RIDEAL LECTURE 2010

A joint award of the

Royal Society of Chemistry and

The Society of Chemical Industry

Controlling the Properties of Aqueous Interfaces

Wednesday 10 March 2010
SCI HQ, London, UK

Organised by SCI's Colloid & Surface Chemistry Group and the RSC's Colloid & Interface Science Group

PFPC

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AUSTRALIAN RESEARCH COUNCIL

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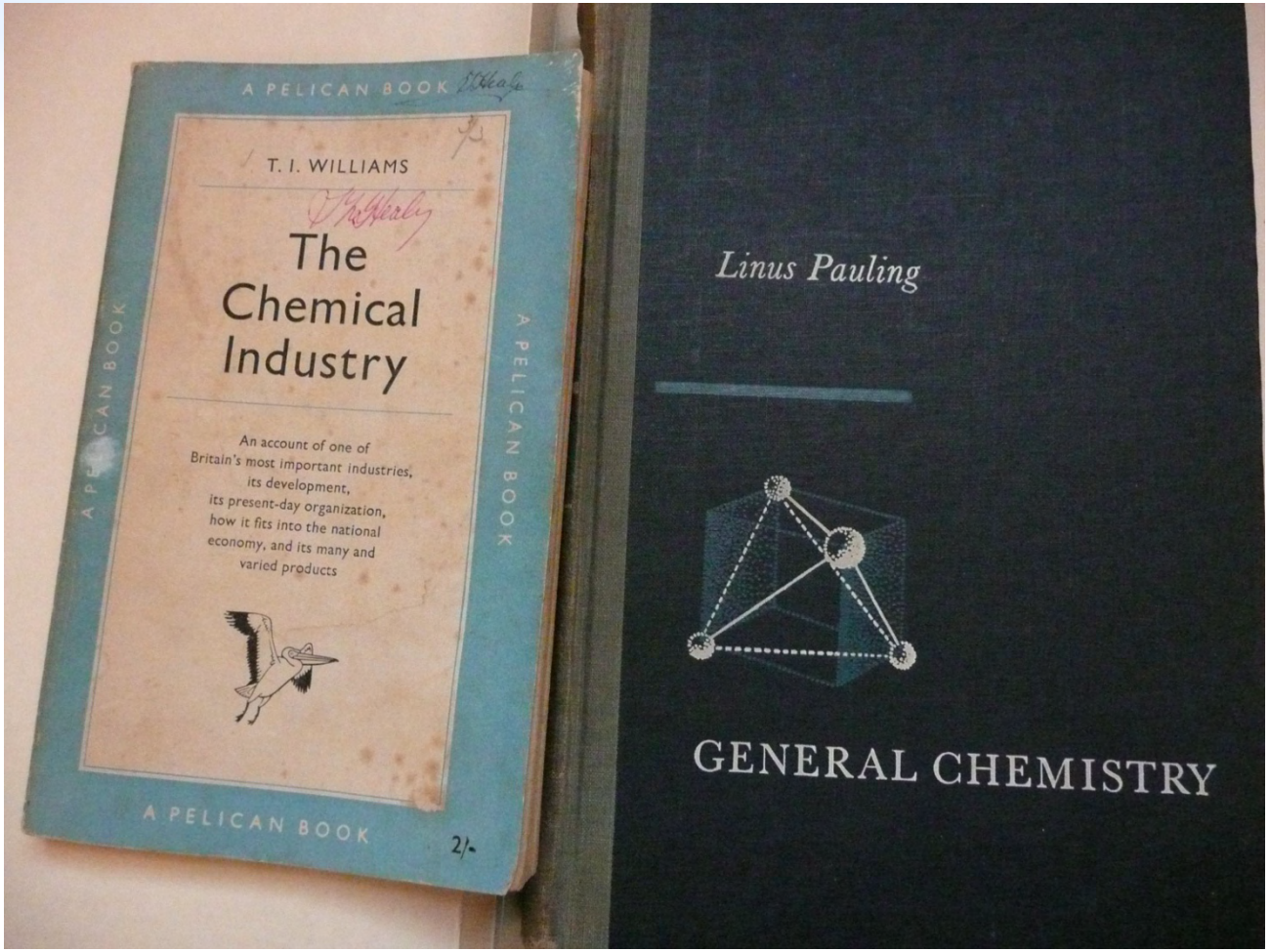
T.W.Healy 1955-present

THE UNIVERSITY OF MELBOURNE

Chemistry 1, 1955
The University of Melbourne
…..Preliminary reading!!



2010 Rideal Award of RSC-SCI

I am delighted !

I am so fortunate to have had such a happy life in chemistry. Why? Due to what ?

1. An amazingly supportive family.

2. I have worked with an amazing cohort of **students**.

and

3. I have worked with an amazing group of **colleagues in industry and academia** around the world

My Special Thank You

1. My Family

My Special Thank You

2. MY STUDENTS

“All my ex-students are perfect”

(Healy 1979)

“Yes, but some are more perfect than others!”

(David Yates 1980)

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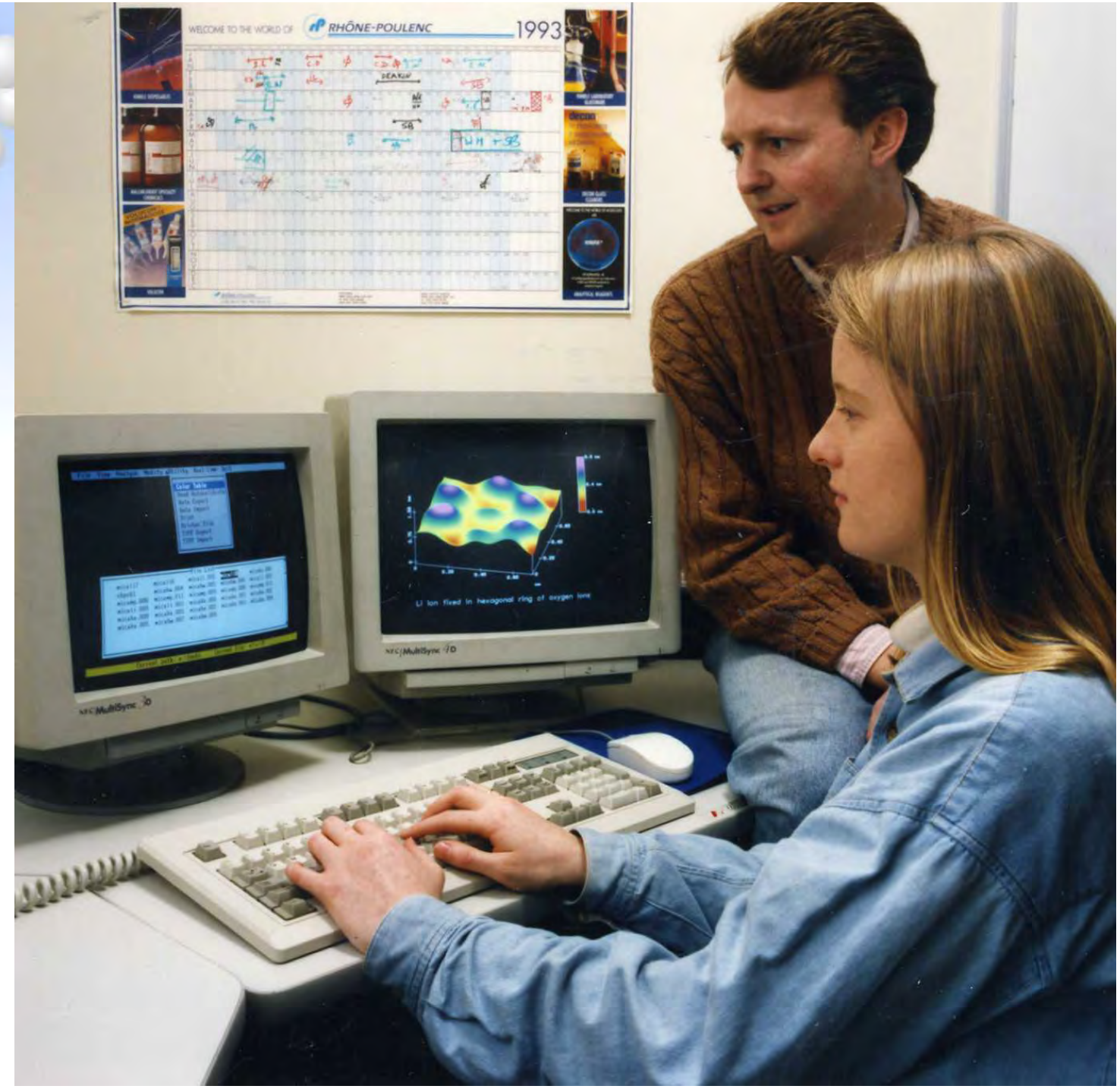
My Special Thank You

3. My Colleagues

My ICI UK Colleagues

My Academic Colleagues



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Pen opening is
Oct. at 7.30PM HERE
BRING YOUR SELF.
1. Stairwell
2. Car Park
3. Only
4. Not
5. Good
DEMONSTRATING
PIG PEN GOLD
$5 Membership
Specials
Coopers Stubby
The Stubbies
LINEA
LINEA

The electrical double layer at the hydrophilic and hydrophobic material-water interfaces----
-------the enemy or salvation of engineers and formulators!

Tom Healy,
Department of Chemical & Biomolecular Engineering,
University of Melbourne, Australia
tomhealy@unimelb.edu.au

The Chemistry Bit

---- Hydrophilic Interfaces First

Electrical Double Layer Charge & Potential controlled by Potential Determining Ions,(pdi)

For AgI, for example, Ag+ or I- are pdi

$$d\,\psi_0 = RT/nF\; d\ln(a_{Ag+})$$

i.e. 59 mv /decade change in Ag+ concn.

Electrical Double Charge & Potential (Cont.)

-For mineral oxides, alkaline earth sulphates or carbonates, clays, latex colloids…….similar reversibility cannot be assigned unambiguously to any pdi species,

-BUT the e.d.l. potentials appear to be controlled by H^+ /OH^- species as if these ions are pdi.

The Chemistry Bit (continued)

Mineral/Metal oxides, clays,latices,……

e.g. TiO_2, SiO_2,Fe_2O_3,Al_2O_3

H+ /OH- are involved in surface site equilibria

$$MOH_2^+ \leftrightarrow MOH \leftrightarrow MO^-$$

where $K+ = (N_0/N_+).a_{H+}$ and $K- = (N-/N_0).a_{H+}$

Where the total number of sites is $N = N_+ + N_0 + N_-$

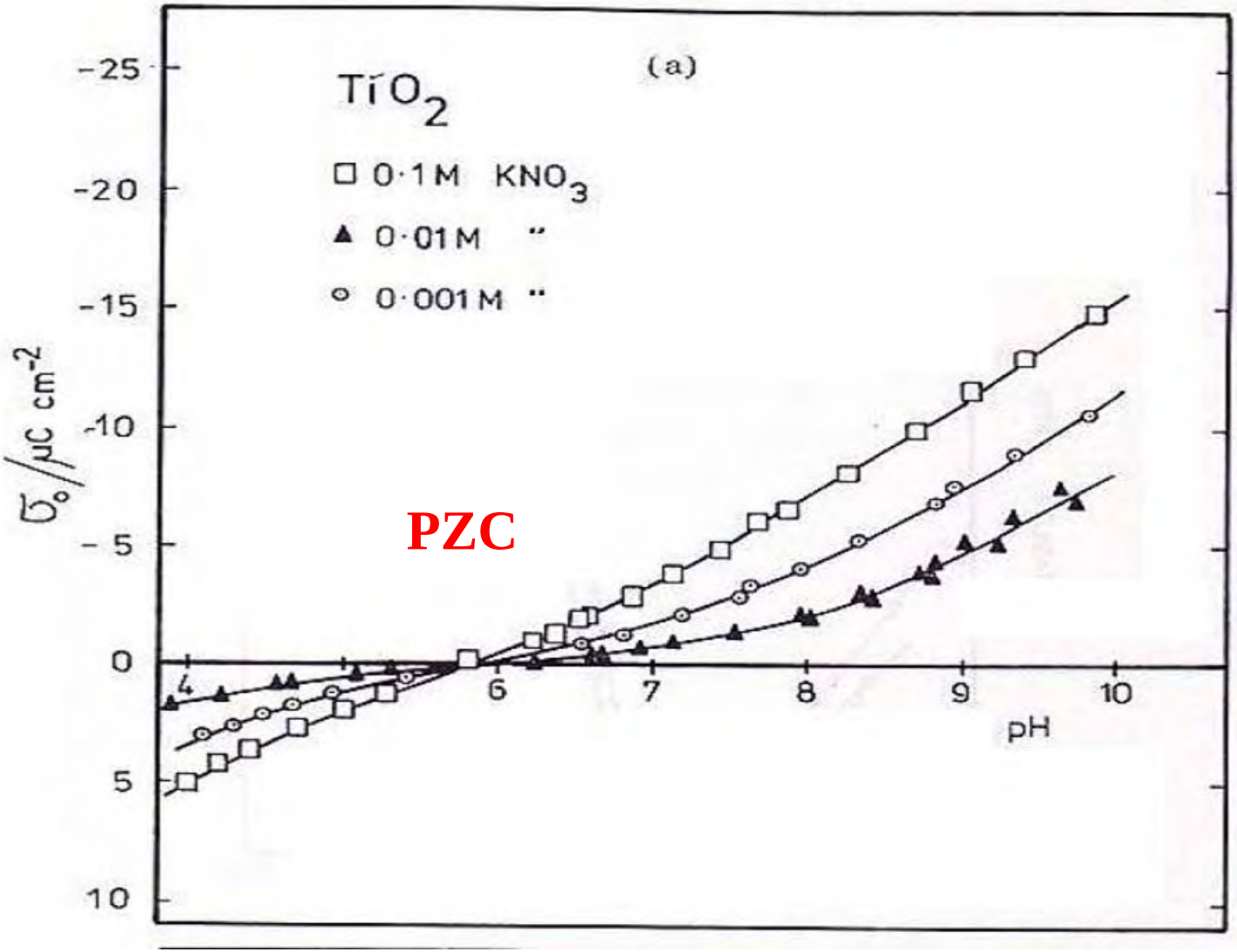
Notice that $K+.K- = (N_-/N_+).\ a_{H+}^2$ and

$N- = N+$ at pH_0 ,the pH of the i.e.p./p.z.c.

