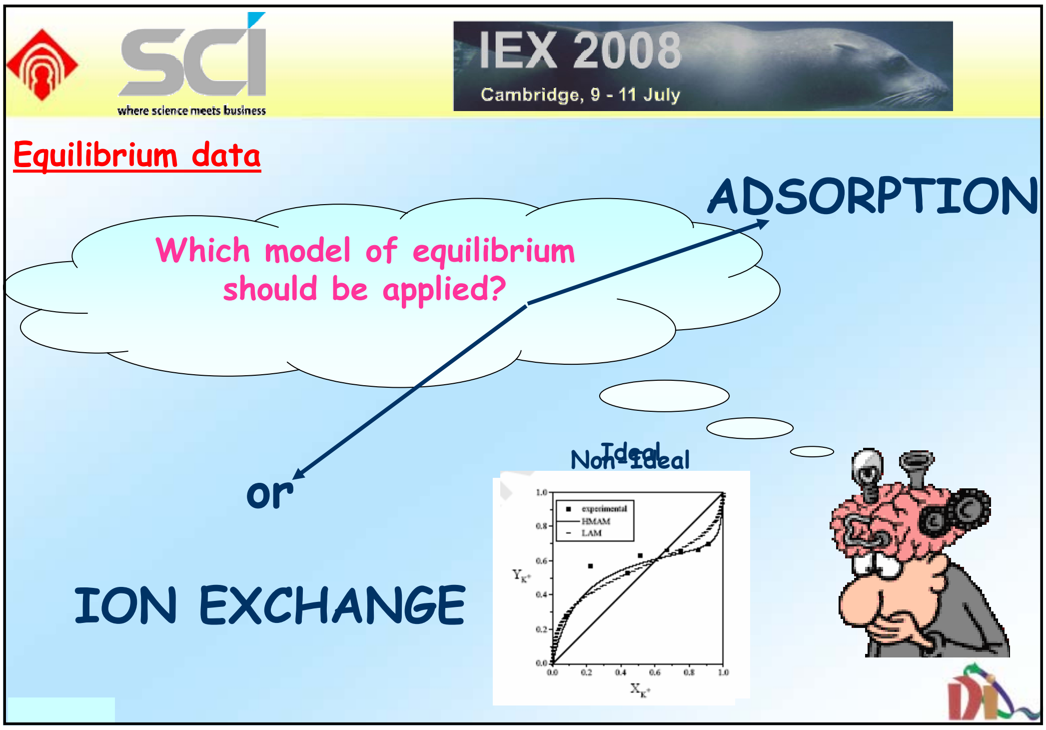
Equilibrium t=∞

Chloride ions
in
liquid phase

Ion chromatography using a conductivity detector

$q^*_{Cl^-} = f(C^*_{Cl^-})$

$$q^* = \frac{(C_0 - C^*)\cdot V}{W} \cdot 10^3$$



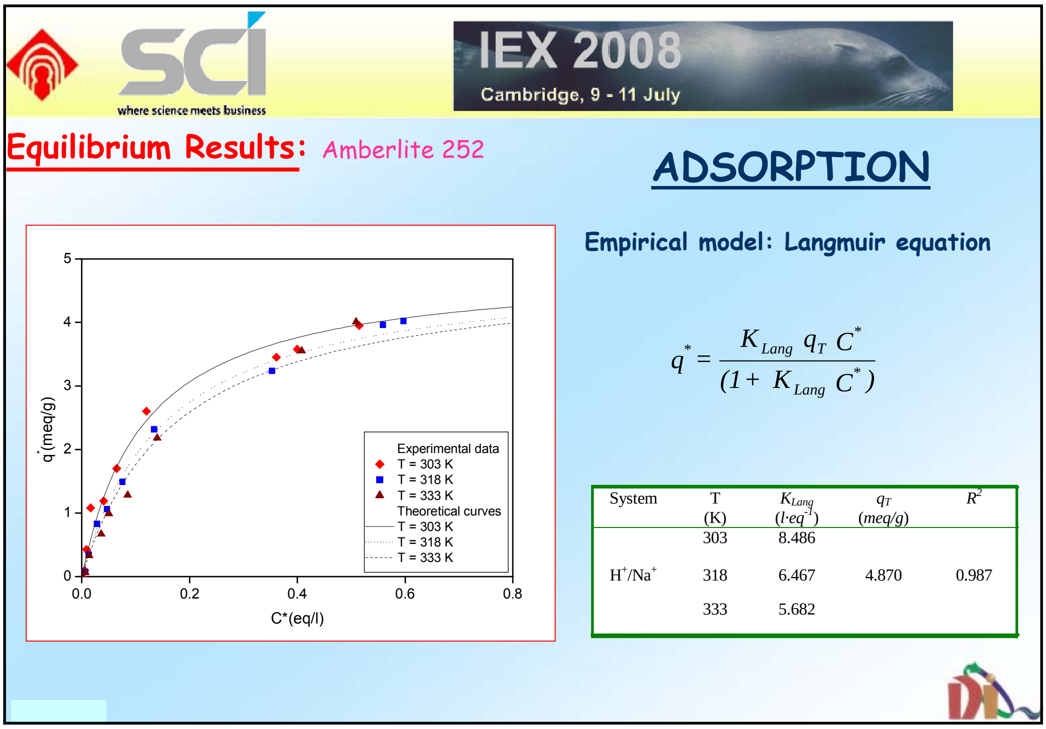
Equilibrium data

Which model of equilibrium should be applied?

