Physical Chemistry of Estuarine Waters

I. Physical Properties

II. Carbonate System

III. Speciation of Metals

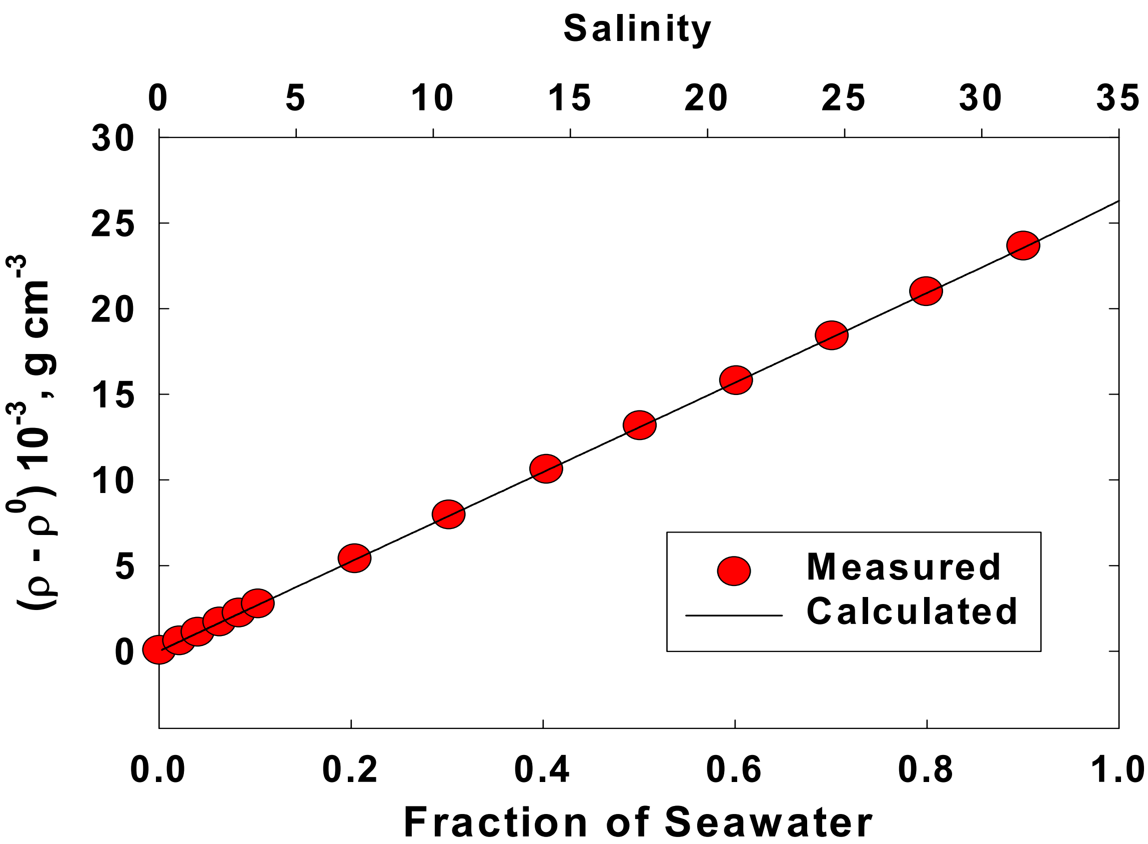
I. Physical Chemical Properties

All the physical chemical properties of Rivers and Estuarine Waters have the same Physical Chemical Properties of seawater at the same absolute salinity

$S(g/kg) = S_R + \Sigma\, n_i\, M_i$ where n_i and M_i are the moles and MW of species i.

$S_R = 35.164$ g/kg for seawater when the Practical Salinity is 35.000.

Density of Estuarine Waters



Pitzer Equations

$P = P^0 + \sum \text{Ion-Water} + \sum \text{Ion-Ion}$

$\sum \text{Ion-Ion} = \sum \text{M-X} + \sum \text{M-N} + \sum \text{X-Y}$

(+ −) (+ +) (− −)

M = Na, Mg, Ca, K, Sr

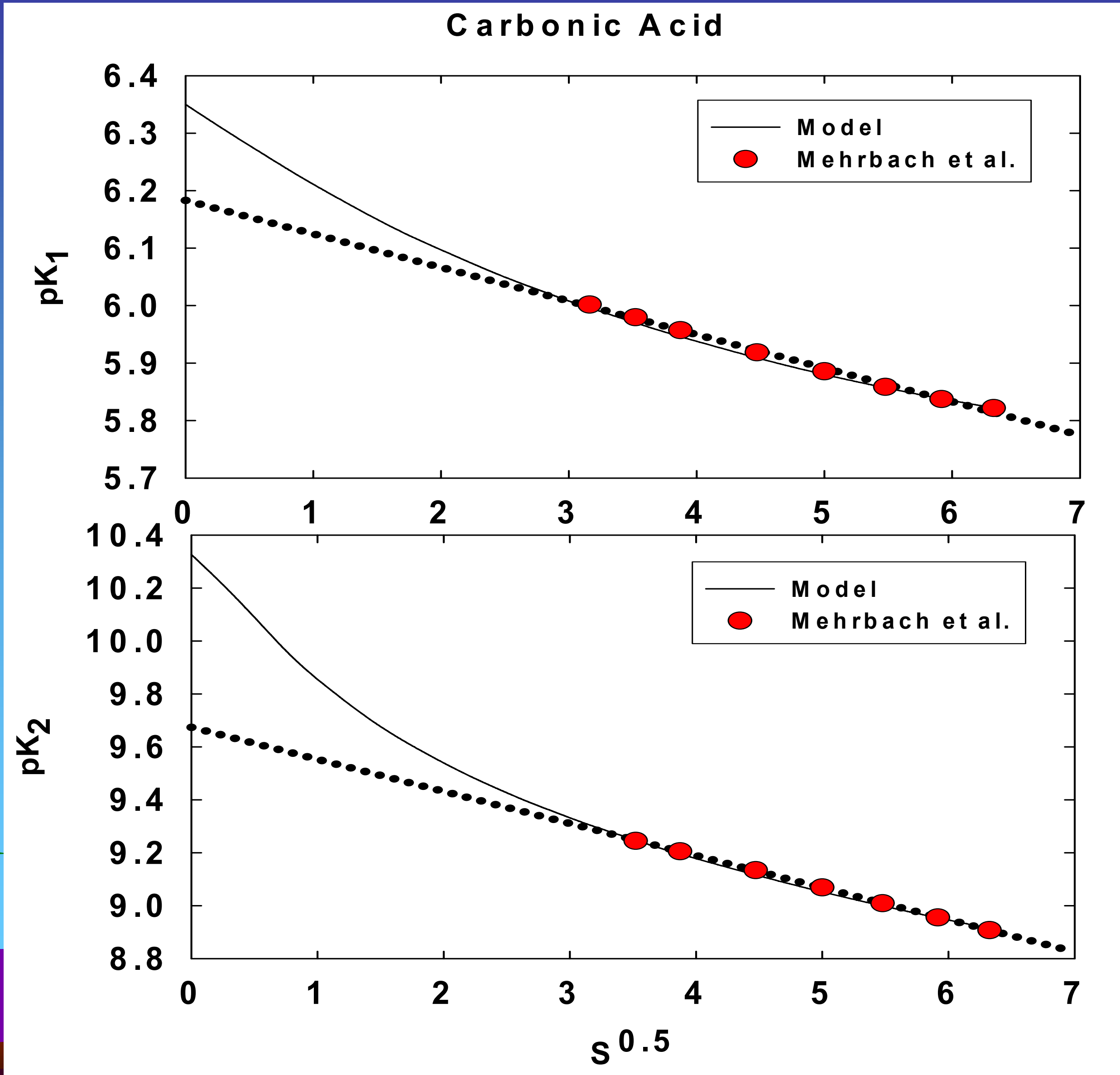
X = Cl, SO_4, HCO_3, Br, CO_3, $B(OH)_4$, F

M-N (Na-Mg) X-Y (Cl-SO_4)