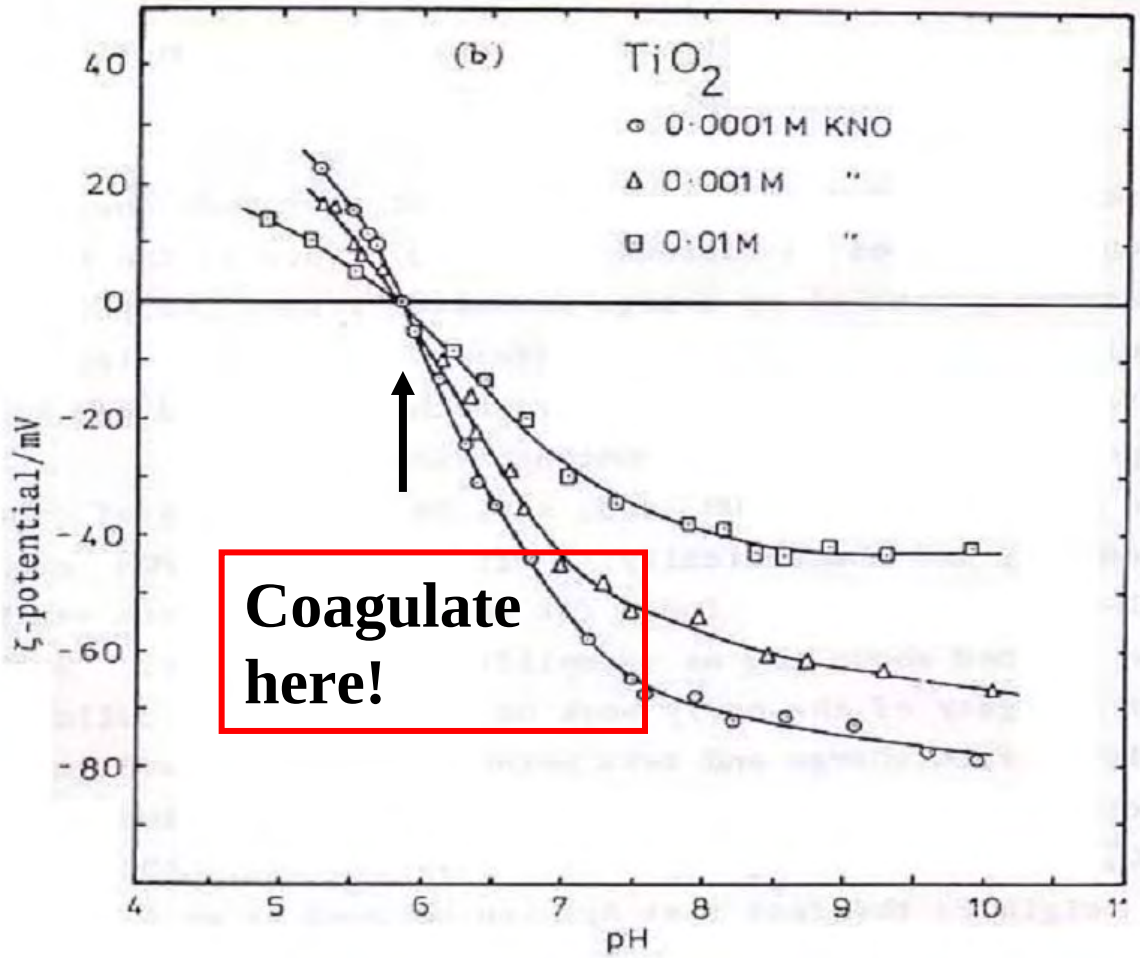
Such that $pHo = ½ (pK_+ + pK_-)$

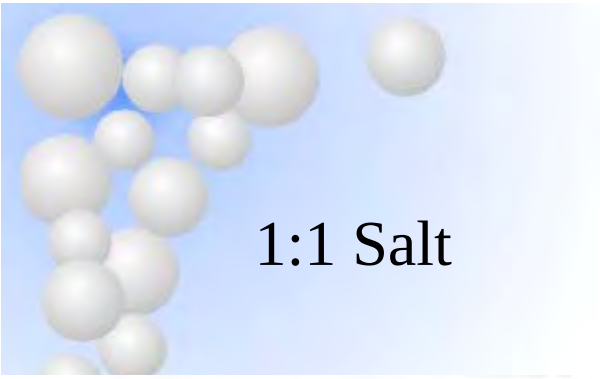
Titratable Surface Charge

Metal Oxides….H^+/OH^- are potential determining ions.



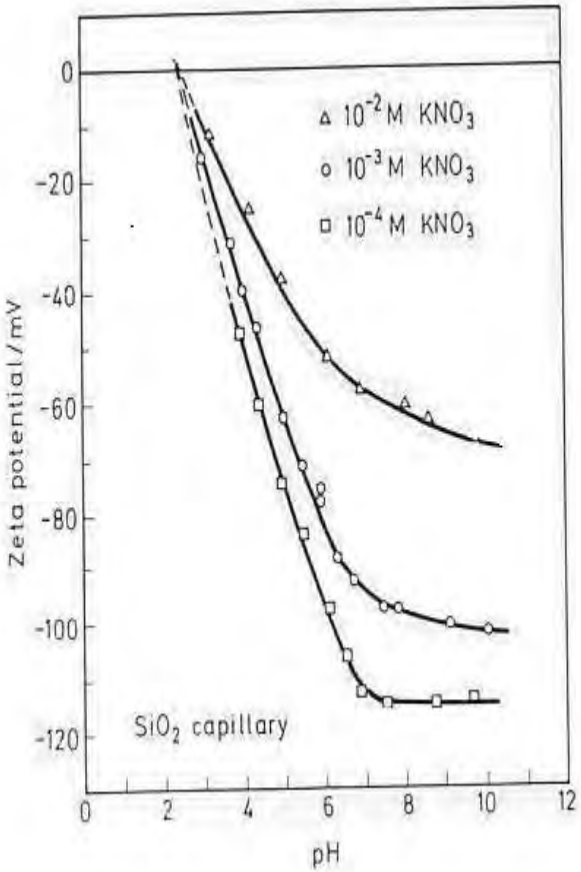
I.E.P/P.Z.C……Titania (rutile)