ADSORPTION

or

ION EXCHANGE



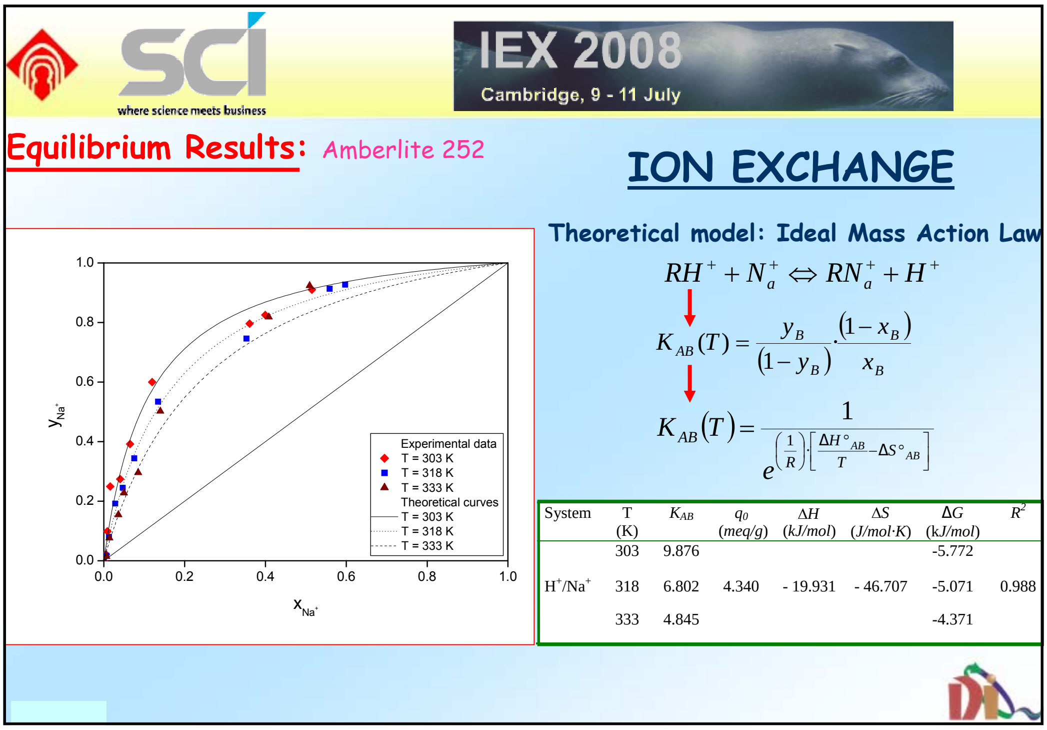
Equilibrium Results: Amberlite 252

ADSORPTION

Empirical model: Langmuir equation

$$q^{*} = \frac{K_{Lang}\ q_T\ C^{*}}{(1 + K_{Lang}\ C^{*})}$$

System	T (K)	K_{Lang} $(l \cdot eq^{-1})$	q_T (meq/g)	R^2
	303	8.486		
H^+/Na^+	318	6.467	4.870	0.987
	333	5.682		



Equilibrium Results: Amberlite 252

ION EXCHANGE

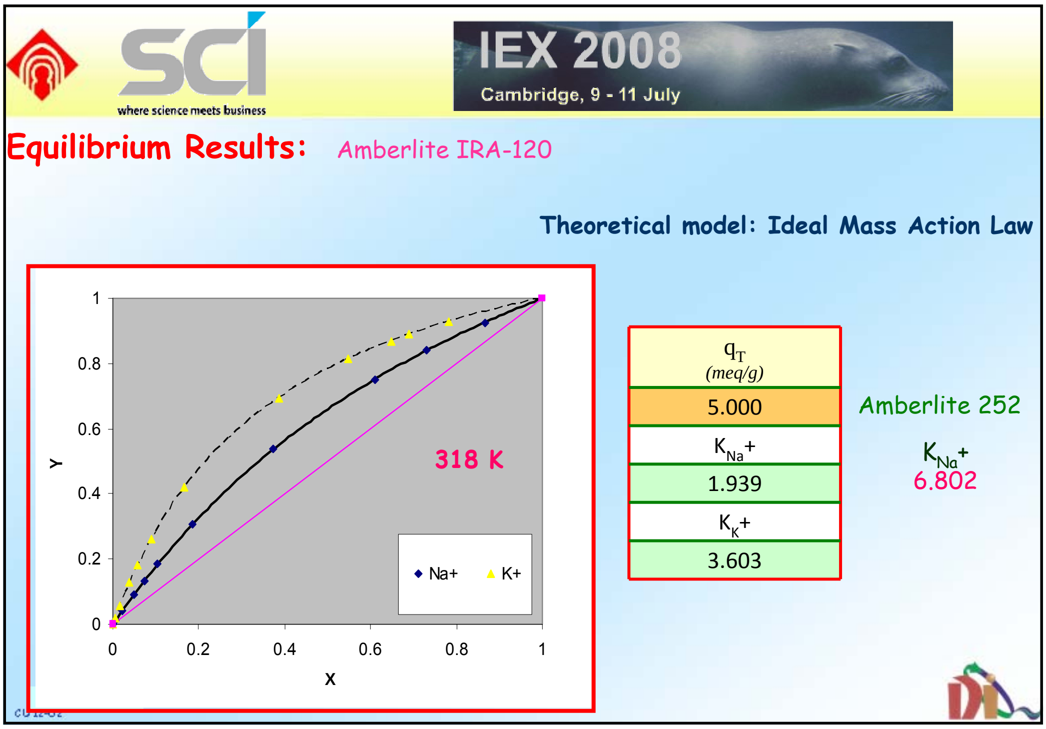
Theoretical model: Ideal Mass Action Law

$$RH^{+} + N_a^{+} \Leftrightarrow RN_a^{+} + H^{+}$$

$$K_{AB}(T) = \frac{y_B}{(1-y_B)} \cdot \frac{(1-x_B)}{x_B}$$

$$K_{AB}(T) = \frac{1}{e^{\left(\frac{1}{R}\right)\cdot\left[\frac{\Delta H^{\circ}_{AB}}{T} - \Delta S^{\circ}_{AB}\right]}}$$