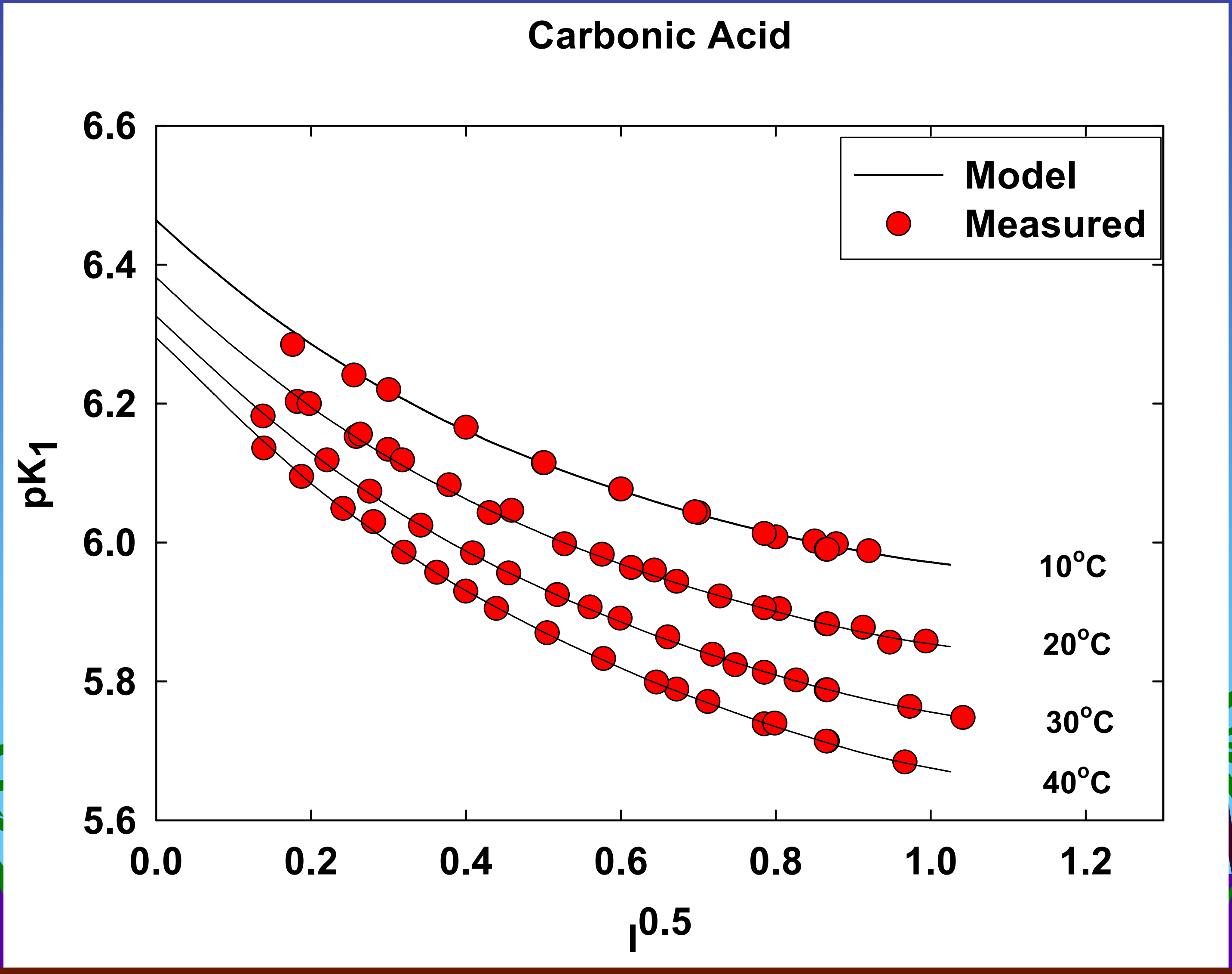
II. Carbonate System

Measurements are presently available for the pK_1 and pK_2 for Carbonic Acid from $S = 0$ to 50 and $t = 0$ to $50^{o}C$

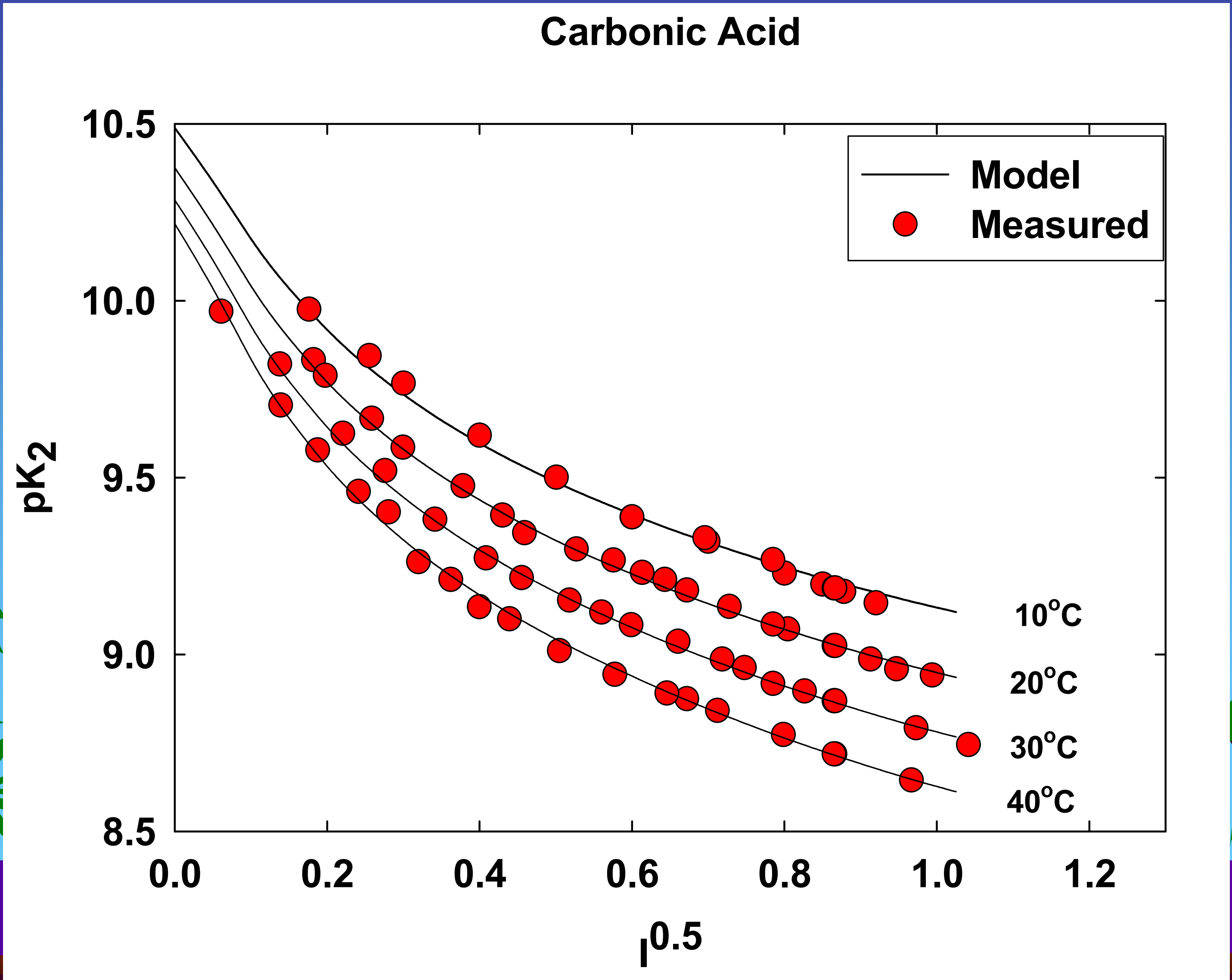
Modeling The CO_2 System



New Measurements



New Measurements



The New CO_2sys Program has these New Constants as Option

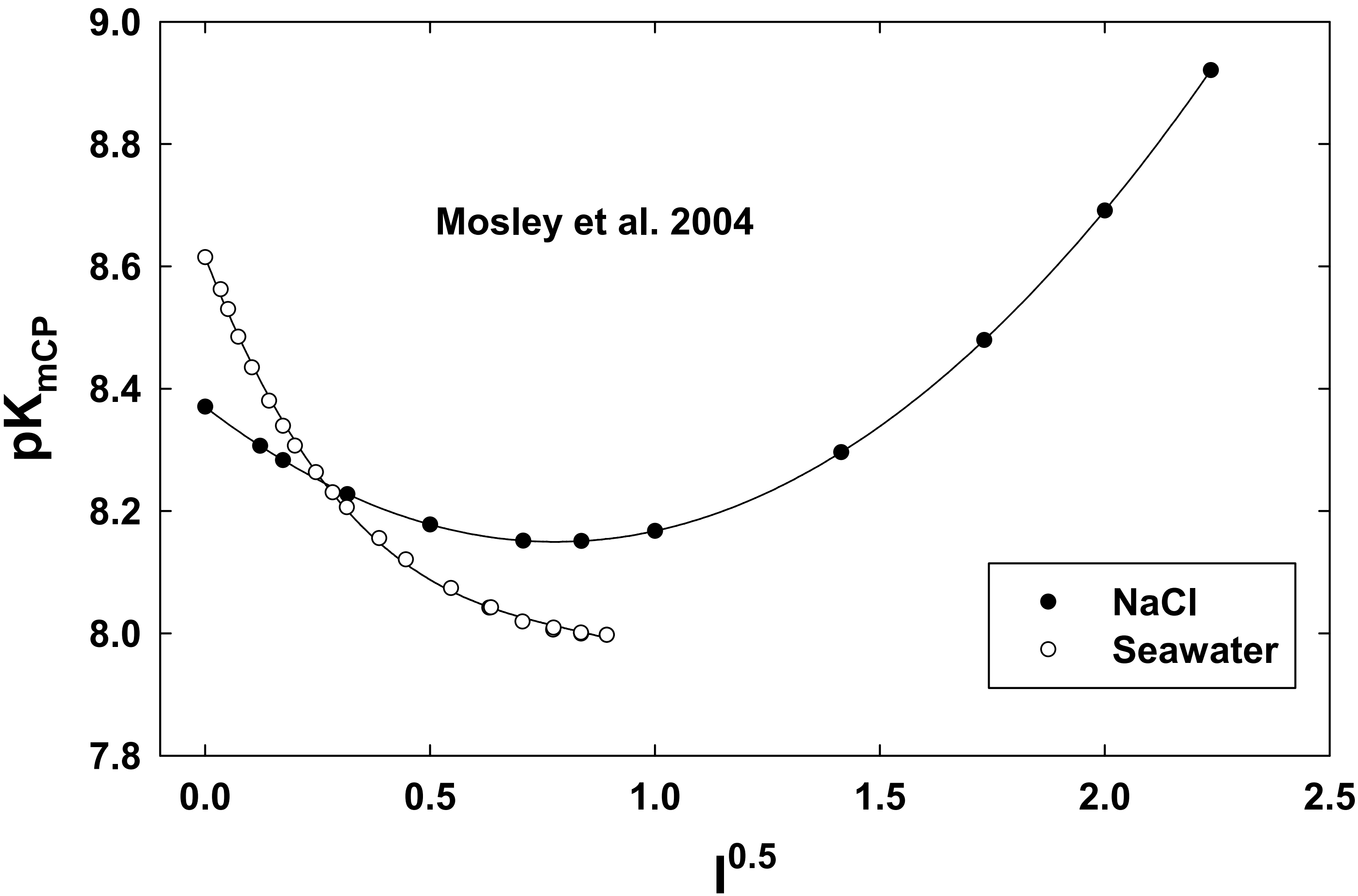
http://cdiac.ornl.gov/ftp/co2sys/co2sys_xls_program/