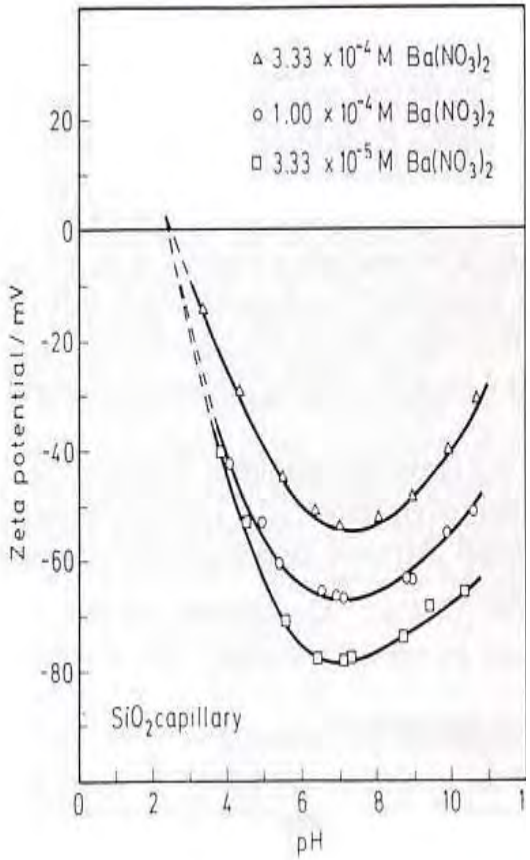


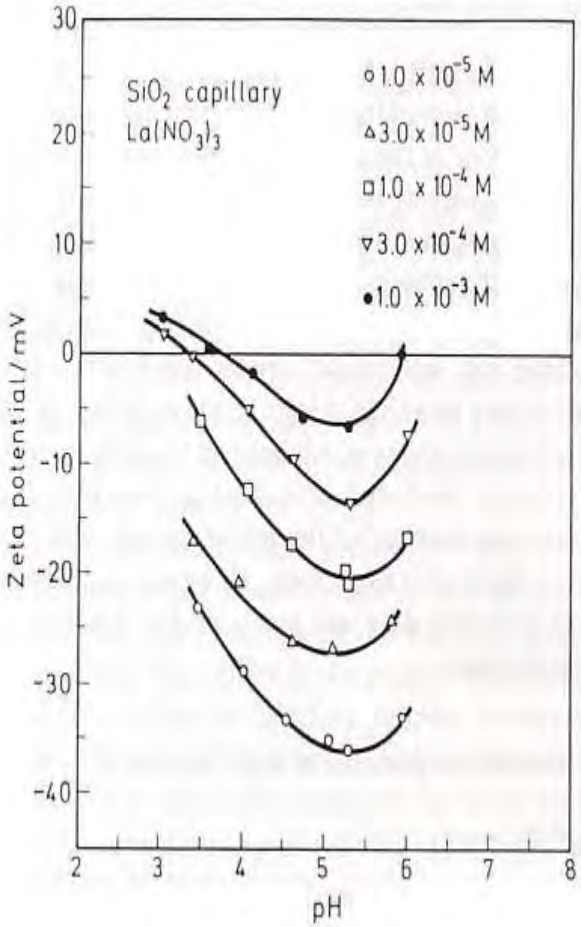


1:1 Salt

2 : 1 Salt





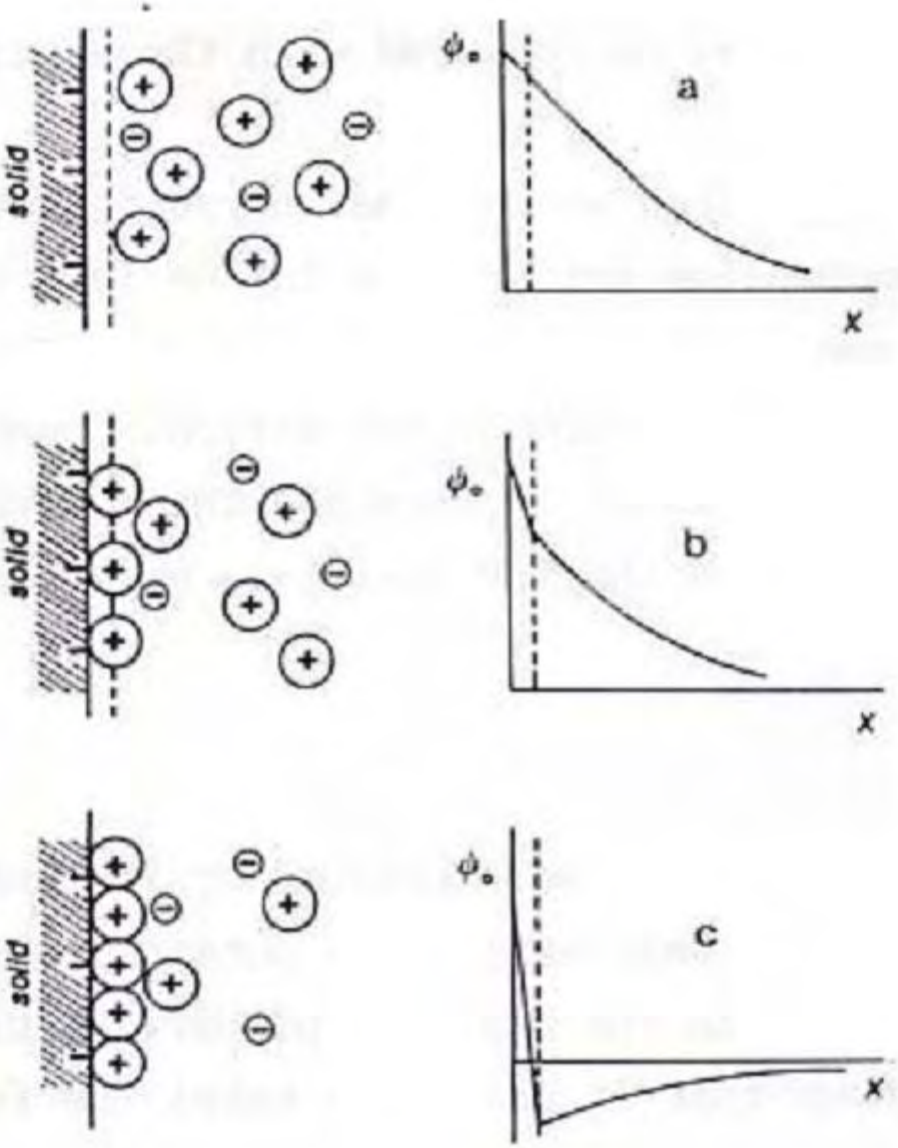


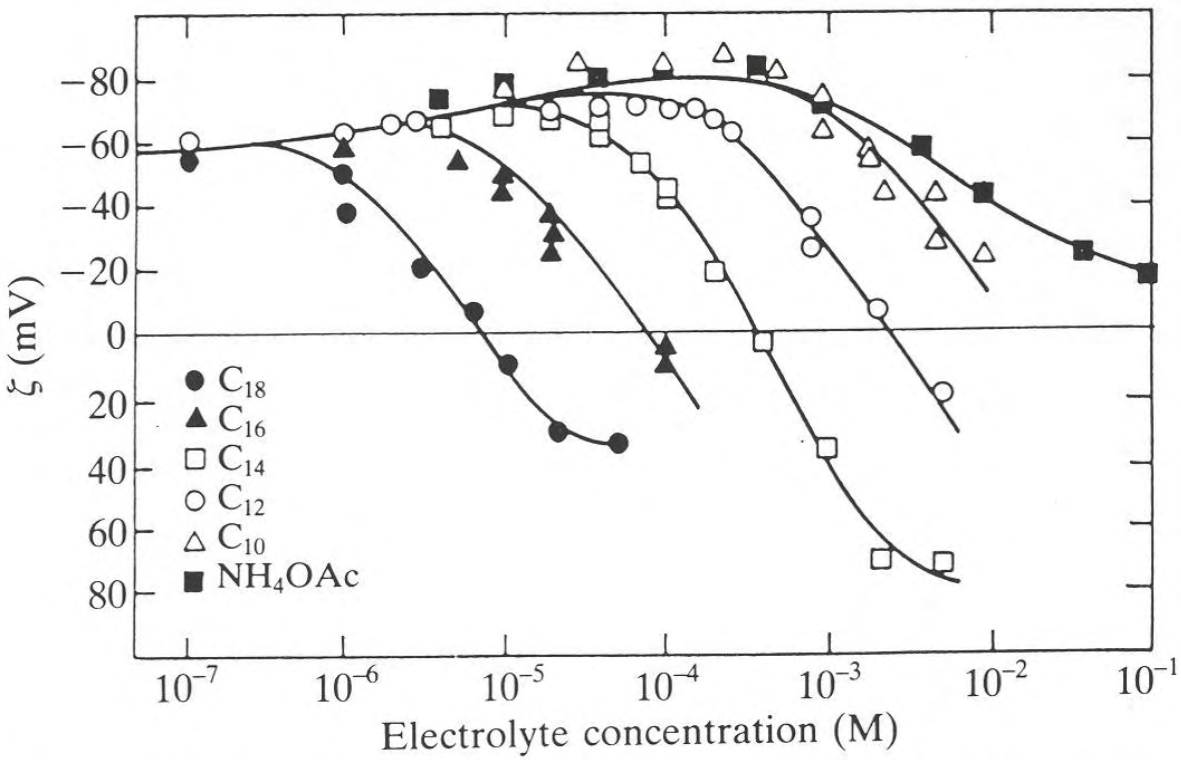
3 : 1 Salt

K^+

Ba^{2+}

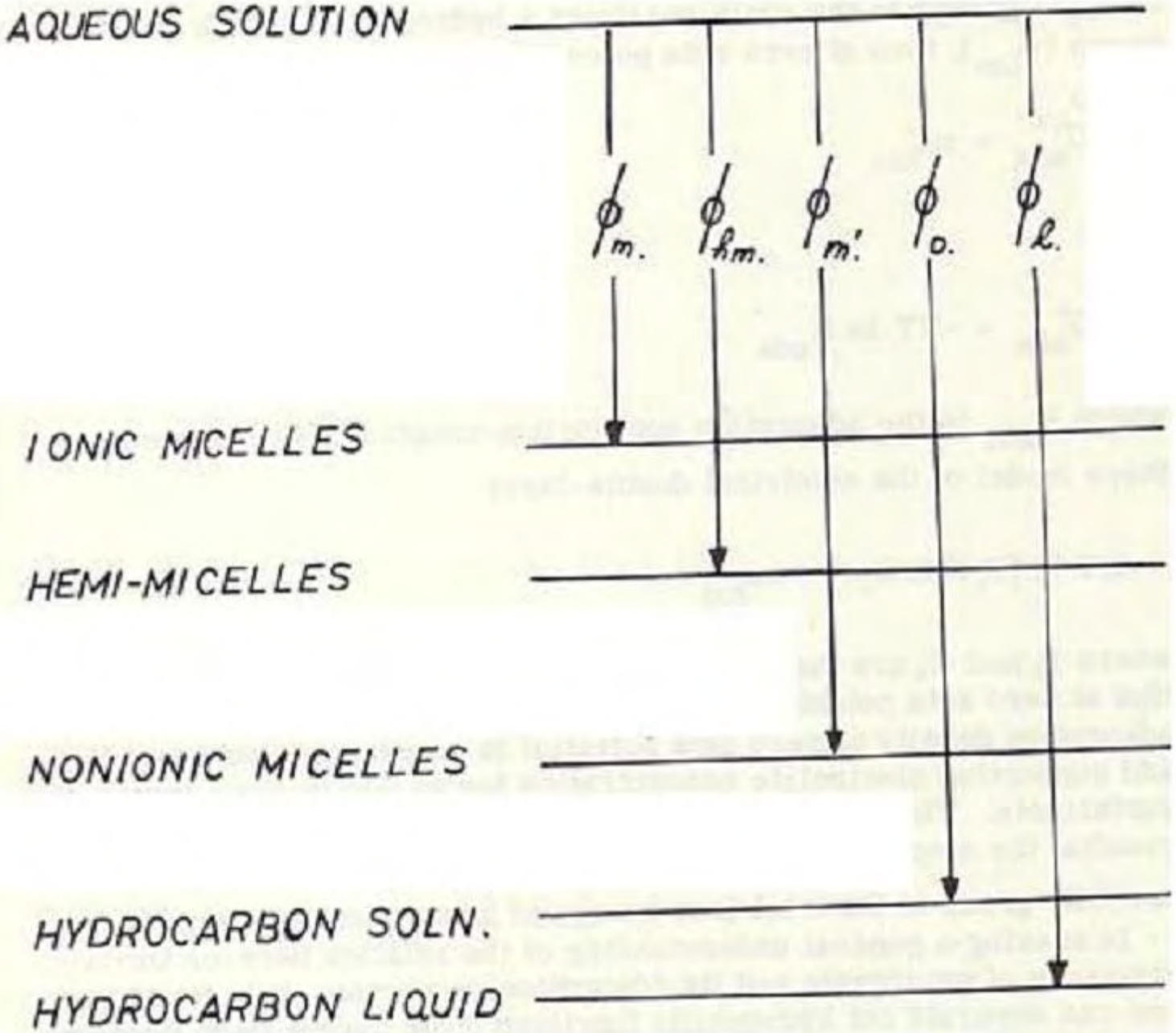
La^{3+}


solid
ψ_o
a
x
solid
ψ_o
b
x
solid
ψ_o
c
x



Effect of hydrocarbon chain length on the ζ-potential of quartz in solutions of onium acetates and in solutions of ammonium acetate.

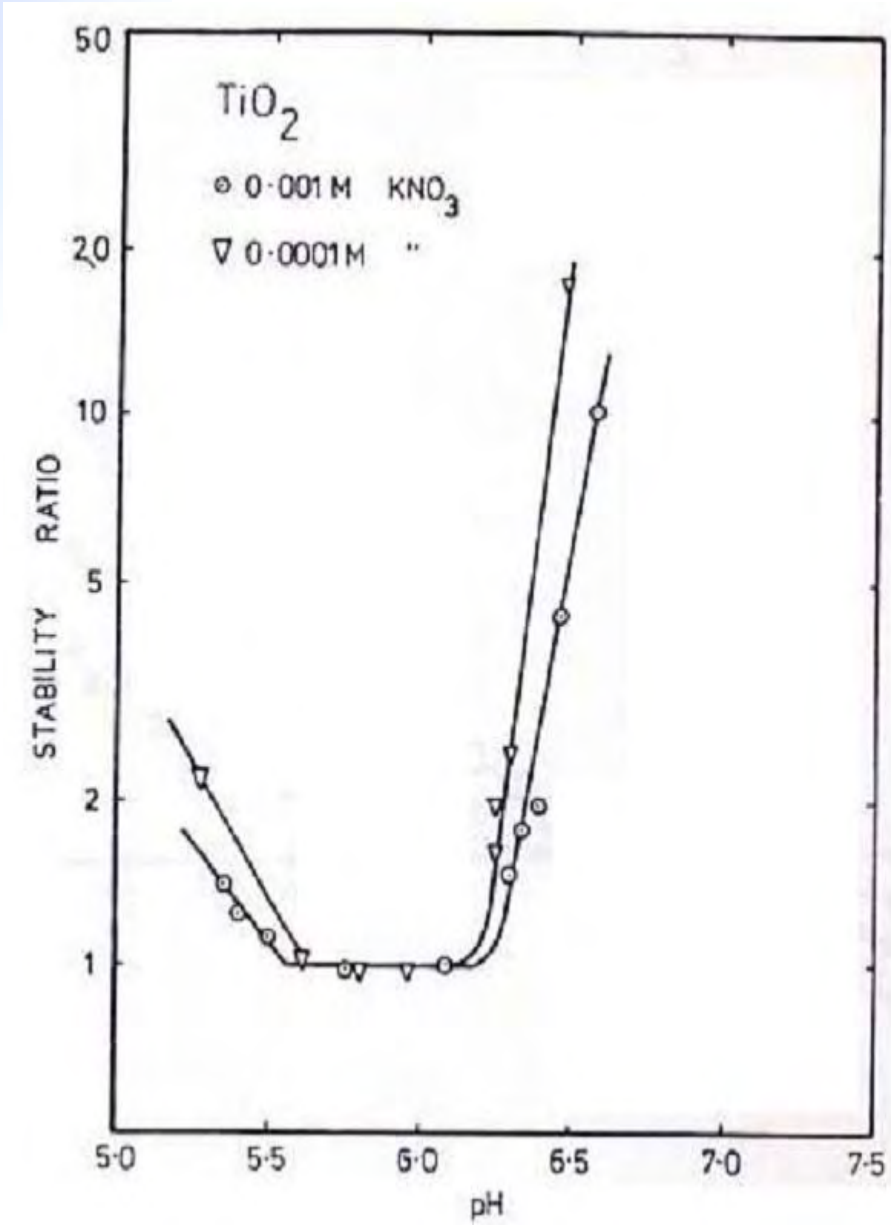
Somasundaran & Fuerstenau


AQUEOUS SOLUTION
$\phi_{m.}$
$\phi_{hm.}$
$\phi_{m'.}$
$\phi_{o.}$
$\phi_{\ell.}$
IONIC MICELLES
HEMI-MICELLES
NONIONIC MICELLES
HYDROCARBON SOLN.
HYDROCARBON LIQUID