System	T (K)	K_{AB}	q_0 (meq/g)	ΔH (kJ/mol)	ΔS $(J/mol \cdot K)$	ΔG (kJ/mol)	R^2
	303	9.876				-5.772	
H^+/Na^+	318	6.802	4.340	- 19.931	- 46.707	-5.071	0.988
	333	4.845				-4.371	



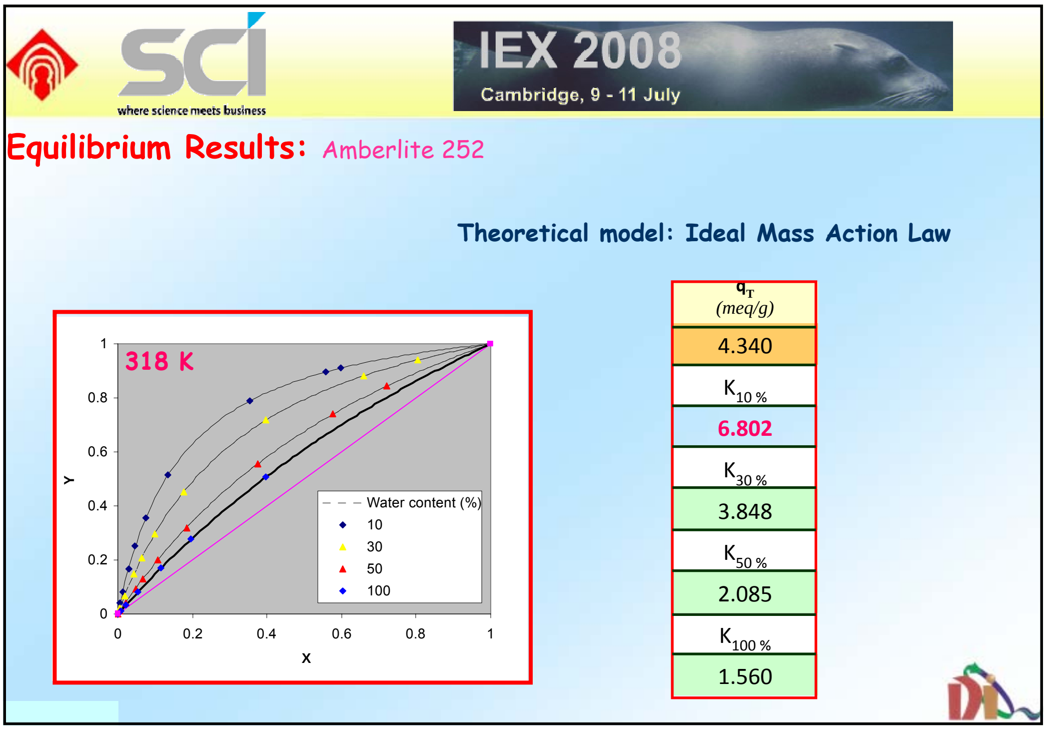
Equilibrium Results: Amberlite IRA-120

Theoretical model: Ideal Mass Action Law

q_T *(meq/g)*
5.000
K_{Na^+}
1.939
K_{K^+}
3.603

Amberlite 252

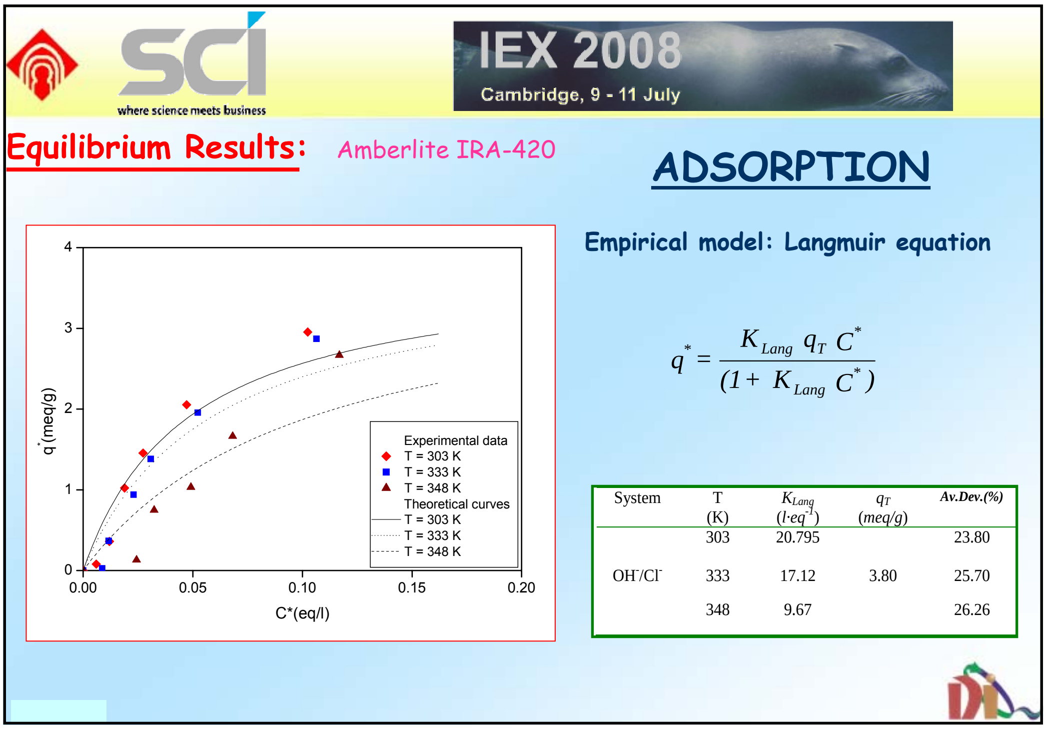
K_{Na^+}
6.802



Equilibrium Results: Amberlite 252

Theoretical model: Ideal Mass Action Law

q_T *(meq/g)*
4.340
$K_{10\,\%}$
6.802
$K_{30\,\%}$
3.848
$K_{50\,\%}$
2.085
$K_{100\,\%}$
1.560