Measurements of CO_2 Parameters

pCO_2, TA and TCO_2 same methods Used for Seawater

Spectroscopic pH Measurements have some problems

NaCl compared to diluted seawater



pK_{mCp} in Various Media

Author	Media	Value
Clayton & Byrne (1993)	SW	8.112
Mosley et al. (2004)	SW	8.000

pK_{Tb} in Various Media

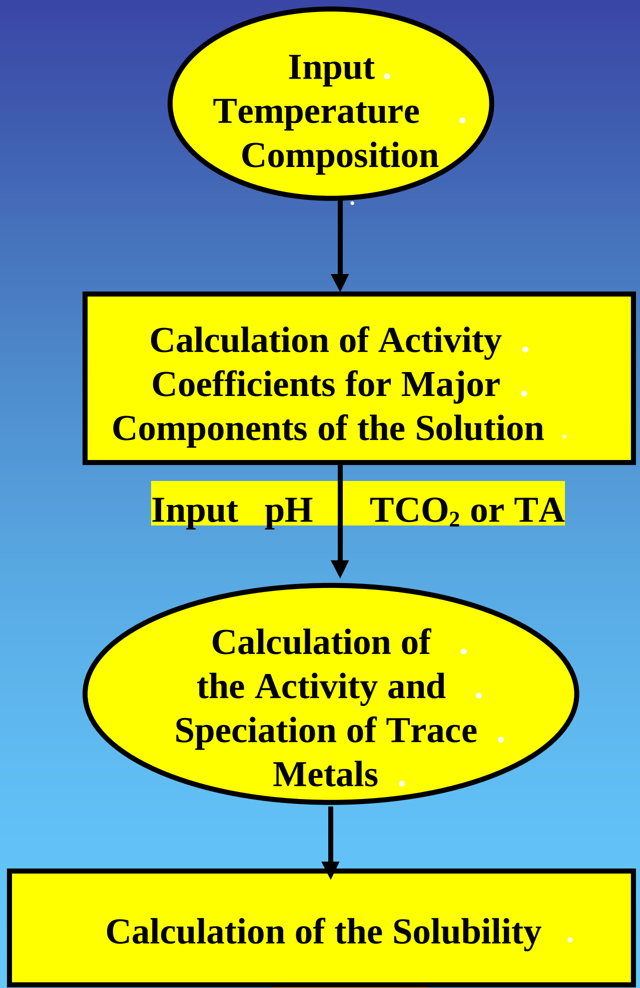
Author	Media	Value
Zhang & Byrne (1996)	SW	8.529
Mosley et al. (2004)	SW	8.534

II. Speciation of Metals

Modeling Ionic Interactions

Some Results for Cu(II), Hg(II) and Al(III) with Cl^- and OH^-

Ionic Interaction Model



Instructions

1 - Enter the Temperature --------------->

Temperature(oC)

50.00

2 - Enter Salinity --------------->

Salinity

50.000

OR Molalities (Delete Salinity Value) --------------->

Molalities

Sr	1.37E-04
Na	0.70544428
K	0.01535131
Mg	0.07944672
Ca	0.01546713
Cl	0.82107401
SO_4	0.04247406
CO_3	0.00028955
HCO_3	0.00279545
Br	0.00126348
F	1.00E-04
$B(OH)_4$	1.26E-04

3 - Select γ Level (1, 2, or 3) (See Comment)

γ level 3

Cations	Molality	Gamma noT	Gamma HOT	Gamma UST
Sr	0.00014	0.17883	0.19607	0.16297
Na	0.70544	0.62616	0.63333	0.62013
K	0.01535	0.57807	0.57282	0.56088
Mg	0.07945	0.19016	0.20853	0.17333
Ca	0.01547	0.18767	0.20153	0.16751
H		0.35341	0.36986	0.36216
Li		0.70255	0.70255	0.70750
Rb		0.56155	0.56155	0.56551
Cs		0.52981	0.50482	0.50838
NH4		0.59090	0.59090	0.59507
Ba		0.14778	0.16132	0.13409
Mn		0.16055	0.17844	0.14900
Fe		0.16423	0.16423	0.16891
Co		0.16580	0.16580	0.17052
Ni		0.17053	0.17053	0.17539
Cu		0.13782	0.13782	0.14174
Zn		0.14713	0.14713	0.15132
UO2		0.20008	0.20008	0.20578
Be		0.04587	0.04587	0.04718
Cd		0.05618	0.05618	0.05778
Pb		0.01498	0.01498	0.01541

Anions	Molality	Gamma noT	Gamma HOT	Gamma UST	Free Fraction (%)
Cl	0.82107	0.68436	0.68787	0.68402	100.00%
SO4	0.04247	0.09606	0.10705	0.08628	100.00%
CO3	0.00029	0.03558	0.03297	0.02657	38.95%
HCO3	0.00280	0.54586	0.57073	0.56754	100.00%
Br	0.00126	0.72121	0.72120	0.71716	
F	0.00010	0.23416	0.23836	0.23702	45.15%
B(OH)4	0.00013	0.36620	0.32764	0.32580	
HSO4		0.61656	0.60837	0.60497	
HS		0.67795	0.67795	0.67416	
OH		0.20945	0.19271	0.19163	35.73%
I		0.77235	0.77235	0.76803	
ClO3		0.63646	0.63646	0.63290	
ClO4		0.71162	0.71162	0.70764	
BrO3		0.58107	0.58107	0.57782	
CNS		0.74794	0.74794	0.74376	
NO2		0.60669	0.60669	0.60330	
NO3		0.60225	0.61609	0.61264	
H2PO4		0.42066	0.48776	0.48503	
HPO4		0.05031	0.04227	0.03407	
PO4		0.00016	0.00007	0.00002	

Neutral	Molality	Gamma
NH3		1.02120
B(OH)3		1.01125
H3PO4		1.12253
H2S		1.16661
SO2		1.05489
CO2		1.16621
HF		1.01564

Acid	pK*1	pK*2	pK*3
CO2	1.77	5.53	8.40
H2S	6.02	N/A	N/A
H3PO4	1.47	5.59	8.21
NH4	8.33	N/A	N/A
H2SO4	1.33	N/A	N/A
H2O	12.10	N/A	N/A
HF	2.57	N/A	N/A
H2SO3	1.53	5.81	N/A
B(OH)3	8.15	N/A	N/A
HAc	4.04	N/A	N/A
Calcite	6.28	N/A	N/A
Aragonite	6.11	N/A	N/A
H3AsO4	1.62	5.31	8.11

Speciation of Mono and Divalent Metals

	Ion Pair	log K	Gamma	log K*	Fraction(tr)
	Cu				5.00%
	CuOH	5.94	0.62942	4.57	6.65%
	Cu(OH)2	11.21	1.99638	8.63	2.68%
	CuHCO3	1.82	1.21399	0.64	0.04%
Cu(II)	CuCO3	7.12	1.32601	4.58	75.09%
	Cu(CO3)2	10.41	0.23602	7.04	8.70%
	CuHS	8.70	0.57726	7.92	0.00%
	Cu(HS)2	14.90	0.78309	13.82	0.00%
	CuSO4	2.61	0.57726	0.93	1.82%

Speciation of Trivalent Metals

	Ion Pair	log K	Gamma	log K*	Fraction(tr)
Al	Al				4.05%
	AlOH	7.61	0.04219	5.20	22.78%
	Al(OH)2	13.93	0.45322	9.77	30.33%
	Al(OH)3	18.79	1.00000	13.57	6.81%
	Al(OH)4	21.29	0.45322	15.70	0.03%
	AlCO3	8.43	0.45322	4.13	21.99%
	AlF	7.01	0.04219	4.69	9.05%
	Al(F)2	12.73	0.45322	8.76	4.73%
	Al(F)3	16.71	1.00000	11.77	0.22%
	Al(F)4	19.67	0.45322	14.45	0.00%
	Al(F)5	20.73	0.04219	15.91	0.00%
	Al(F)6	20.46	0.00081	16.74	0.00%