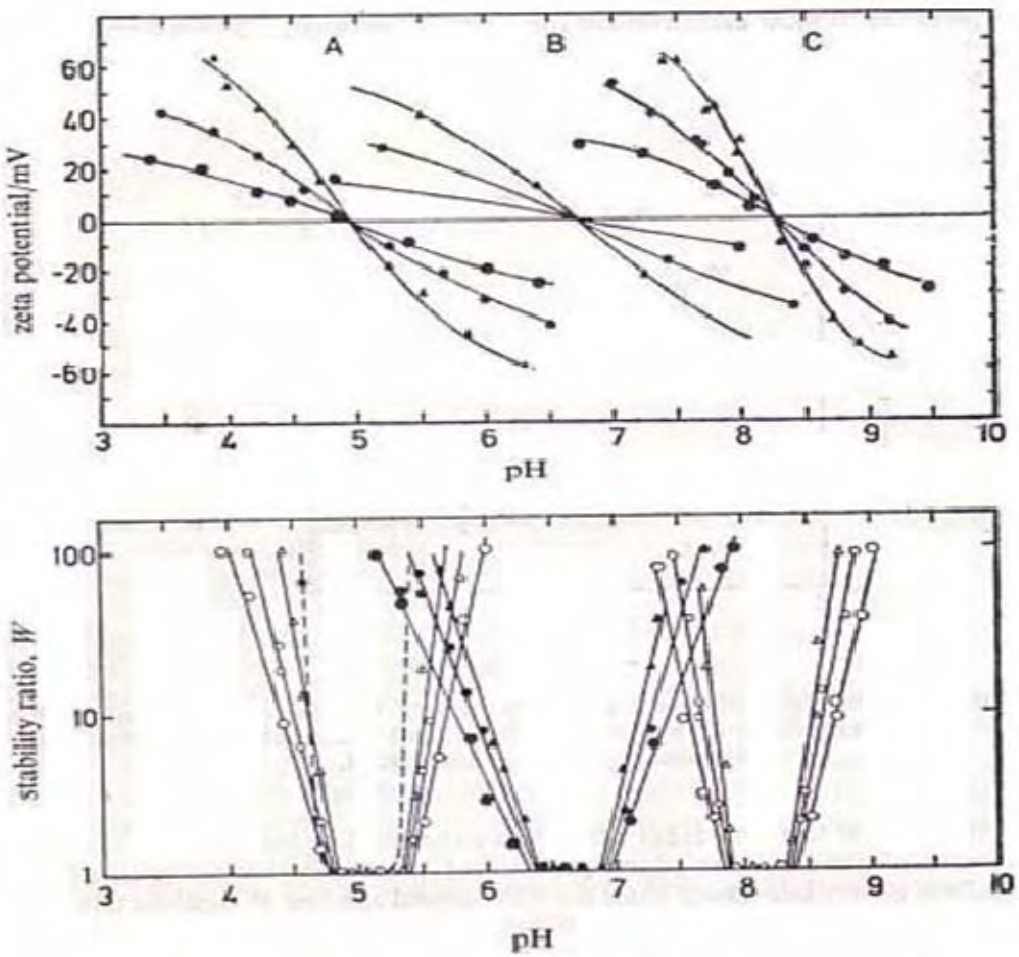
Colloidal Forces

ATTRACTIVE	REPULSIVE
Van der Waals	Van der Waals
Electrostatic	Electrostatic
Bridging	Steric/Structural
Depletion	
Viscous/Hydrodynamic	Viscous/Hydrodynamic

"Hydrophobic"