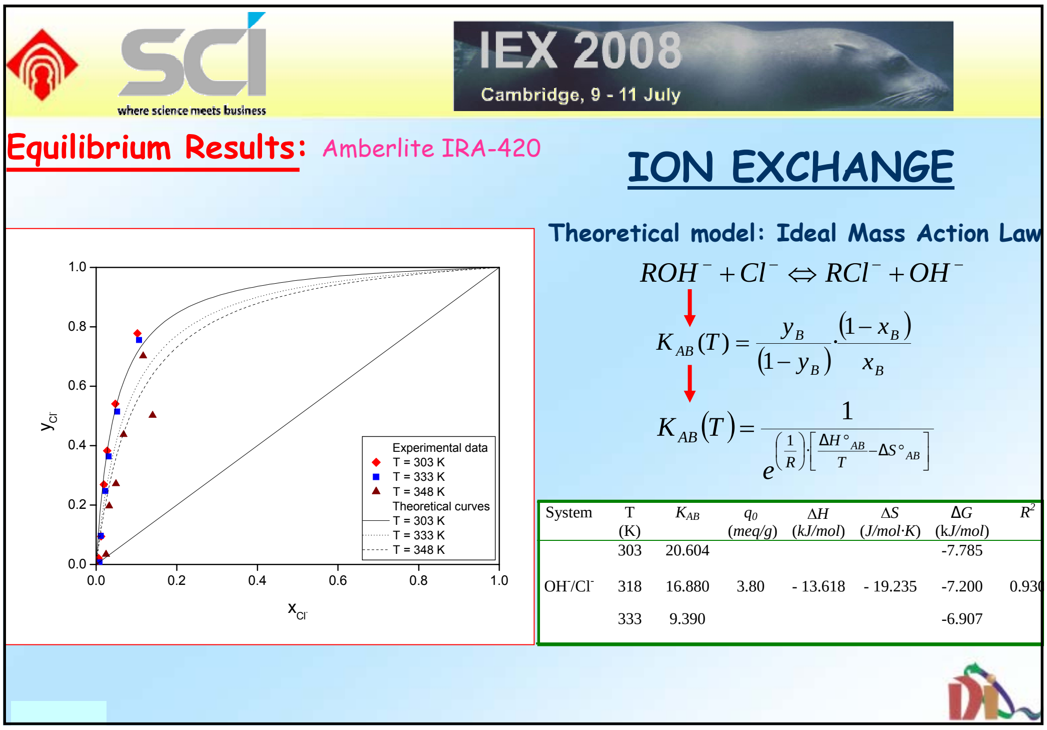
Equilibrium Results: Amberlite IRA-420

ADSORPTION

Empirical model: Langmuir equation

$$q^* = \frac{K_{Lang}\ q_T\ C^*}{(1 + K_{Lang}\ C^*)}$$

System	T (K)	K_{Lang} ($l \cdot eq^{-1}$)	q_T (*meq/g*)	***Av.Dev.(%)***
	303	20.795		23.80
OH^-/Cl^-	333	17.12	3.80	25.70
	348	9.67		26.26



Equilibrium Results: Amberlite IRA-420

ION EXCHANGE

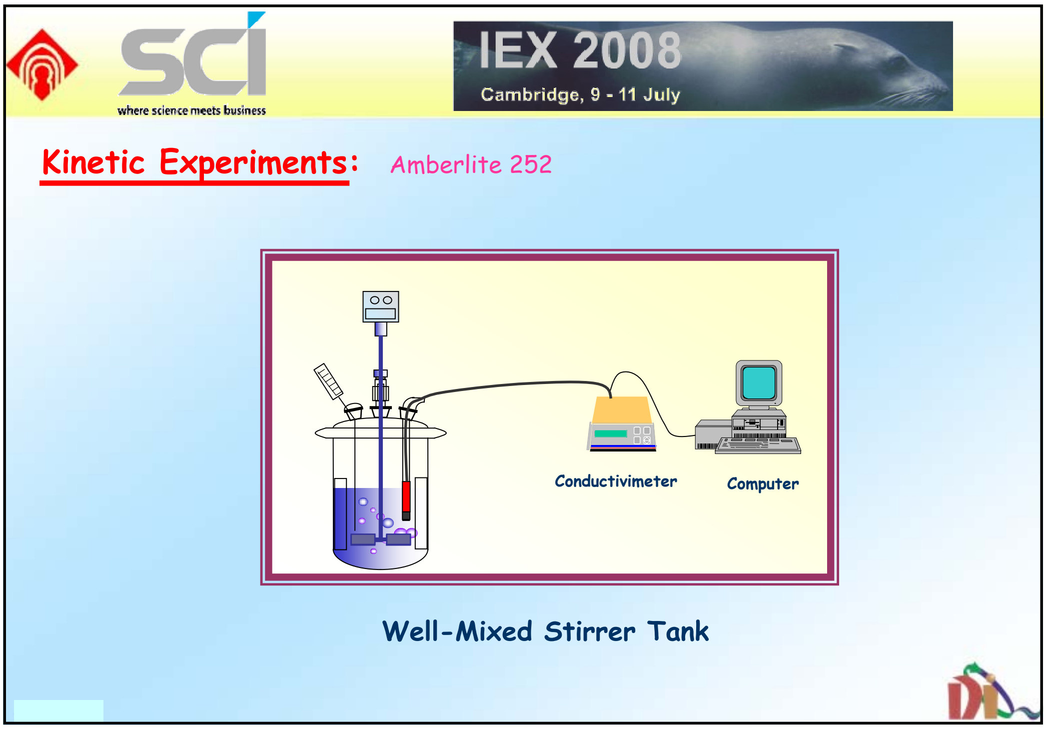
Theoretical model: Ideal Mass Action Law

$$ROH^- + Cl^- \Leftrightarrow RCl^- + OH^-$$

$$K_{AB}(T) = \frac{y_B}{(1-y_B)} \cdot \frac{(1-x_B)}{x_B}$$

$$K_{AB}(T) = \frac{1}{e^{\left(\frac{1}{R}\right) \cdot \left[\frac{\Delta H^\circ_{AB}}{T} - \Delta S^\circ_{AB}\right]}}$$