Calculation of Speciation

$$Cu^{2+} + CO_3^{2-} = MCO_3$$

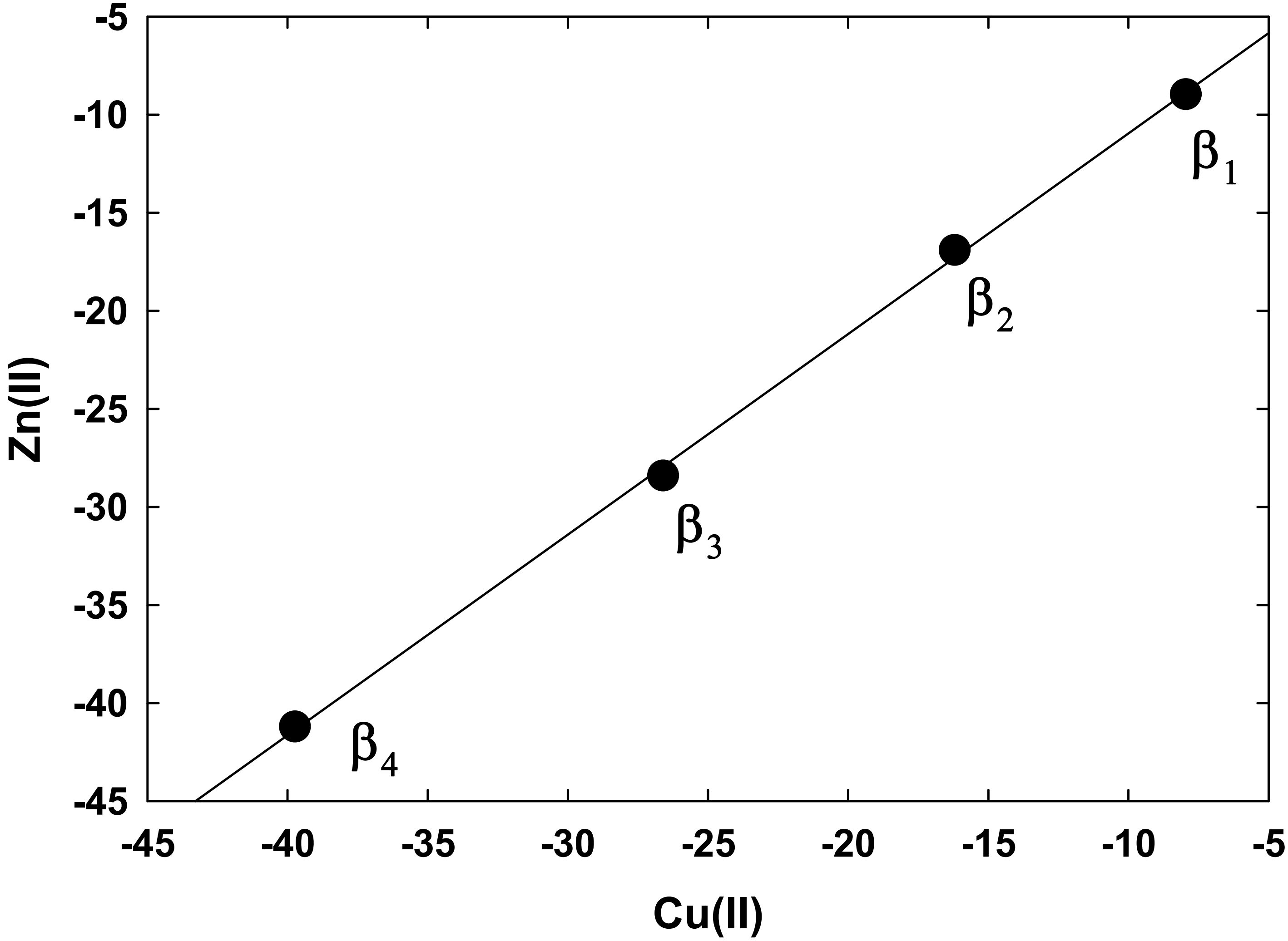
$$K^*_{CuCO3} = K_{CuCO3}\ \{\gamma_{Cu}\gamma_{CO3}/\gamma_{MCO3}\}$$

γ_M = activity coefficient of Cu^{2+}

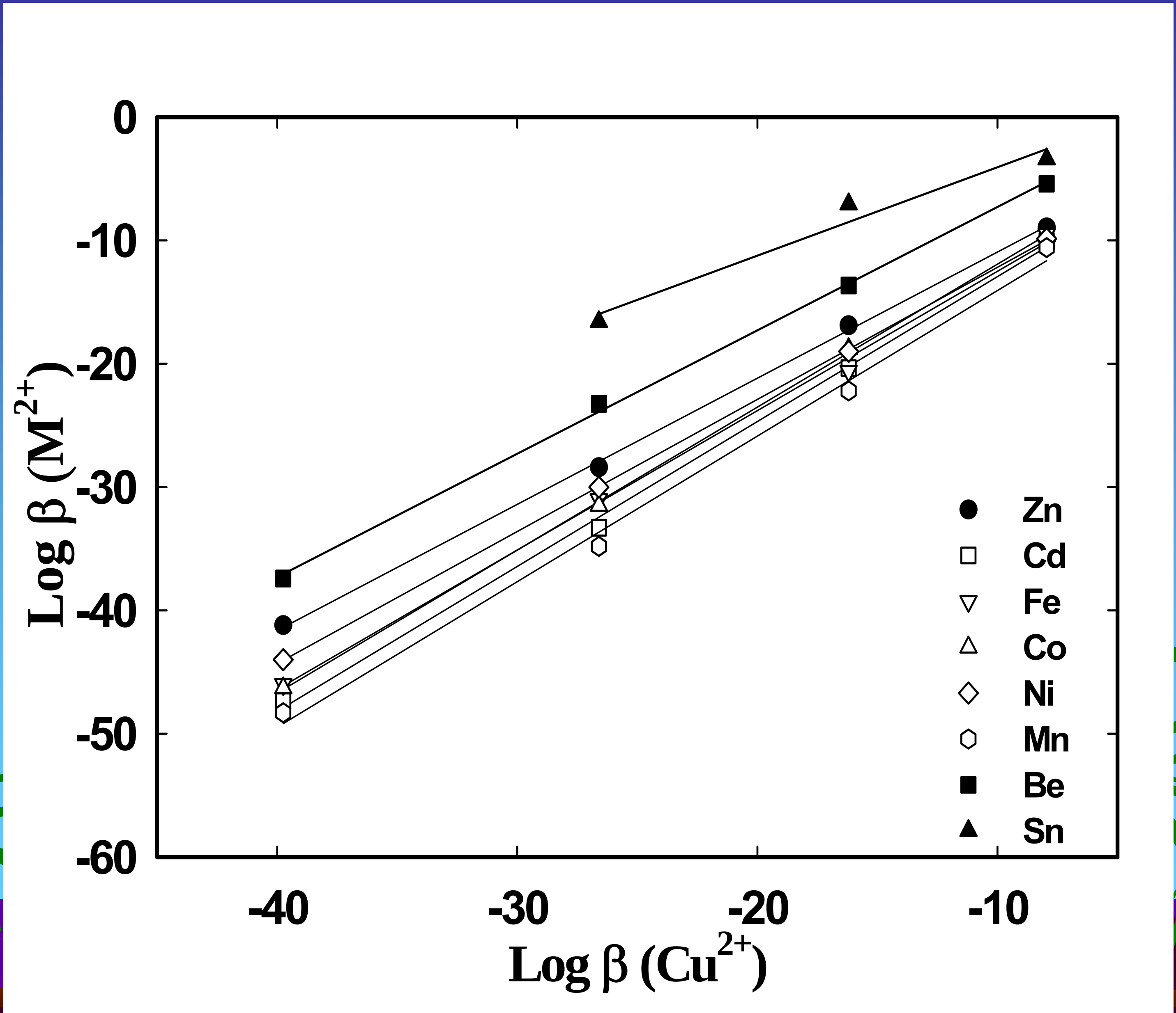
γ_{CO3} = activity coefficient of CO_3^{2-}