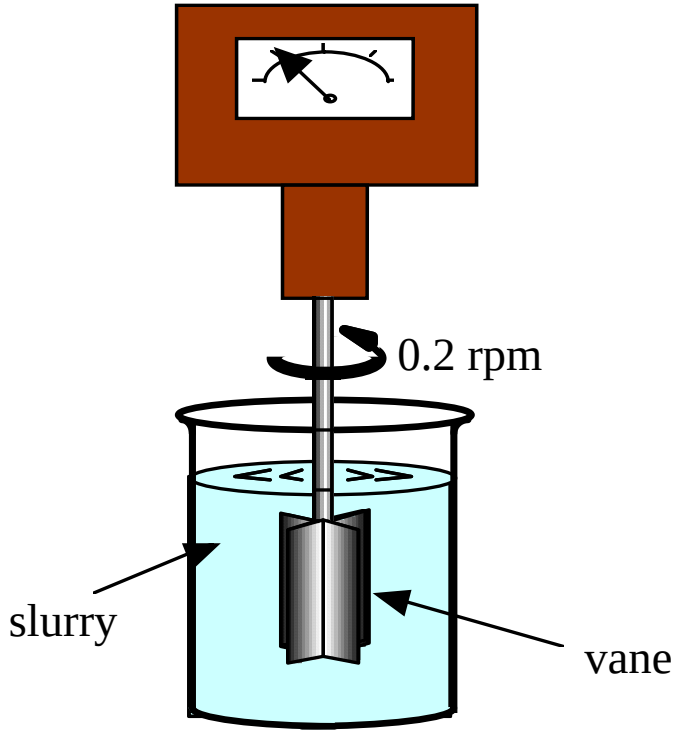

TiO2
0·001 M KNO3
0·0001 M "
STABILITY RATIO
50
20
10
5
2
1
5·0
5·5
6·0
6·5
7·0
7·5
pH

Amphoteric Latices

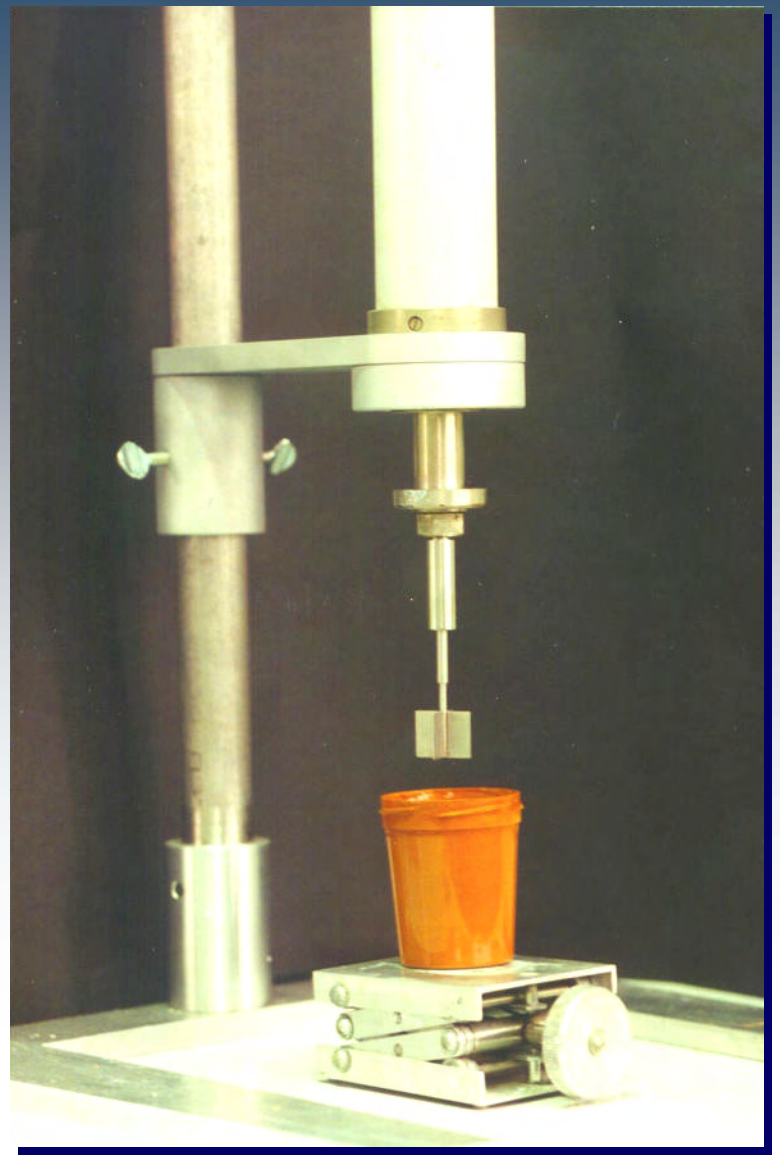


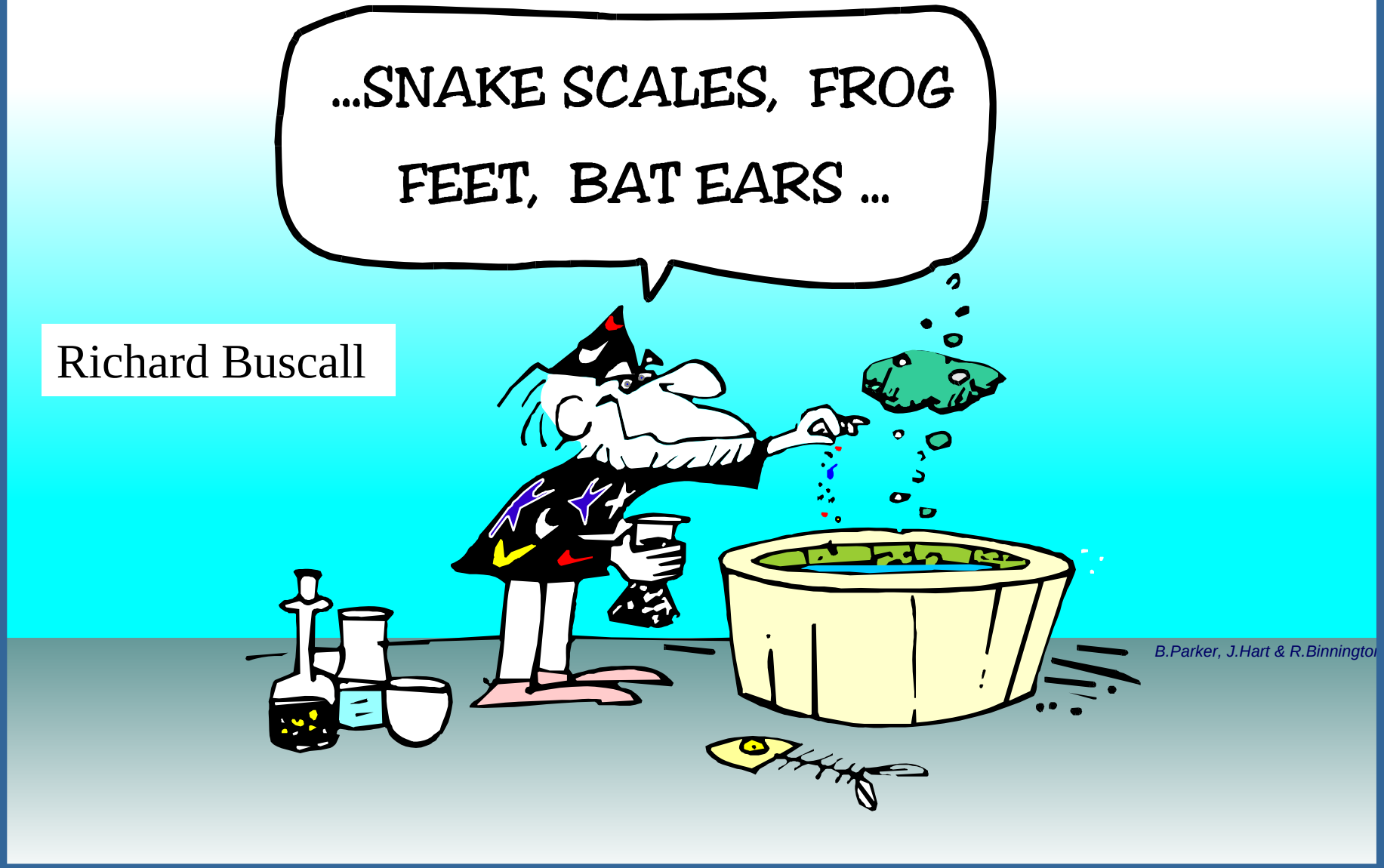
Harding

Shear Yield Stress

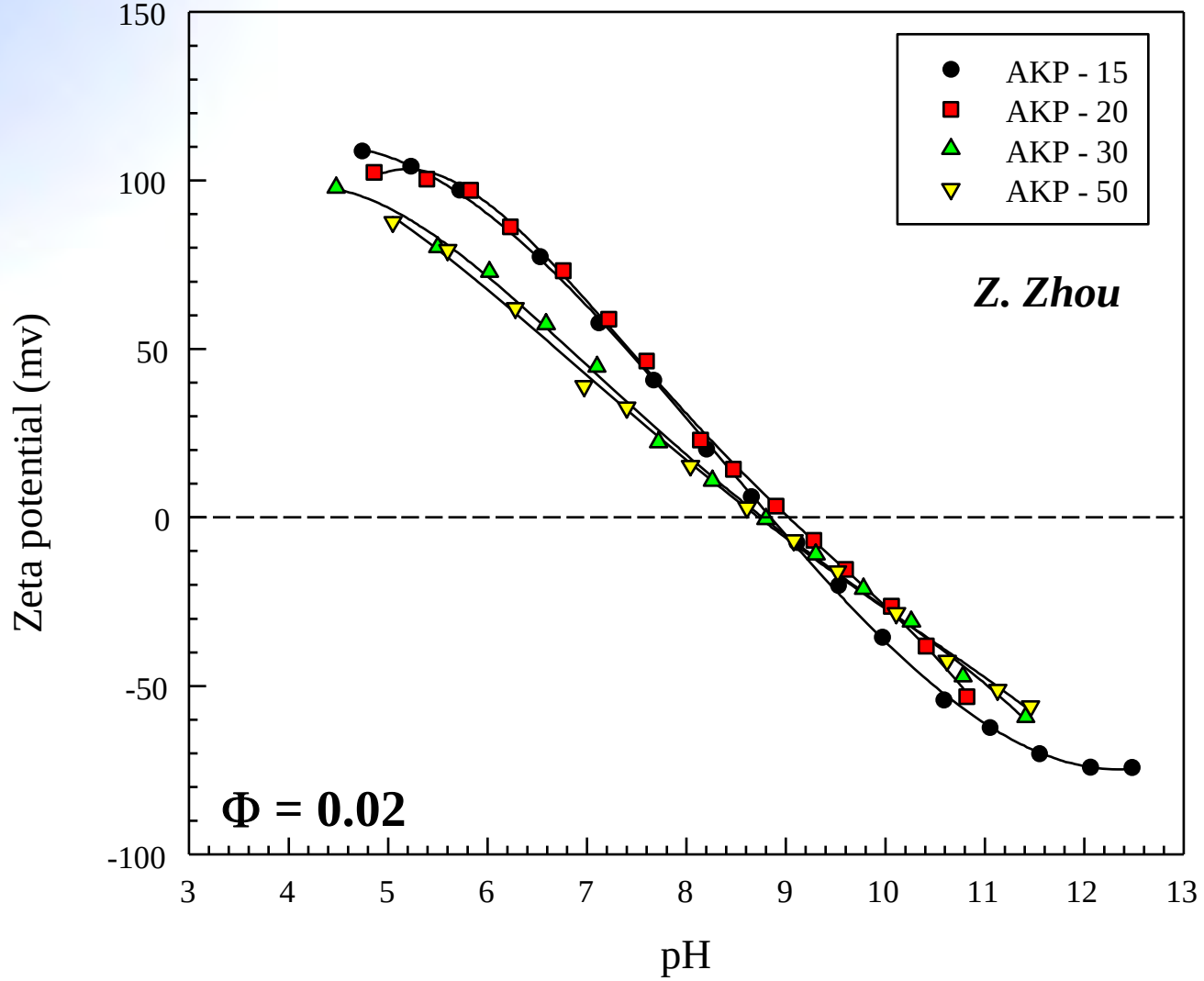


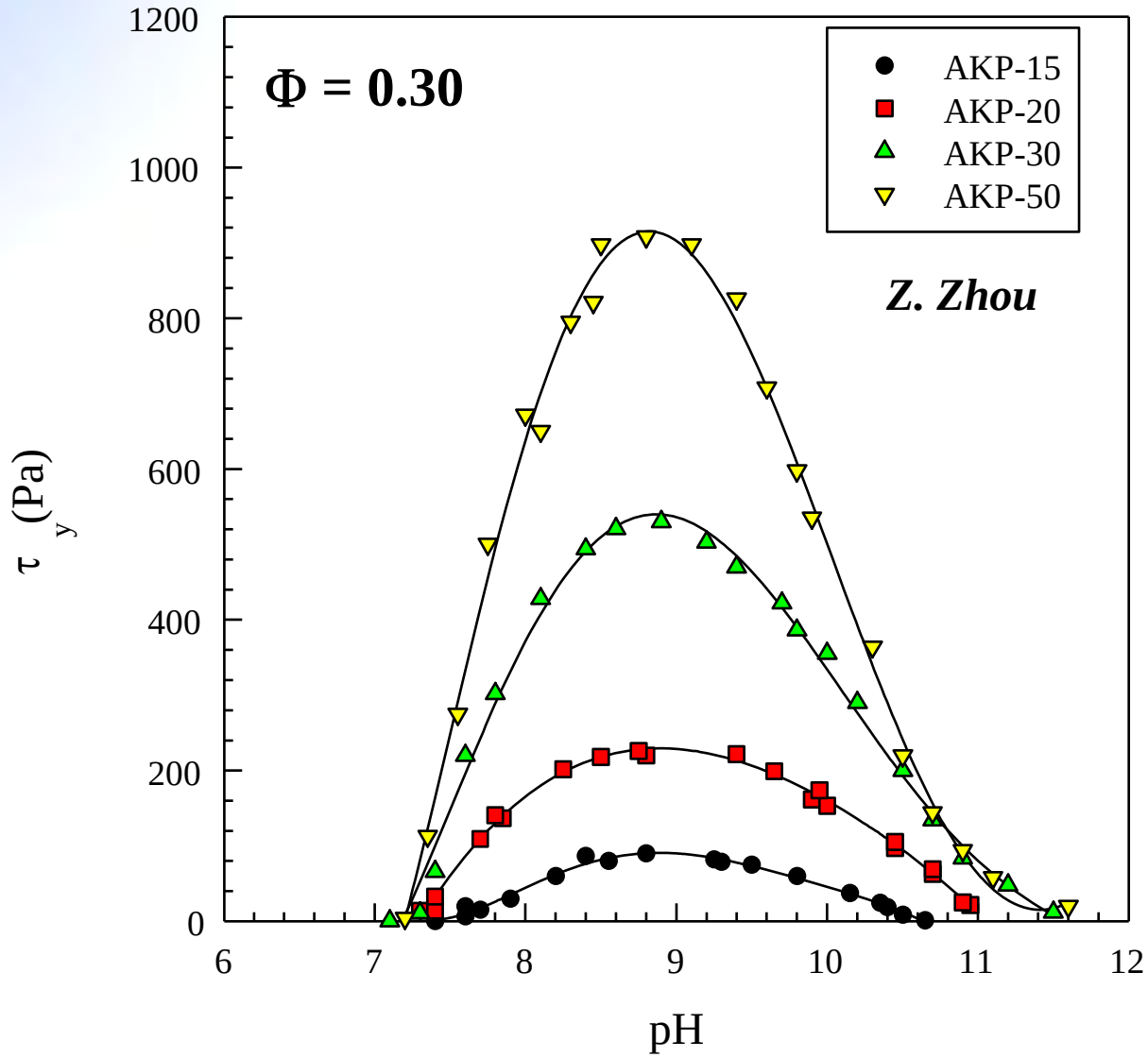
Nyghun & Boger





Richard Buscall

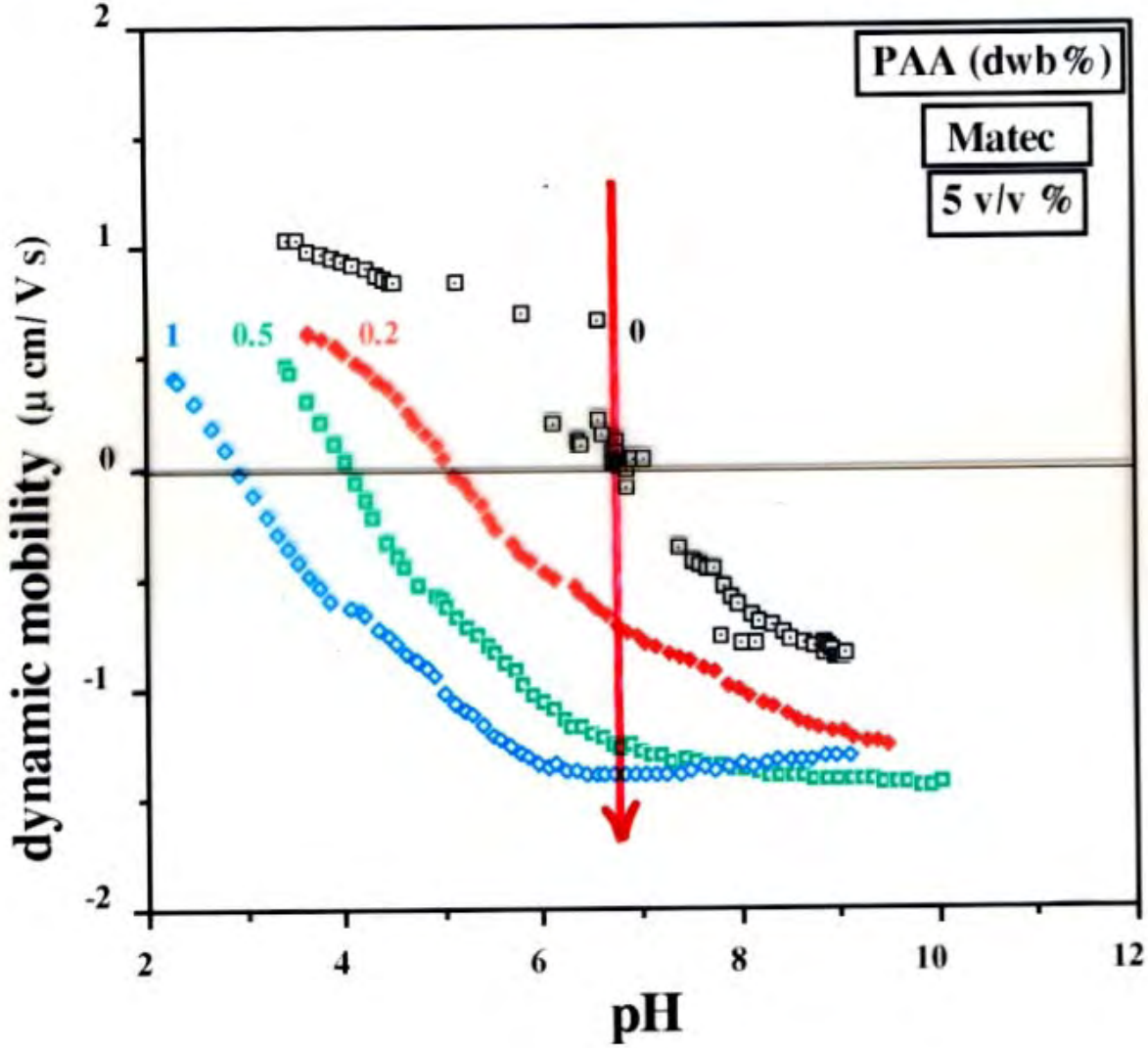

150
100
50
0
-50
-100
Zeta potential (mv)
3
4
5
6
7
8
9
10
11
12
13
pH
AKP - 15
AKP - 20
AKP - 30
AKP - 50
Z. Zhou
Φ = 0.02


Φ = 0.30
AKP-15
AKP-20
AKP-30
AKP-50
Z. Zhou
τ y (Pa)
pH
0
200
400
600
800
1000
1200
6
7
8
9
10
11
12