System	T (K)	K_{AB}	q_0 (*meq/g*)	ΔH (*kJ/mol*)	ΔS (*J/mol·K*)	ΔG (kJ/mol)	R^2
	303	20.604				-7.785	
OH^-/Cl^-	318	16.880	3.80	- 13.618	- 19.235	-7.200	0.930
	333	9.390				-6.907	



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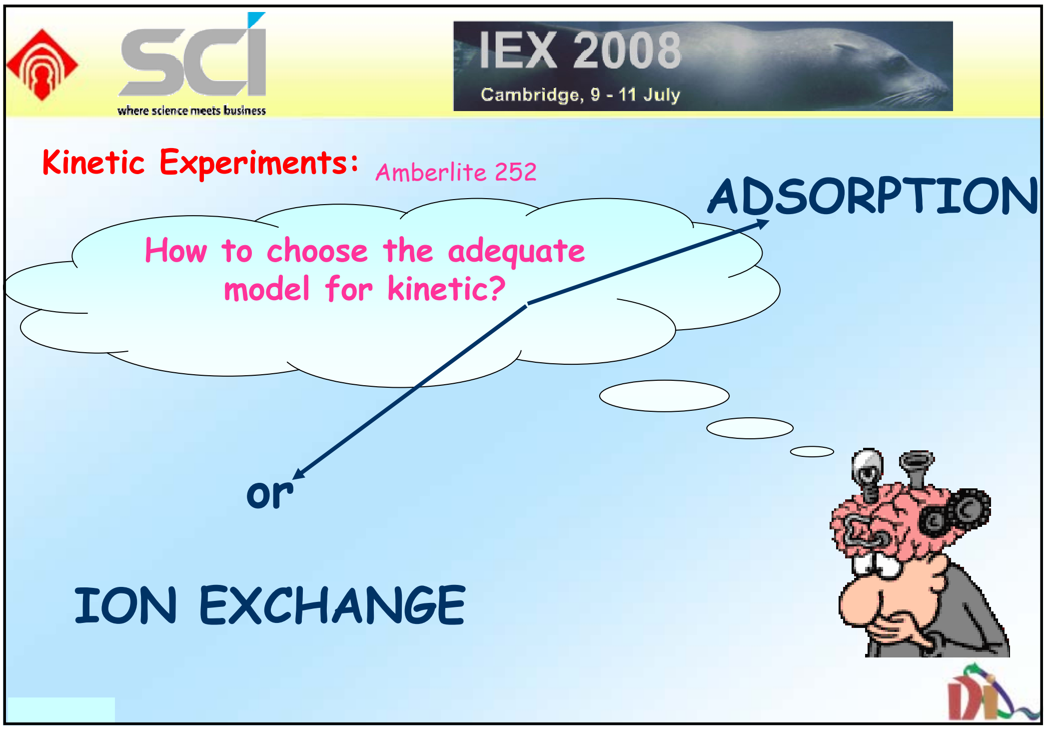
Kinetic Experiments: Amberlite 252

Well-Mixed Stirrer Tank



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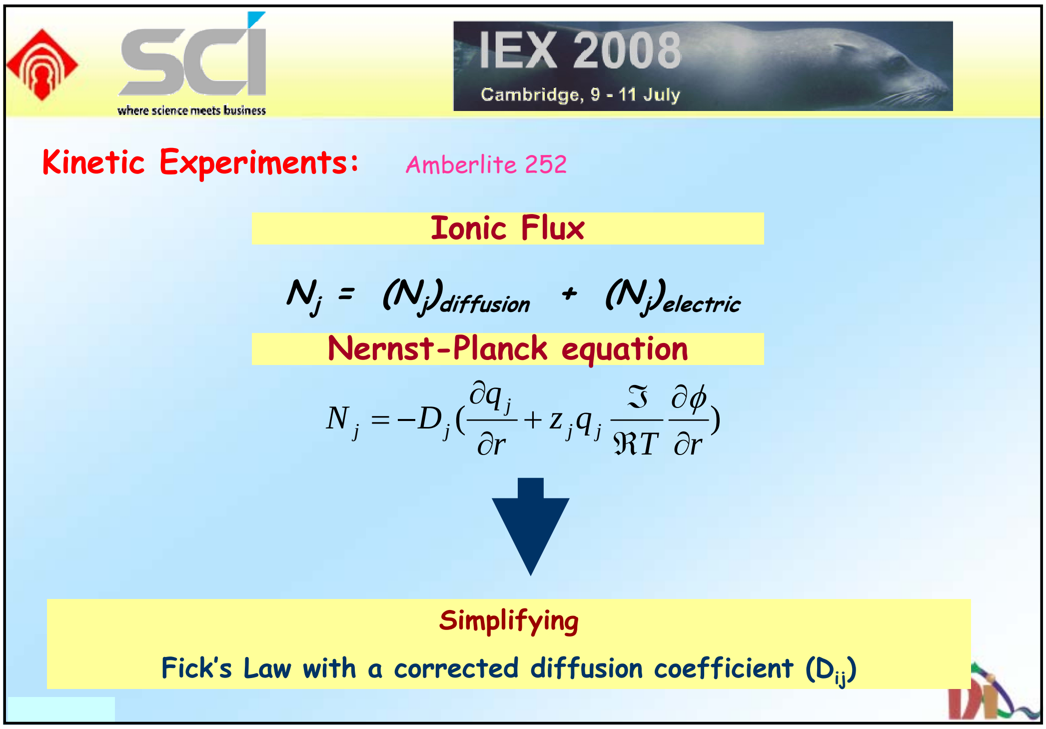
Kinetic Experiments: Amberlite 252

How to choose the adequate model for kinetic?