γ_{MCO3} = activity coefficient of $CuCO_3$

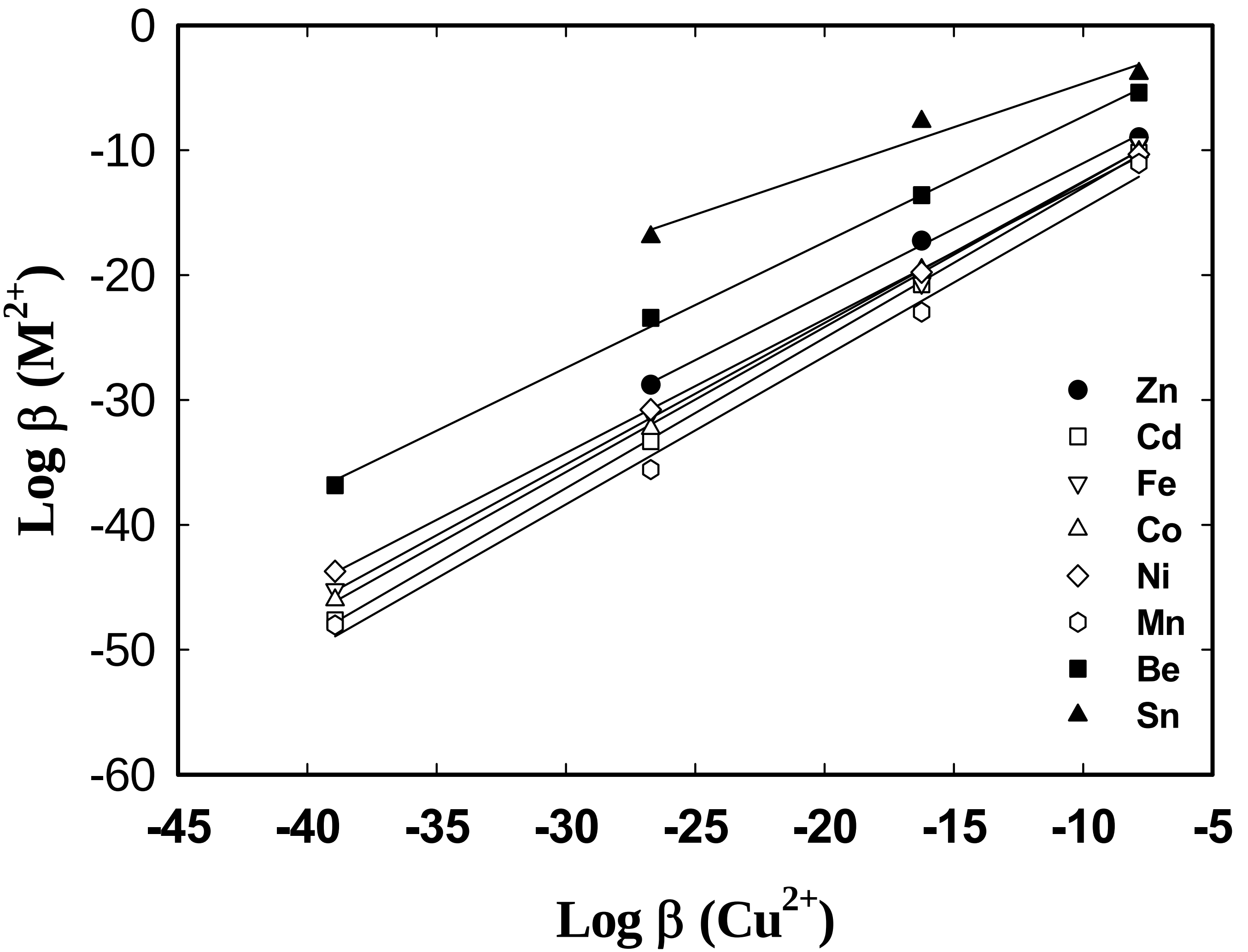
Hydrolysis Constants



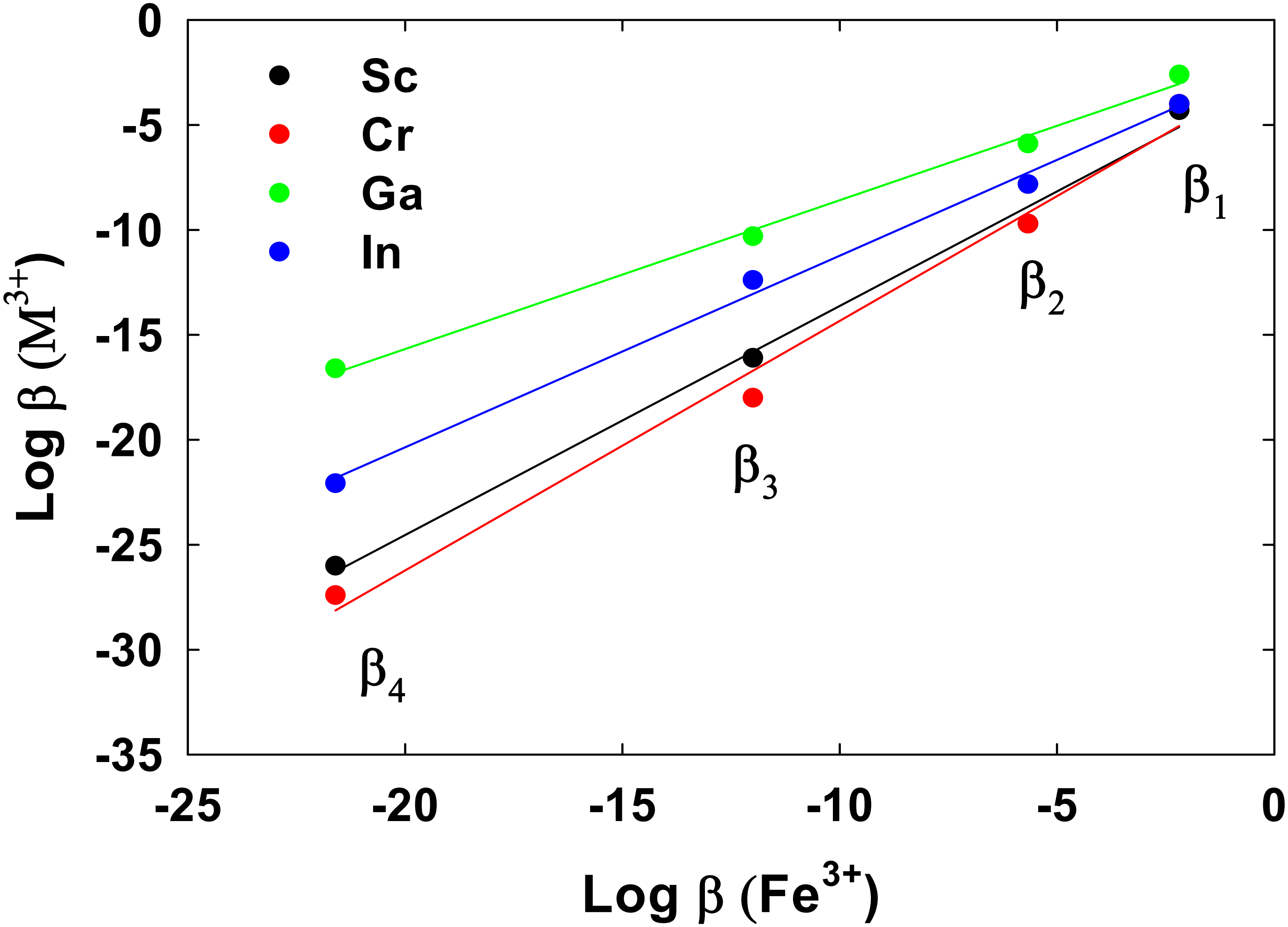
Hydrolysis Constants I = 0 m



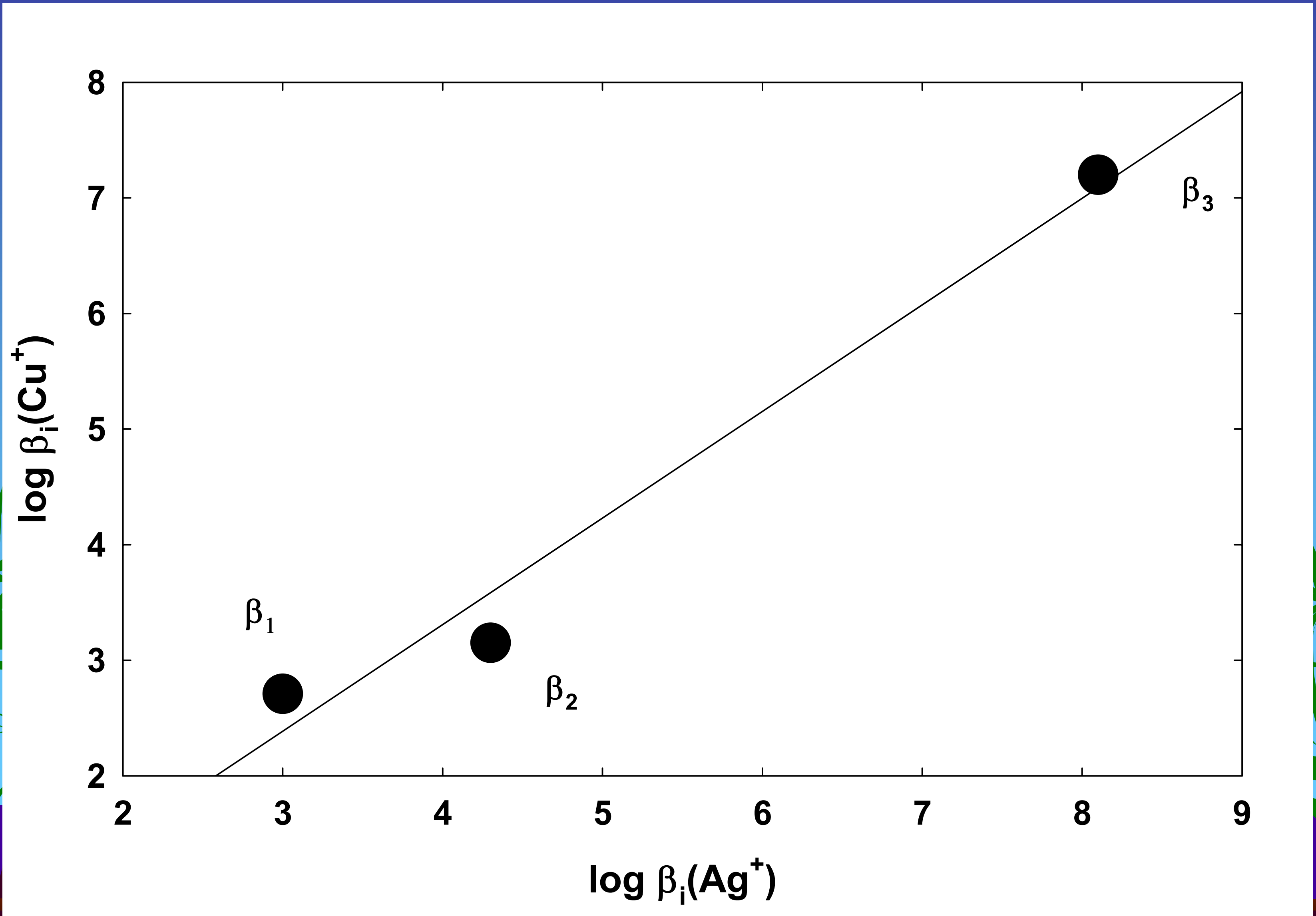
Hydrolysis Constants I = 3 m