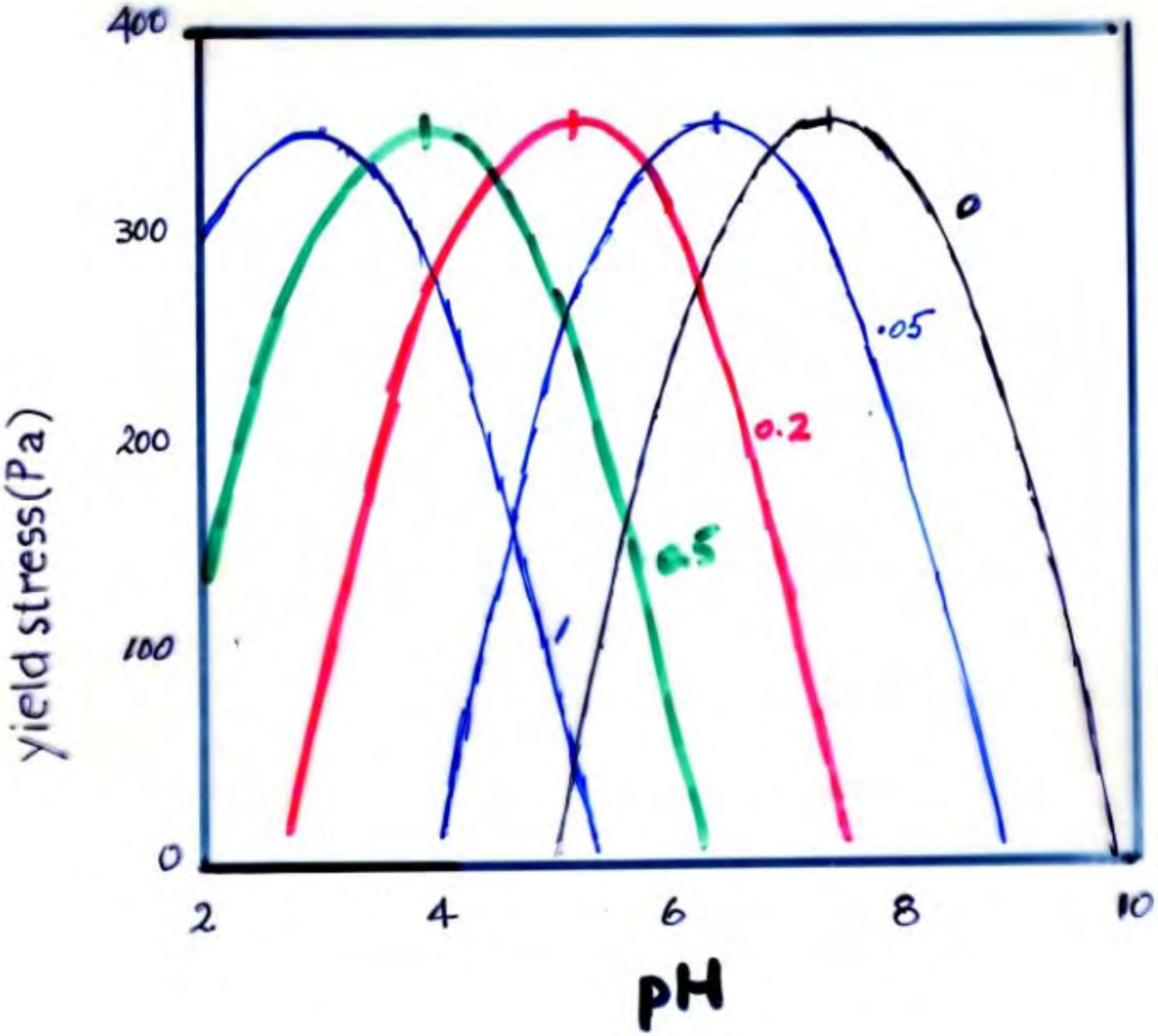
2. Electrokinetics

Colloidal Ceramic grade Zirconia

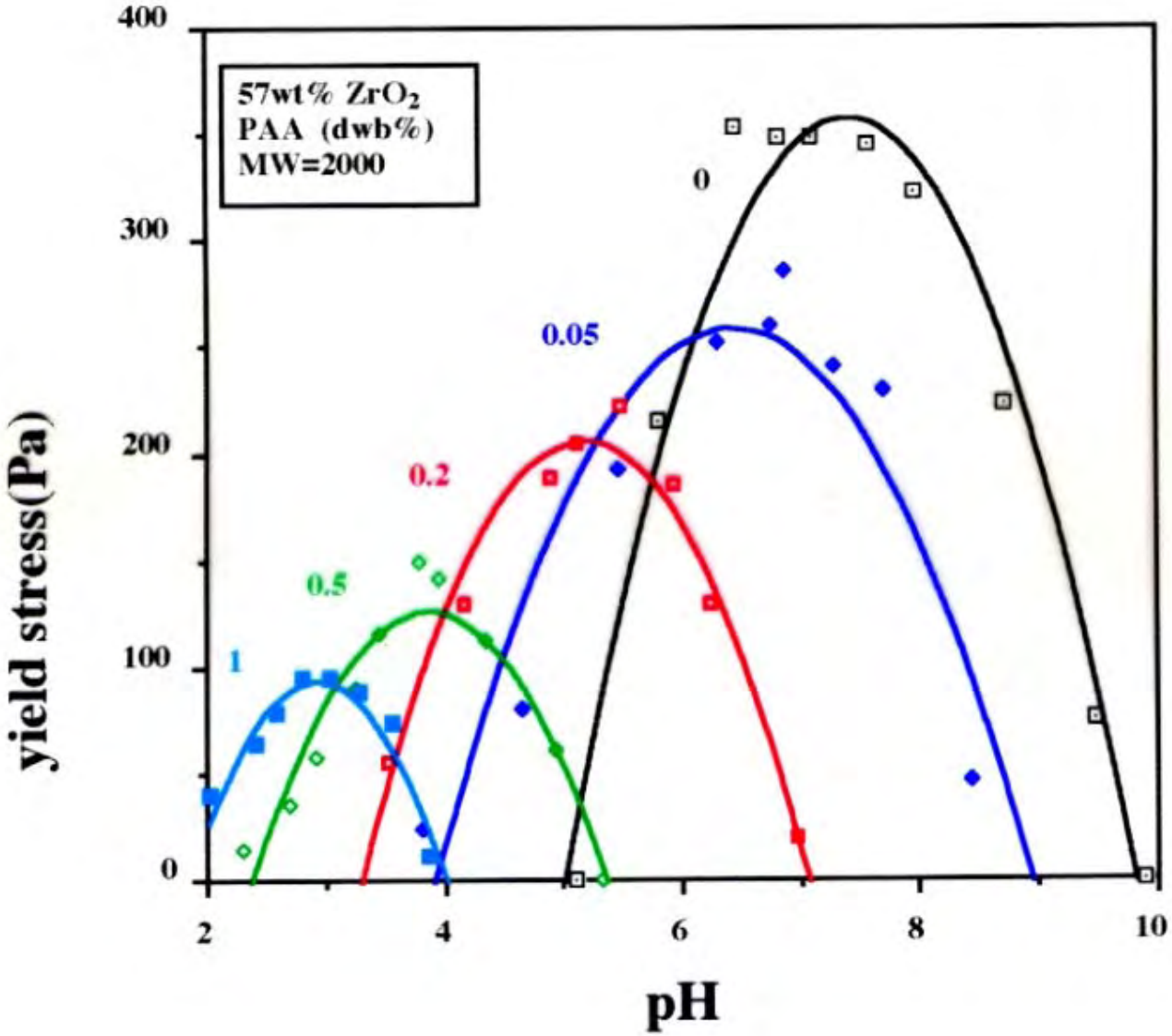
Low Mol.Wt. polyacrylic acid.



EXPECTED

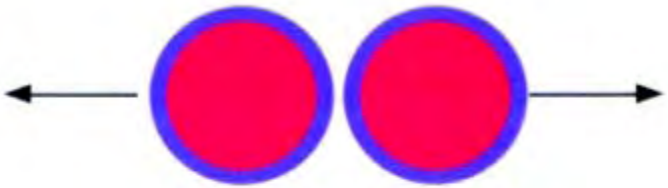


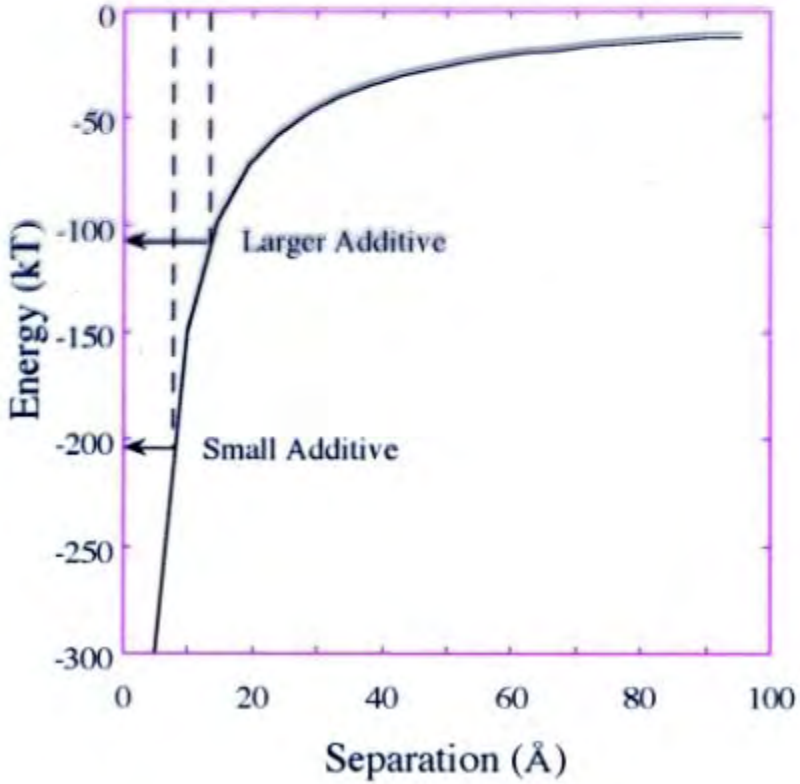
OBSERVED RHEOLOGY.

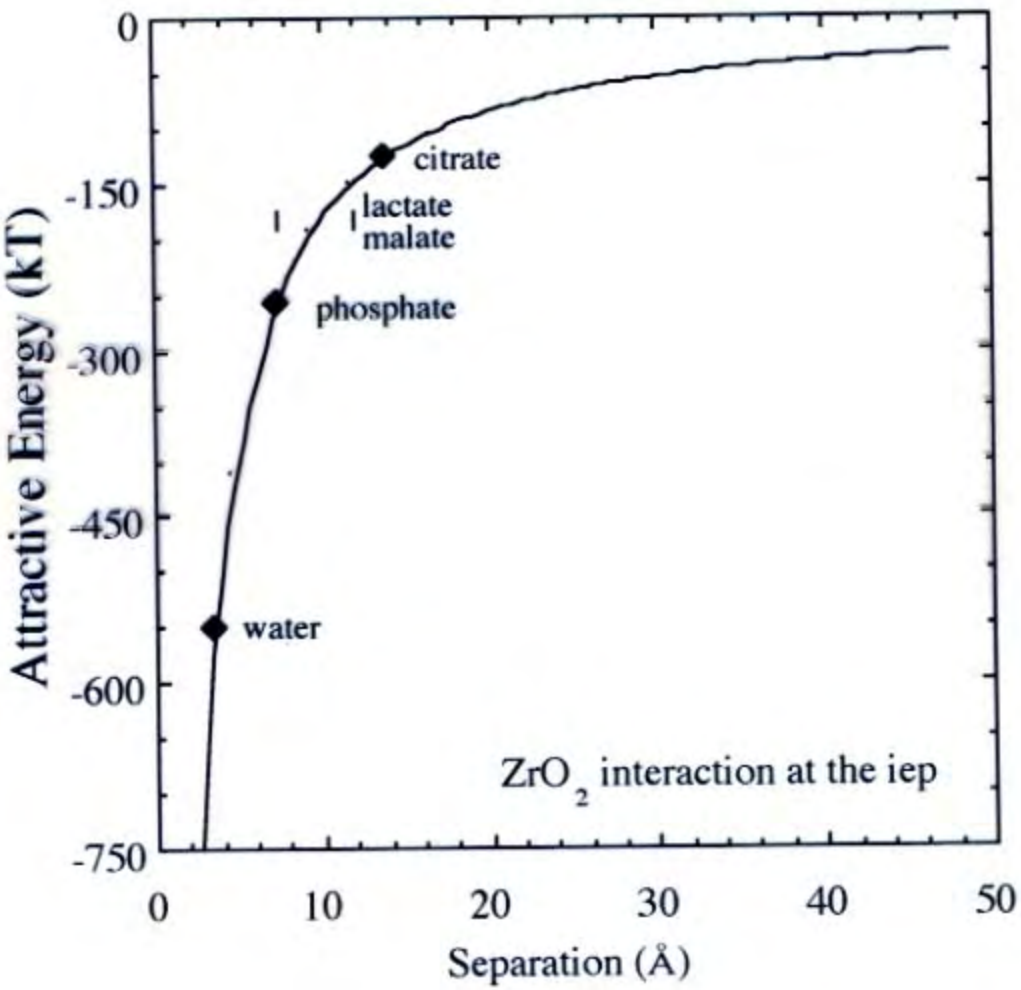


Effect of Additives

Citrate
Phosphate
PAA 2000
Lactate
Malate.....