ADSORPTION

or

ION EXCHANGE



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Kinetic Experiments: Amberlite 252

Ionic Flux

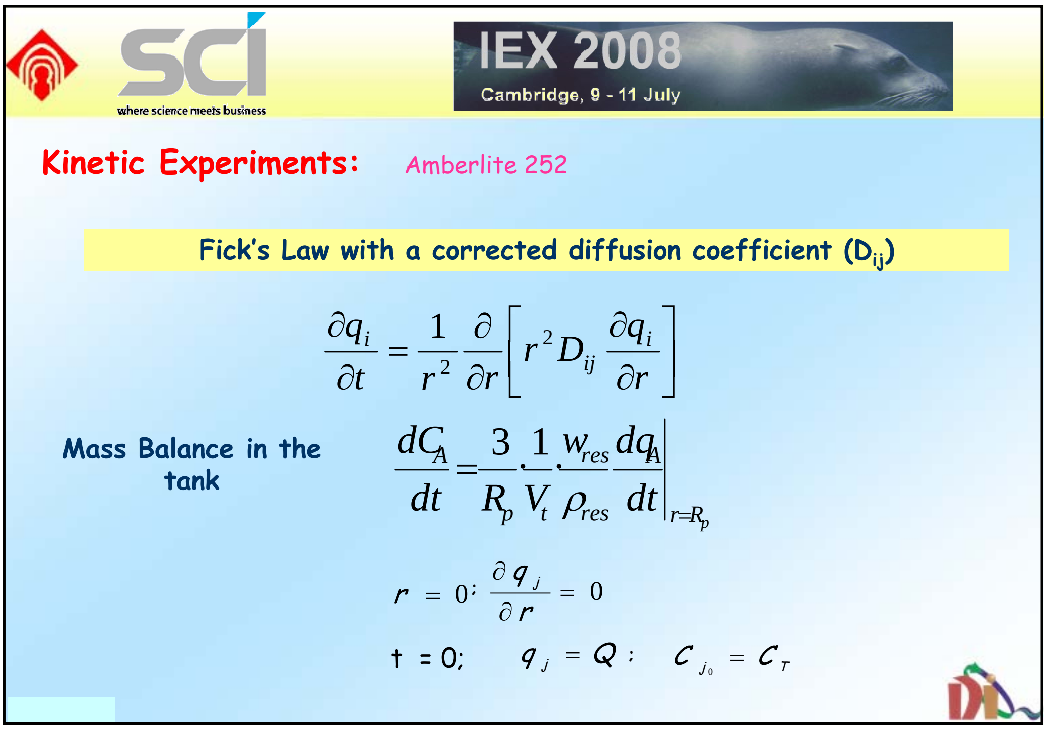
$$N_j = (N_j)_{diffusion} + (N_j)_{electric}$$

Nernst-Planck equation

$$N_j = -D_j \left(\frac{\partial q_j}{\partial r} + z_j q_j \frac{\Im}{\Re T} \frac{\partial \phi}{\partial r} \right)$$

Simplifying

Fick's Law with a corrected diffusion coefficient (D_{ij})



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Kinetic Experiments: Amberlite 252

Fick's Law with a corrected diffusion coefficient (D_{ij})

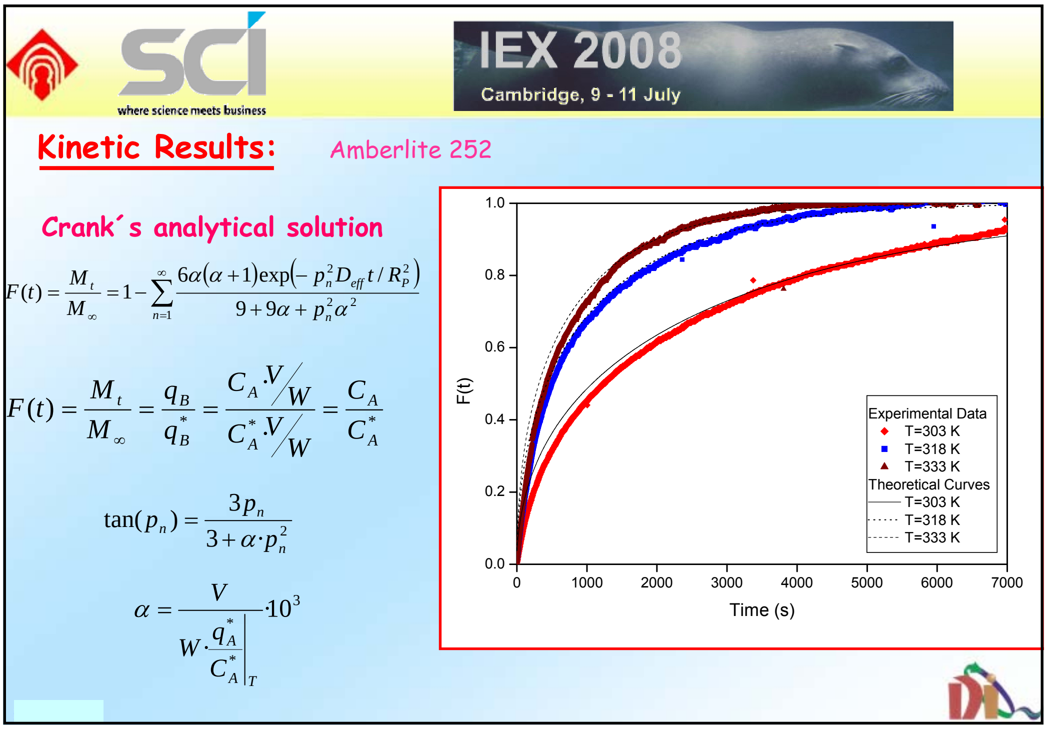
$$\frac{\partial q_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_{ij} \frac{\partial q_i}{\partial r} \right]$$