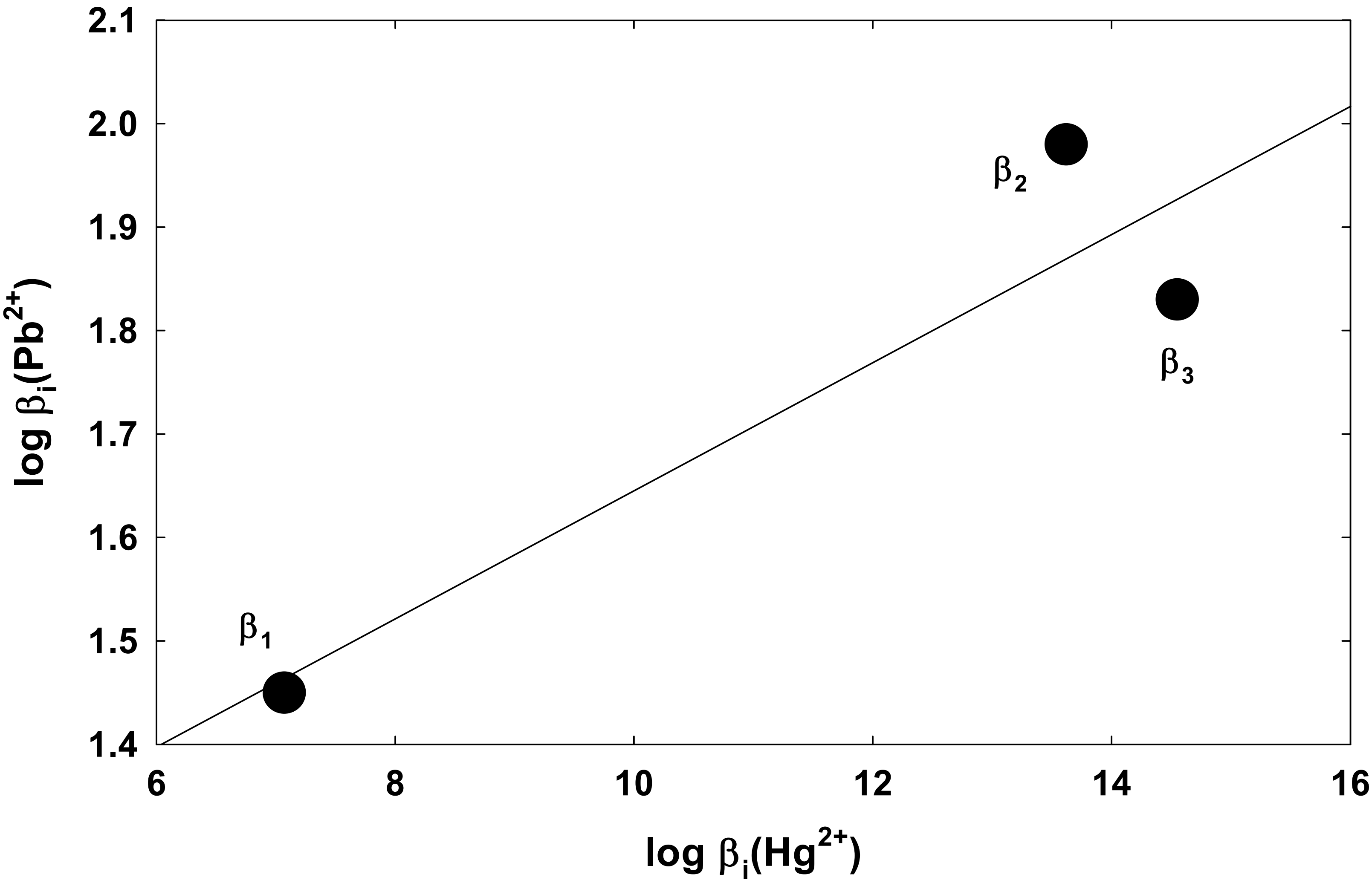
Hydrolysis Constants I = 0 m



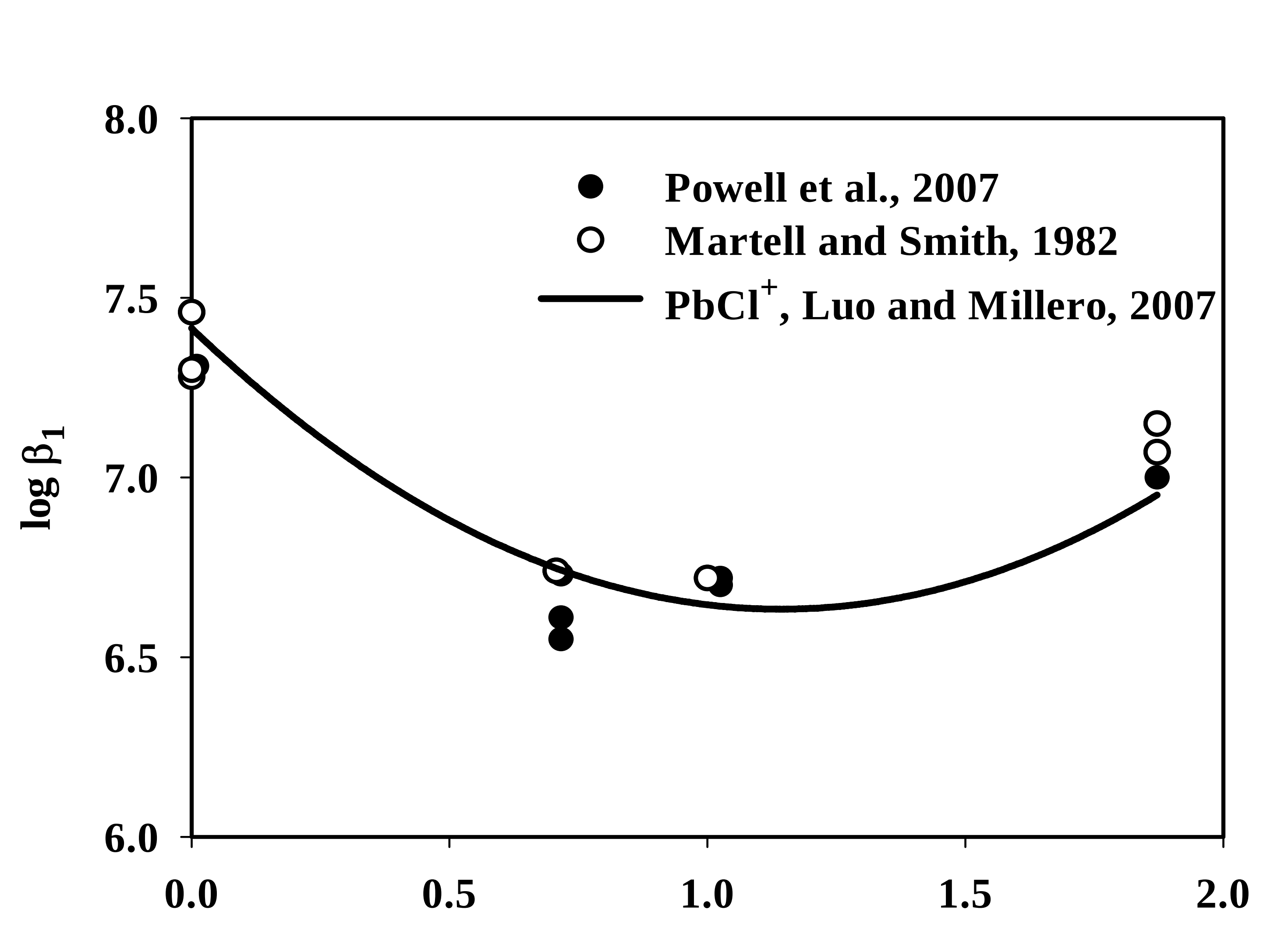
Chloride Constants for Ag(I) and Cu(I)



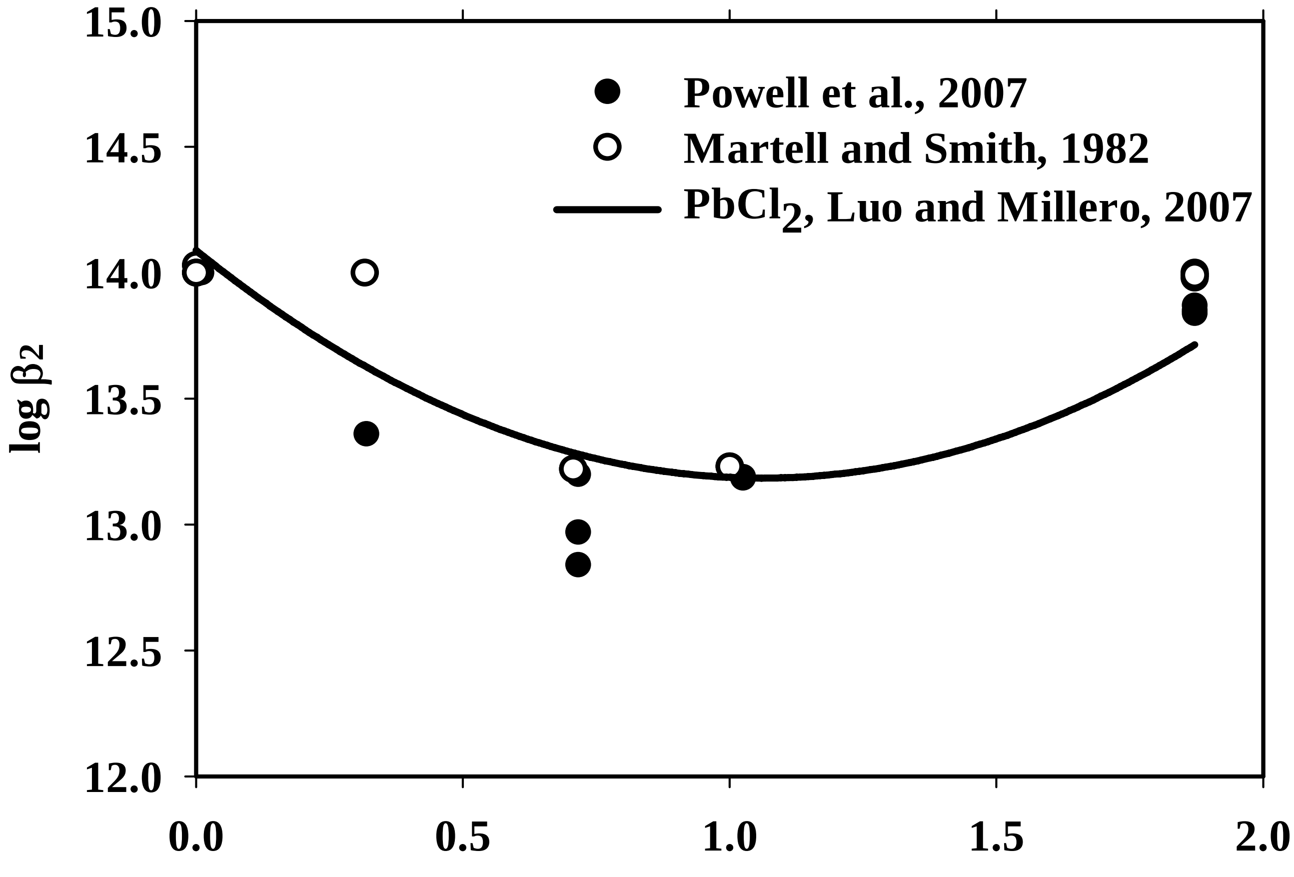
Chloride Constants for Hg(II) and Pb(II)