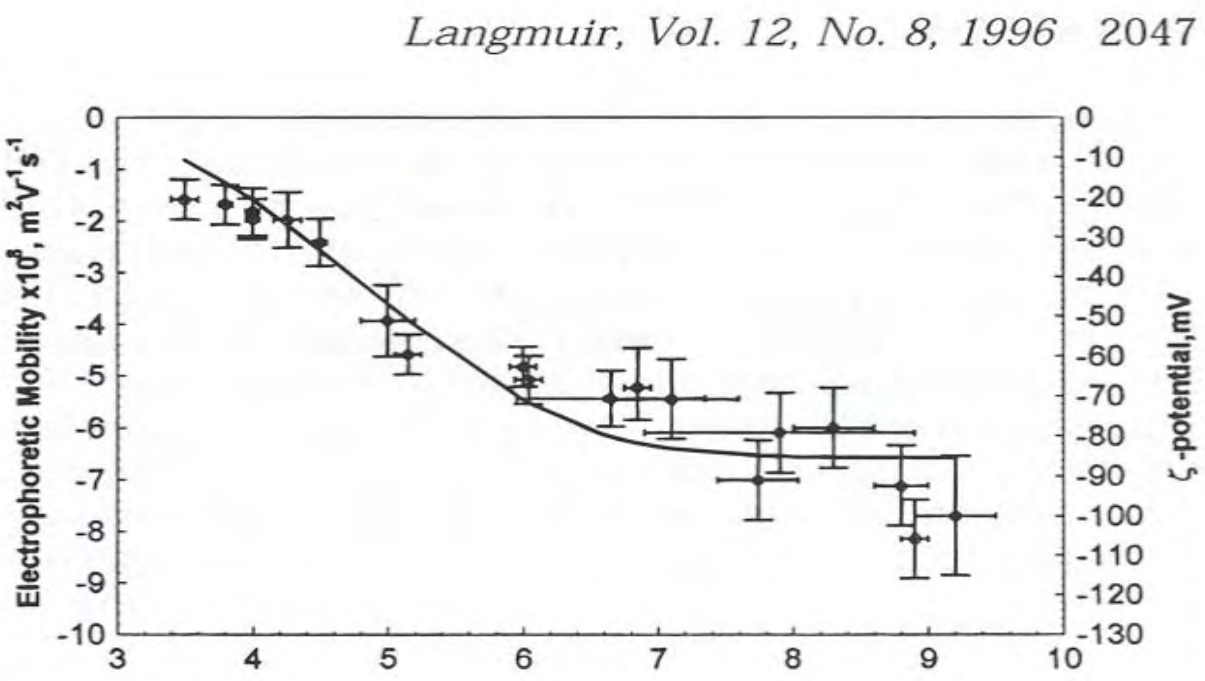

0
-150
-300
-450
-600
-750
Attractive Energy (kT)
citrate
lactate
malate
phosphate
water
ZrO2 interaction at the iep
0
10
20
30
40
50
Separation (Å)

What about Hydrophobic (Non-Polar) Materials Suspended in Water?

RESPONSES

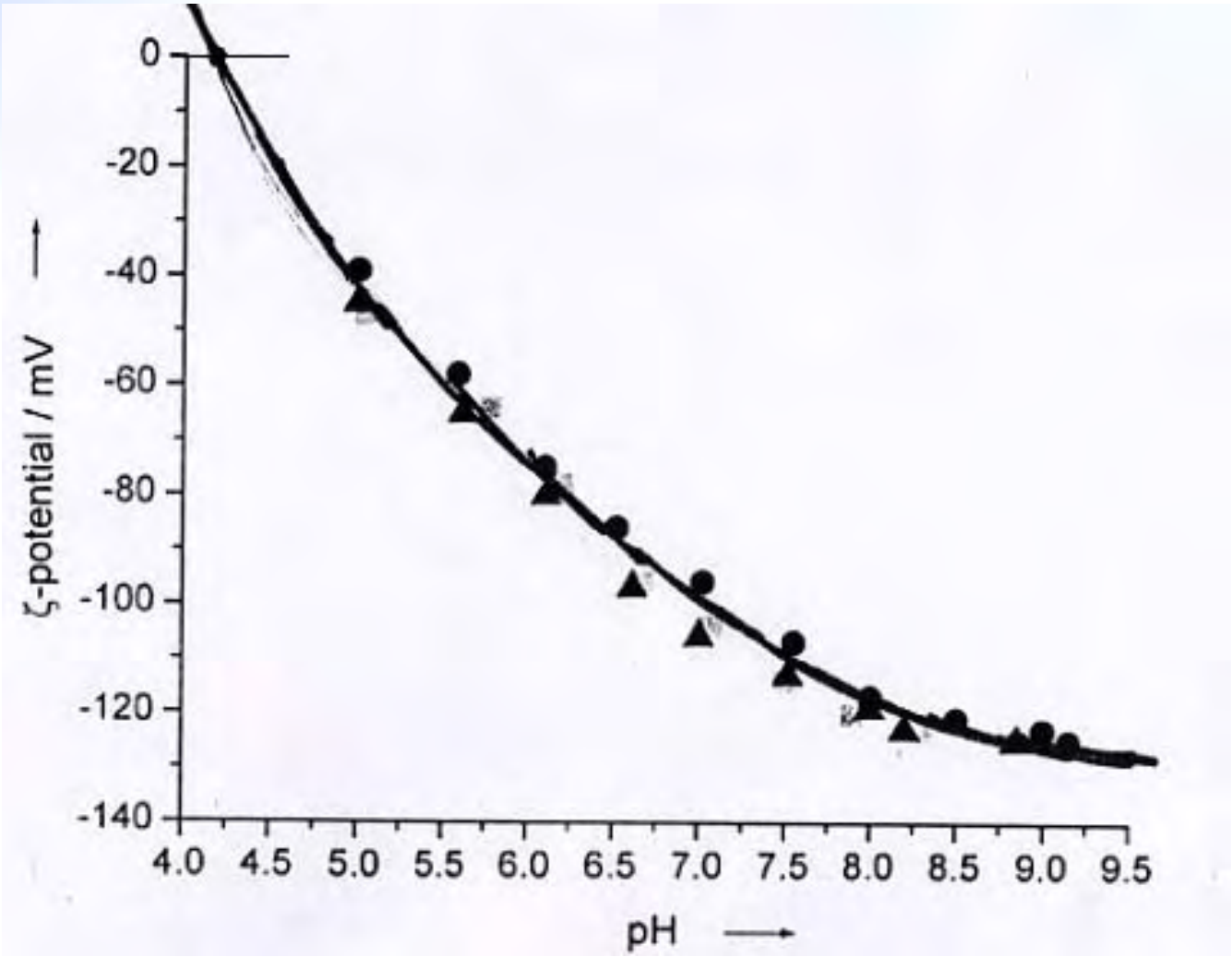
- An oxy-moron perhaps!!!
- Things like graphite, oil drops, paraffin etc do not have electrical double layers!!
- Need to pretreat such materials with an amphipathic molecule (surfactant).
- Make sure the surfactant is high molecular weigh and insoluble in water.

XYLENE-WATER,
(after Marinova et al,1996)

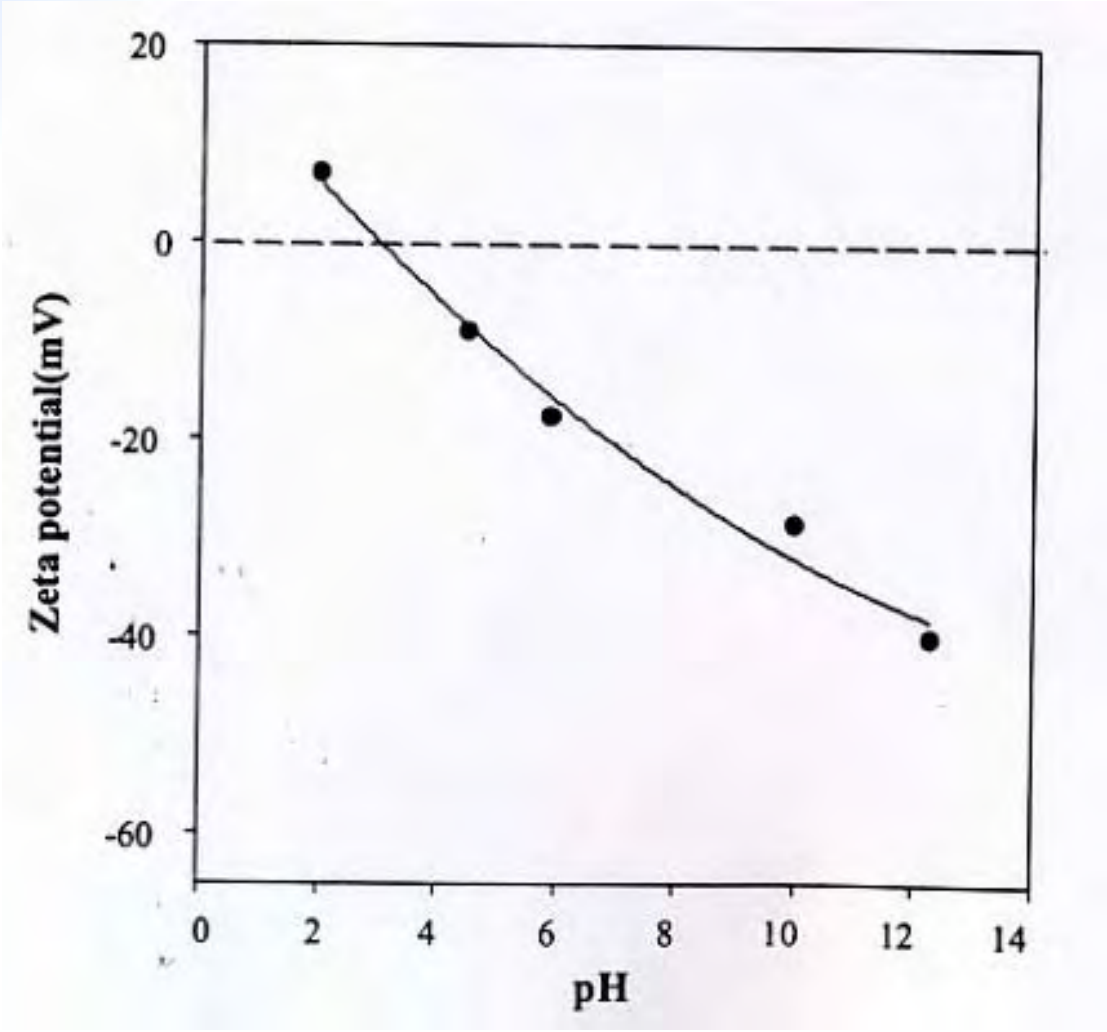


pH

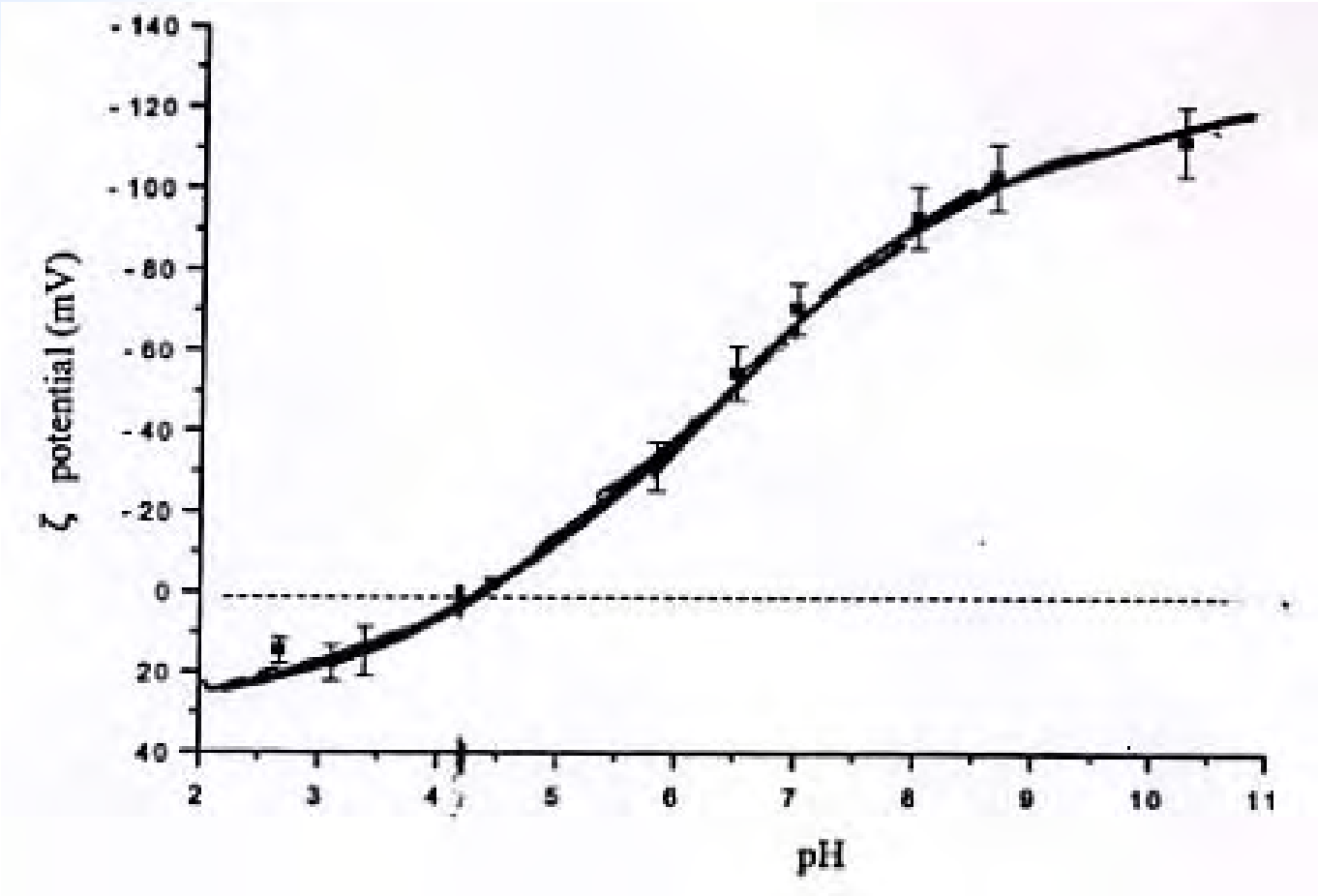
HEXADECANE EMULSIONS, (After Beattie and Djerdjev, 2004)