Mass Balance in the tank

$$\frac{dC_A}{dt} = \frac{3}{R_p} \cdot \frac{1}{V_t} \cdot \frac{w_{res}}{\rho_{res}} \left. \frac{dq_A}{dt} \right|_{r=R_p}$$

$$r = 0; \quad \frac{\partial q_j}{\partial r} = 0$$

$$t = 0; \quad q_j = Q; \quad C_{j_0} = C_T$$



Kinetic Results: Amberlite 252

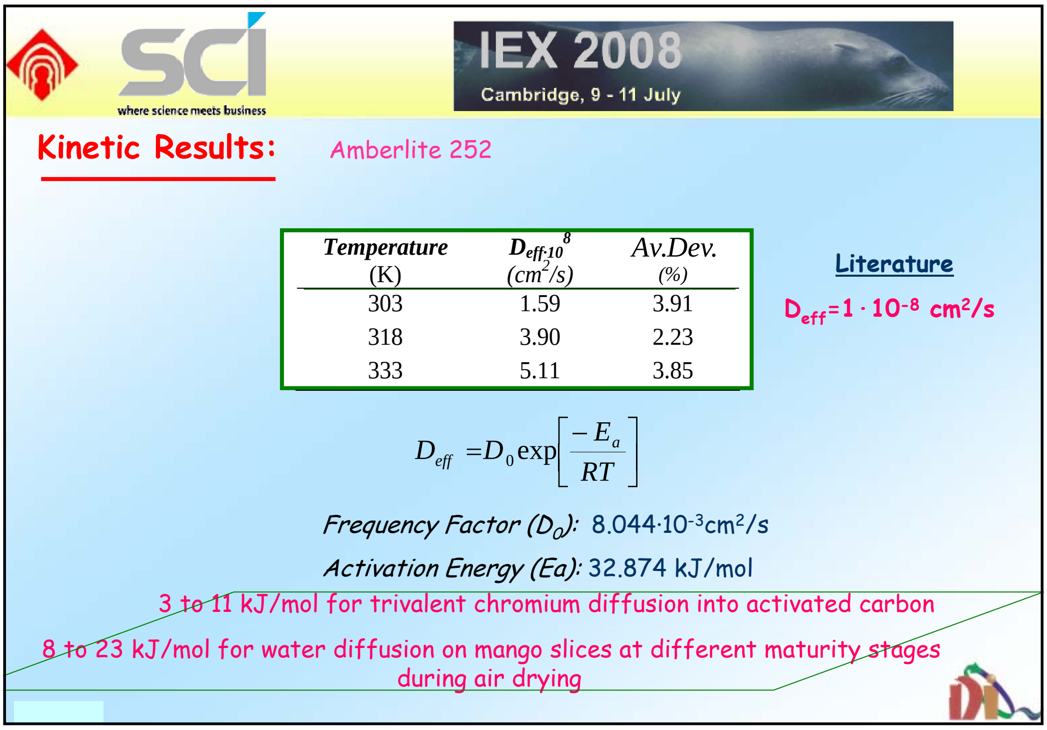
Crank´s analytical solution

$$F(t)=\frac{M_t}{M_\infty}=1-\sum_{n=1}^{\infty}\frac{6\alpha(\alpha+1)\exp\left(-p_n^2 D_{eff}t/R_P^2\right)}{9+9\alpha+p_n^2\alpha^2}$$

$$F(t)=\frac{M_t}{M_\infty}=\frac{q_B}{q_B^*}=\frac{C_A.V/W}{C_A^*.V/W}=\frac{C_A}{C_A^*}$$

$$\tan(p_n)=\frac{3p_n}{3+\alpha\cdot p_n^2}$$

$$\alpha=\frac{V}{W\cdot\left.\frac{q_A^*}{C_A^*}\right|_T}\cdot 10^3$$



Kinetic Results: Amberlite 252

Temperature (K)	$D_{eff}\cdot10^8$ (cm^2/s)	*Av.Dev.* (%)
303	1.59	3.91
318	3.90	2.23
333	5.11	3.85