Chloride Constants for Hg(II) and Pb(II)



Chloride Constants for Hg(II) and Pb(II)



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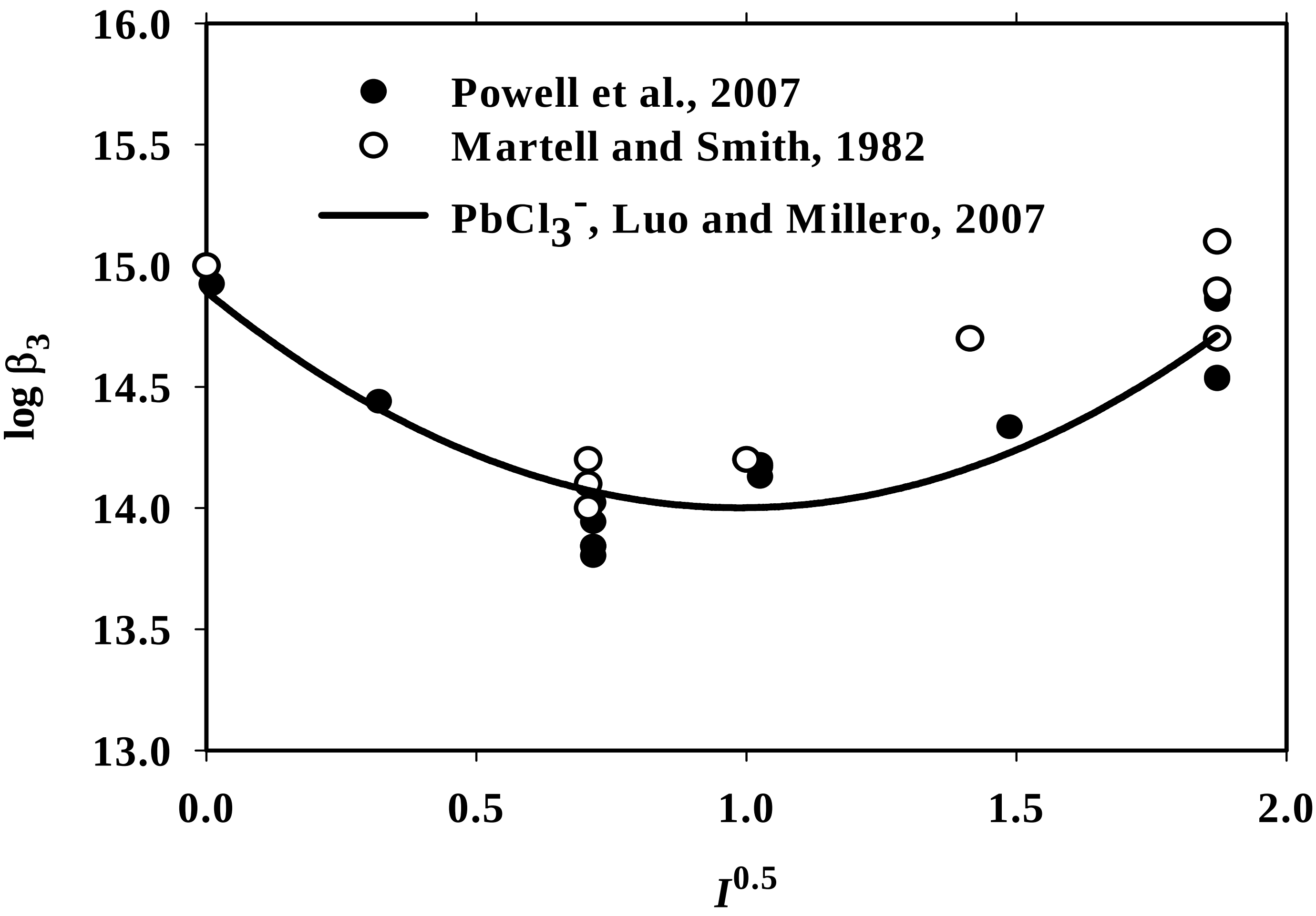
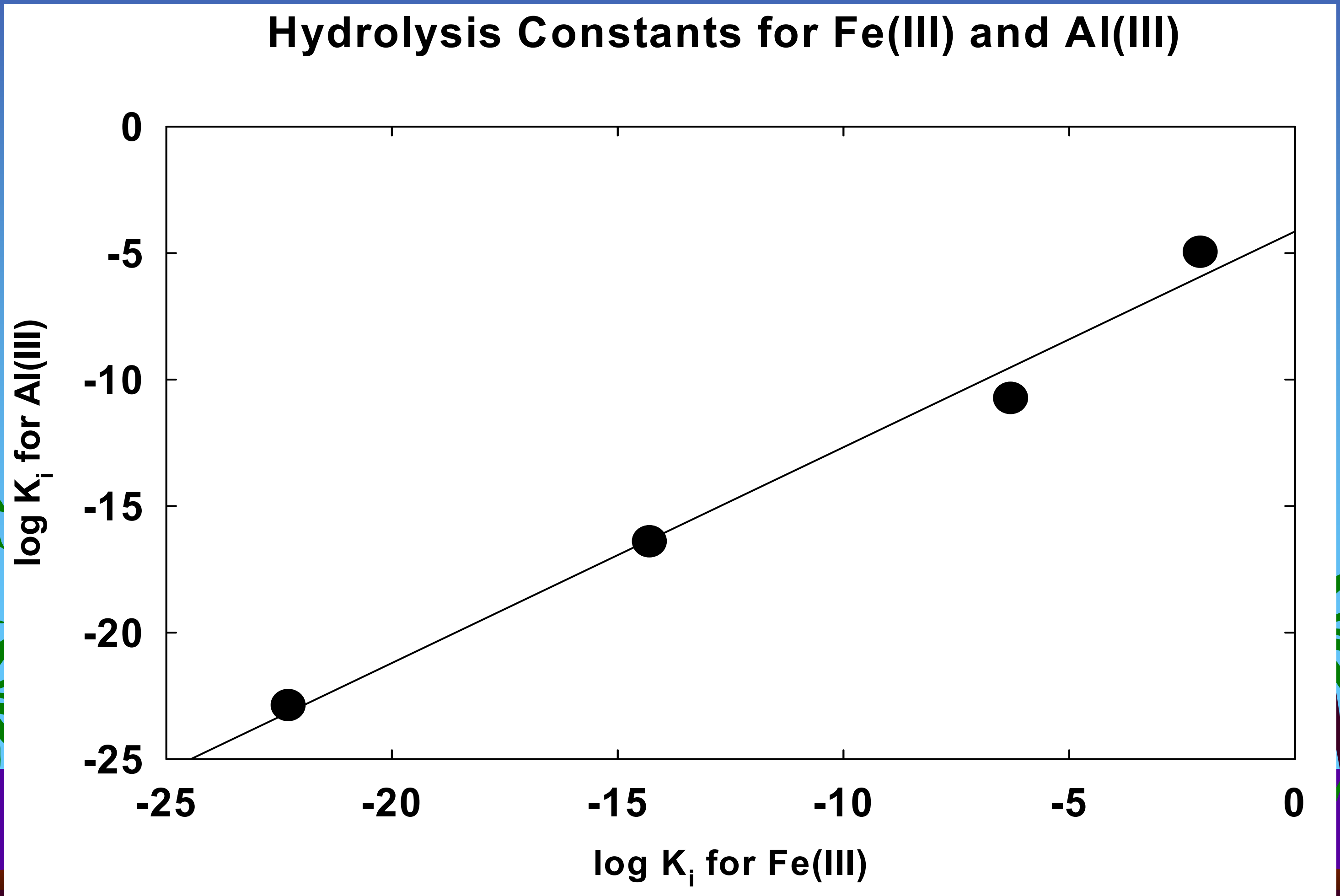


Hydrolysis of Al(III) and Fe(III)