NANOBUBBLES,(AFTER Cho et al, 2005)

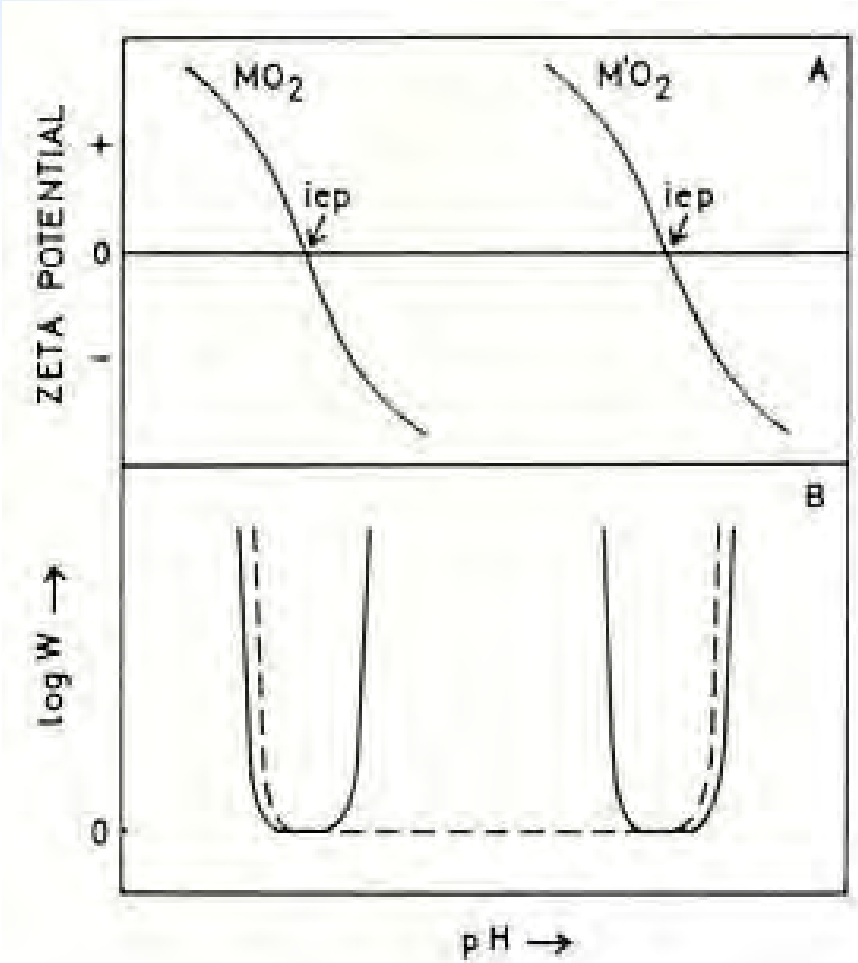


MICROBUBBLES, (after Takahashi,2005)

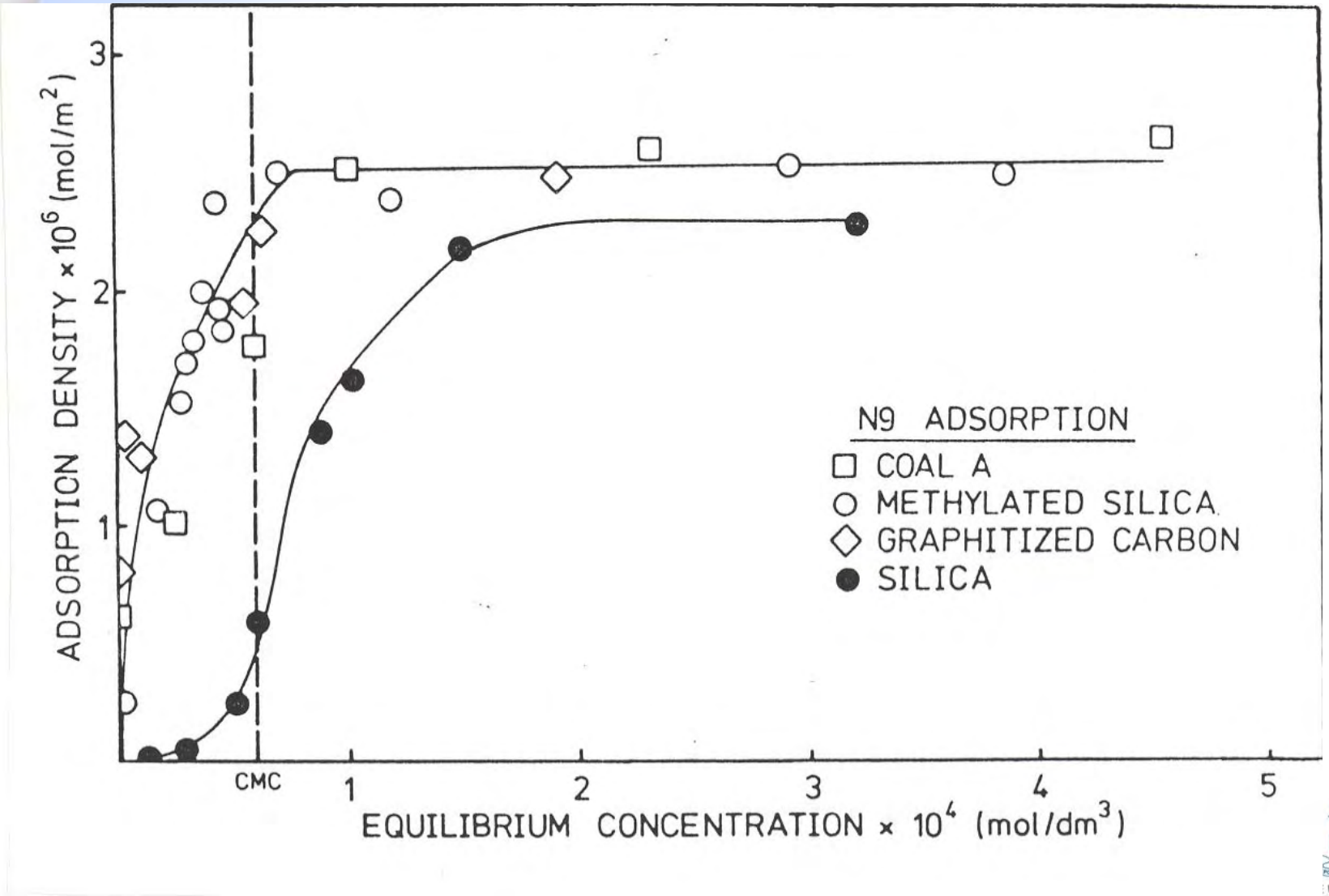


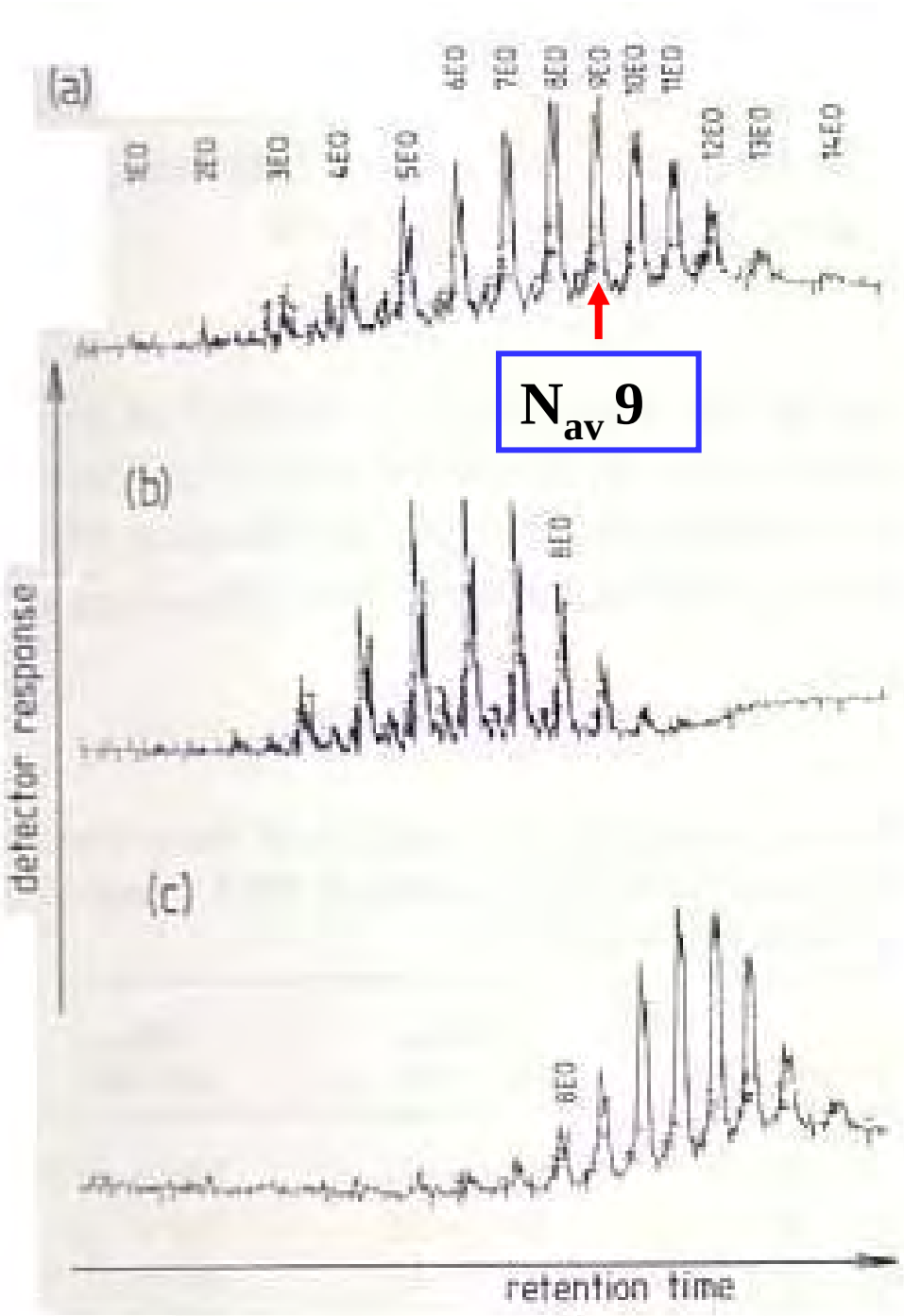
pHpzc of Non-polar Solid-Water Interfaces

Graphite, graphitized carbons	pH 0.5 to less than 6
Molybdenite	pH 1.5-3.0
Stibnite	pH 2
Paraffin Wax	pH 4-5
Talc, pyrophilite,	pH 1-2
Sulphur	pH 1.5-2.5


MO2
M'O2
A
iep
iep
ZETA POTENTIAL
+
0
-
B
log W →
0
pH →

N9 Alkyl ethoxylate




(a)
1EO
2EO
3EO
4EO
5EO
6EO
7EO
8EO
9EO
10EO
11EO
12EO
13EO
14EO
(b)
8EO
(c)
8EO
detector response
retention time

N_{av} 9

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- Make sure the surfactant is high molecular weigh and insoluble in water.

Thank You

RSC-SCI

including Laura Grimsley

Speakers…coming from far away

Audience