Literature

$D_{eff}=1\cdot10^{-8}$ cm^2/s

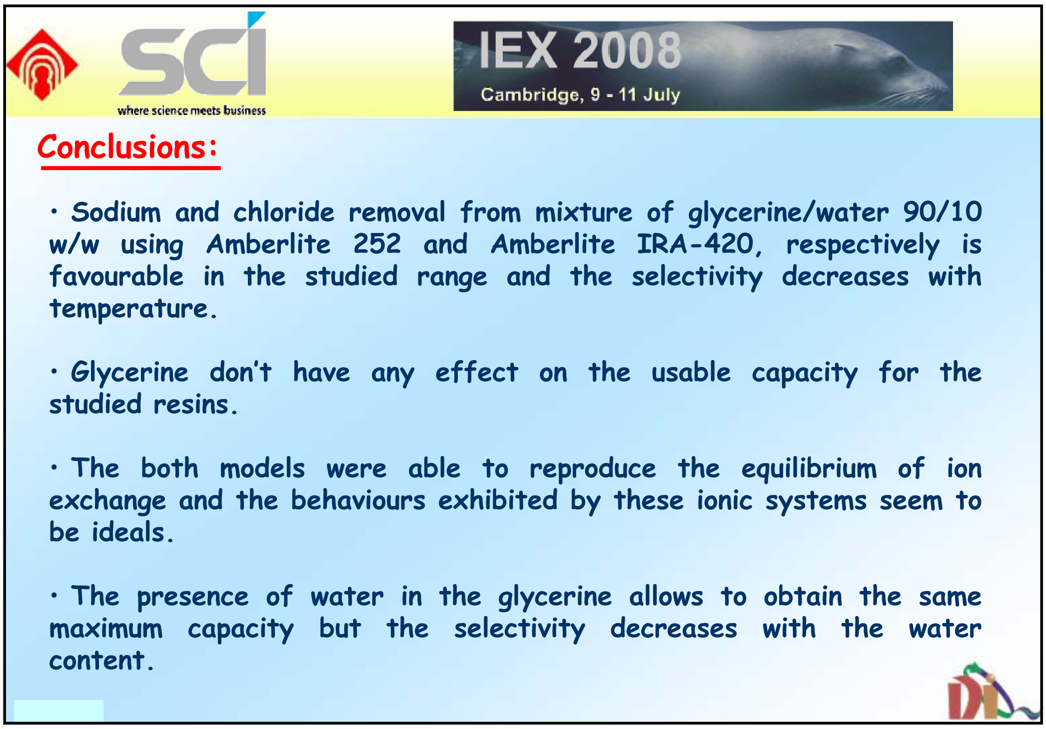
$$D_{eff}=D_0\exp\left[\frac{-E_a}{RT}\right]$$

Frequency Factor (D_0): $8.044\cdot10^{-3}cm^2/s$

Activation Energy (Ea): 32.874 kJ/mol

3 to 11 kJ/mol for trivalent chromium diffusion into activated carbon

8 to 23 kJ/mol for water diffusion on mango slices at different maturity stages during air drying



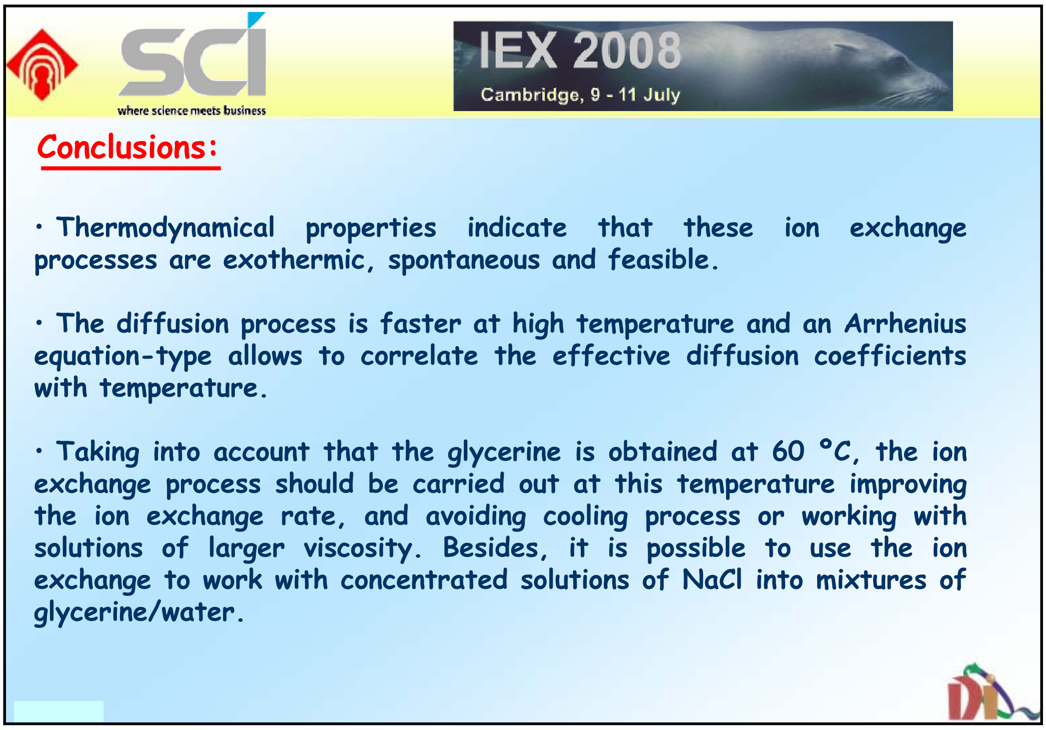
Conclusions:

- Sodium and chloride removal from mixture of glycerine/water 90/10 w/w using Amberlite 252 and Amberlite IRA-420, respectively is favourable in the studied range and the selectivity decreases with temperature.

- Glycerine don't have any effect on the usable capacity for the studied resins.

- The both models were able to reproduce the equilibrium of ion exchange and the behaviours exhibited by these ionic systems seem to be ideals.

- The presence of water in the glycerine allows to obtain the same maximum capacity but the selectivity decreases with the water content.



Conclusions:

- Thermodynamical properties indicate that these ion exchange processes are exothermic, spontaneous and feasible.

- The diffusion process is faster at high temperature and an Arrhenius equation-type allows to correlate the effective diffusion coefficients with temperature.

- Taking into account that the glycerine is obtained at 60 °C, the ion exchange process should be carried out at this temperature improving the ion exchange rate, and avoiding cooling process or working with solutions of larger viscosity. Besides, it is possible to use the ion exchange to work with concentrated solutions of NaCl into mixtures of glycerine/water.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Thank you for your attention

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