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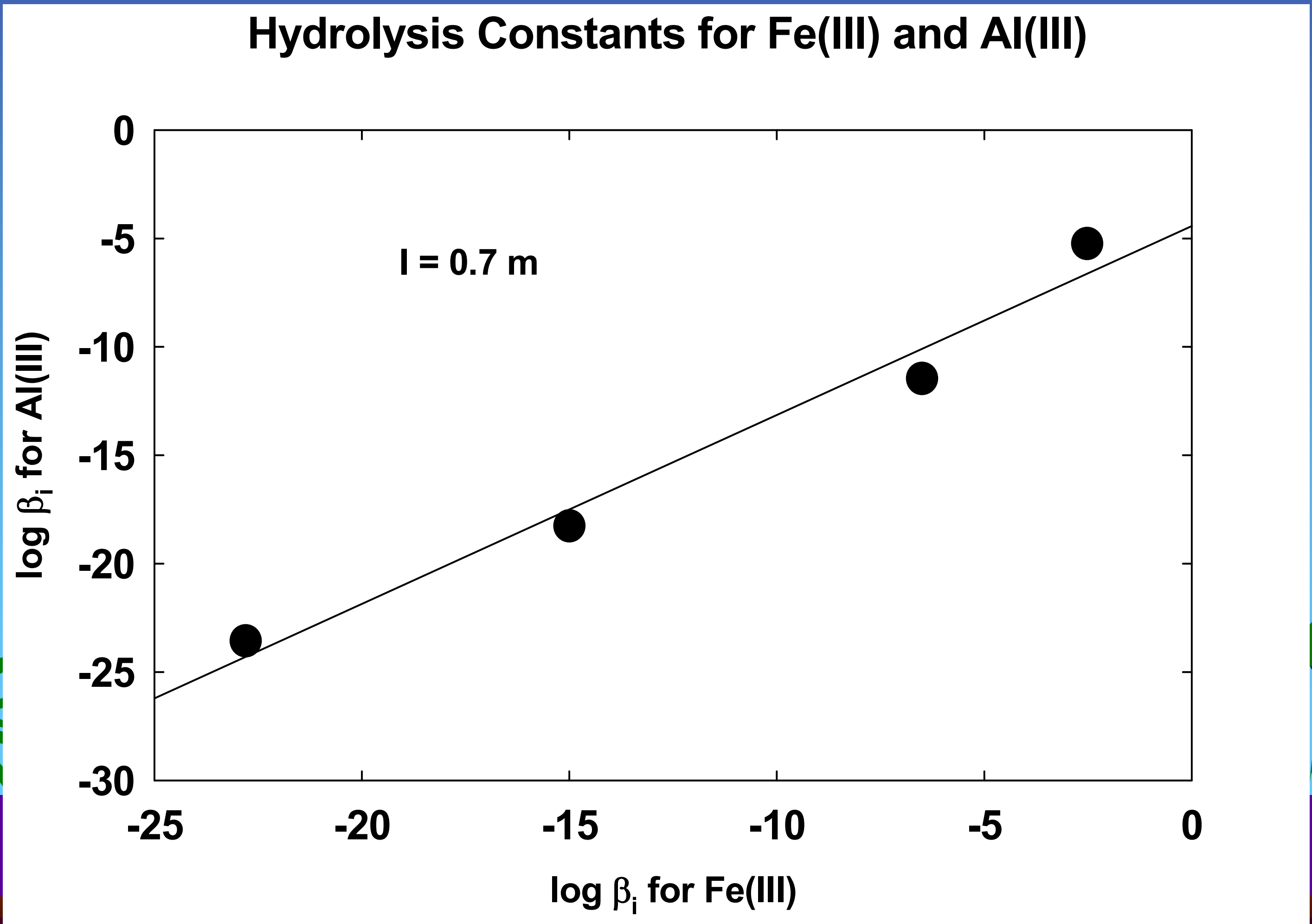

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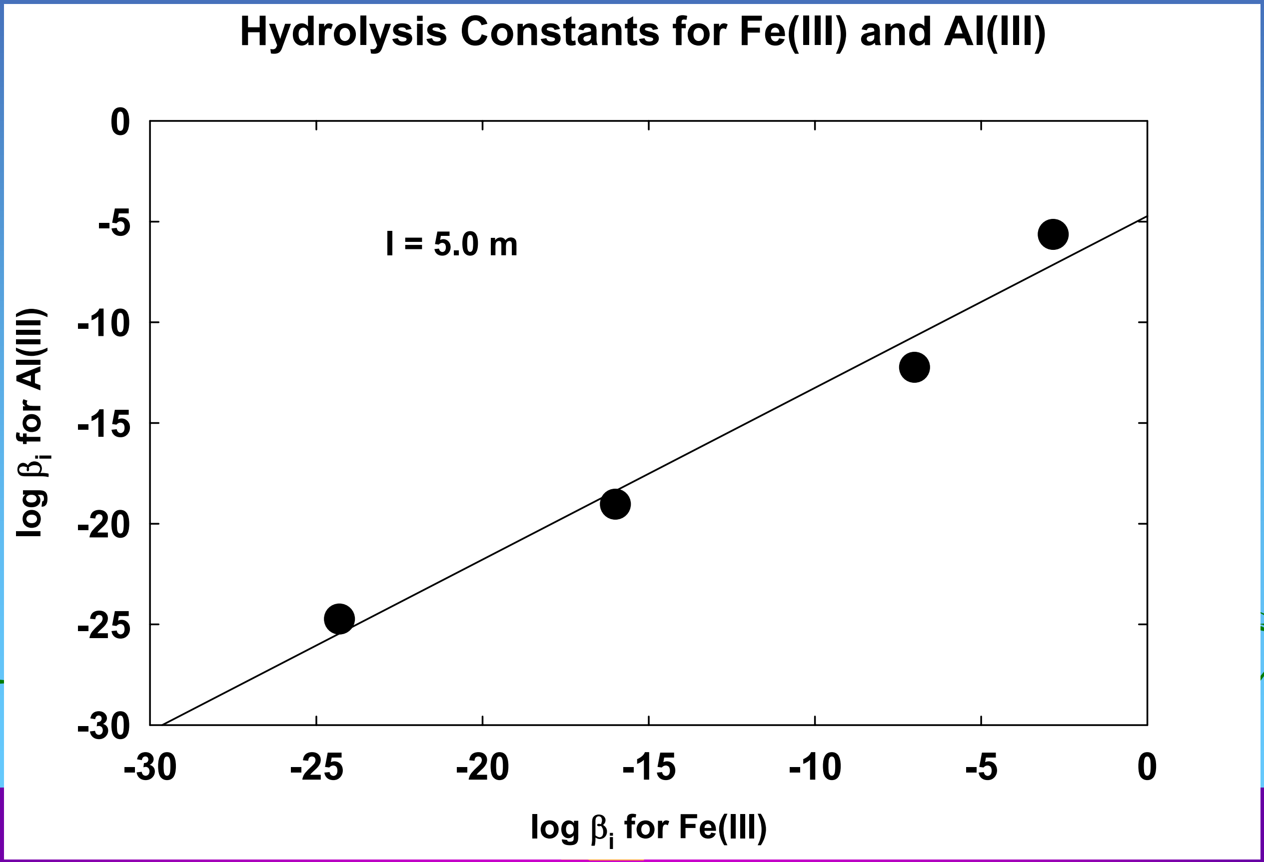

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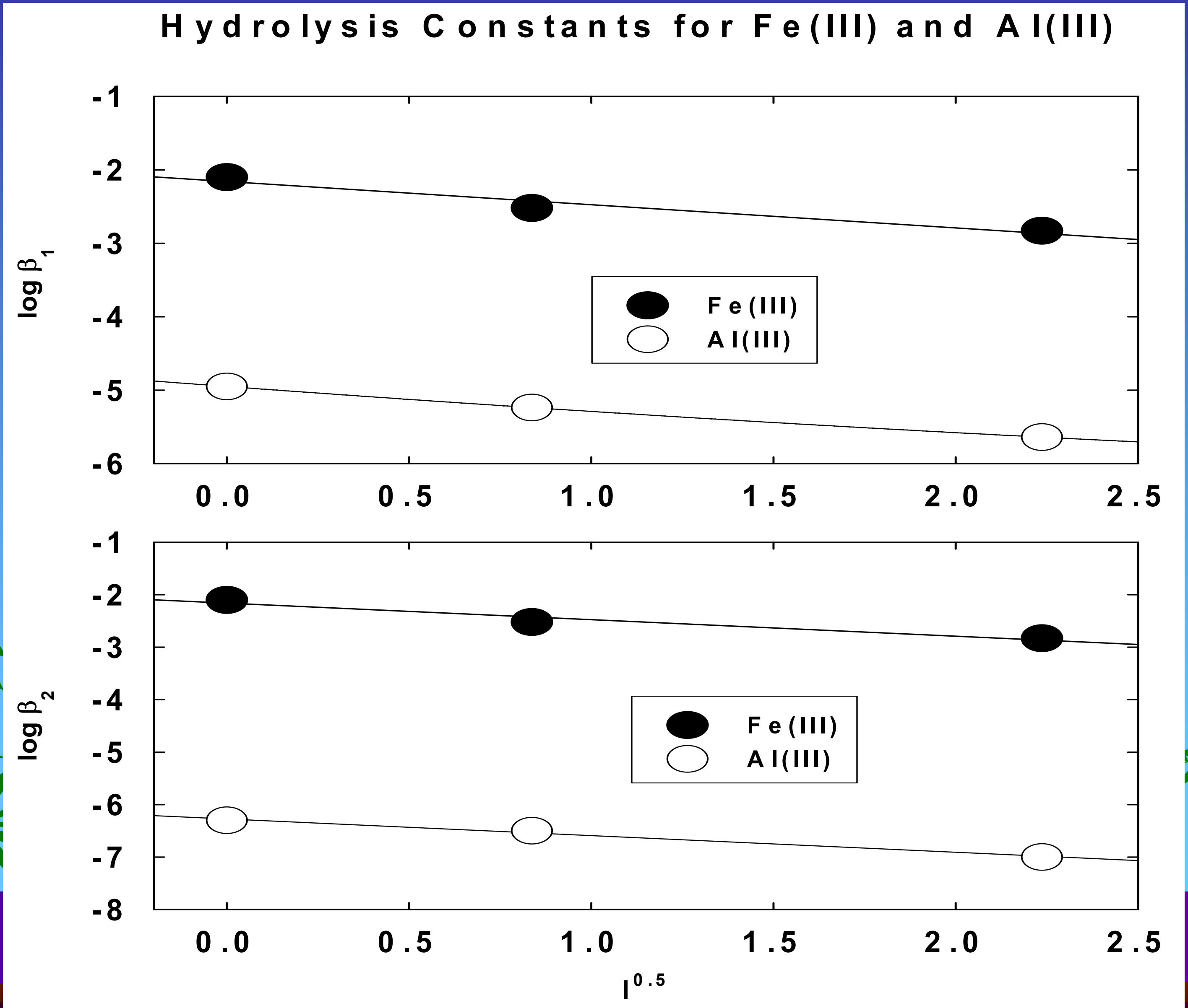
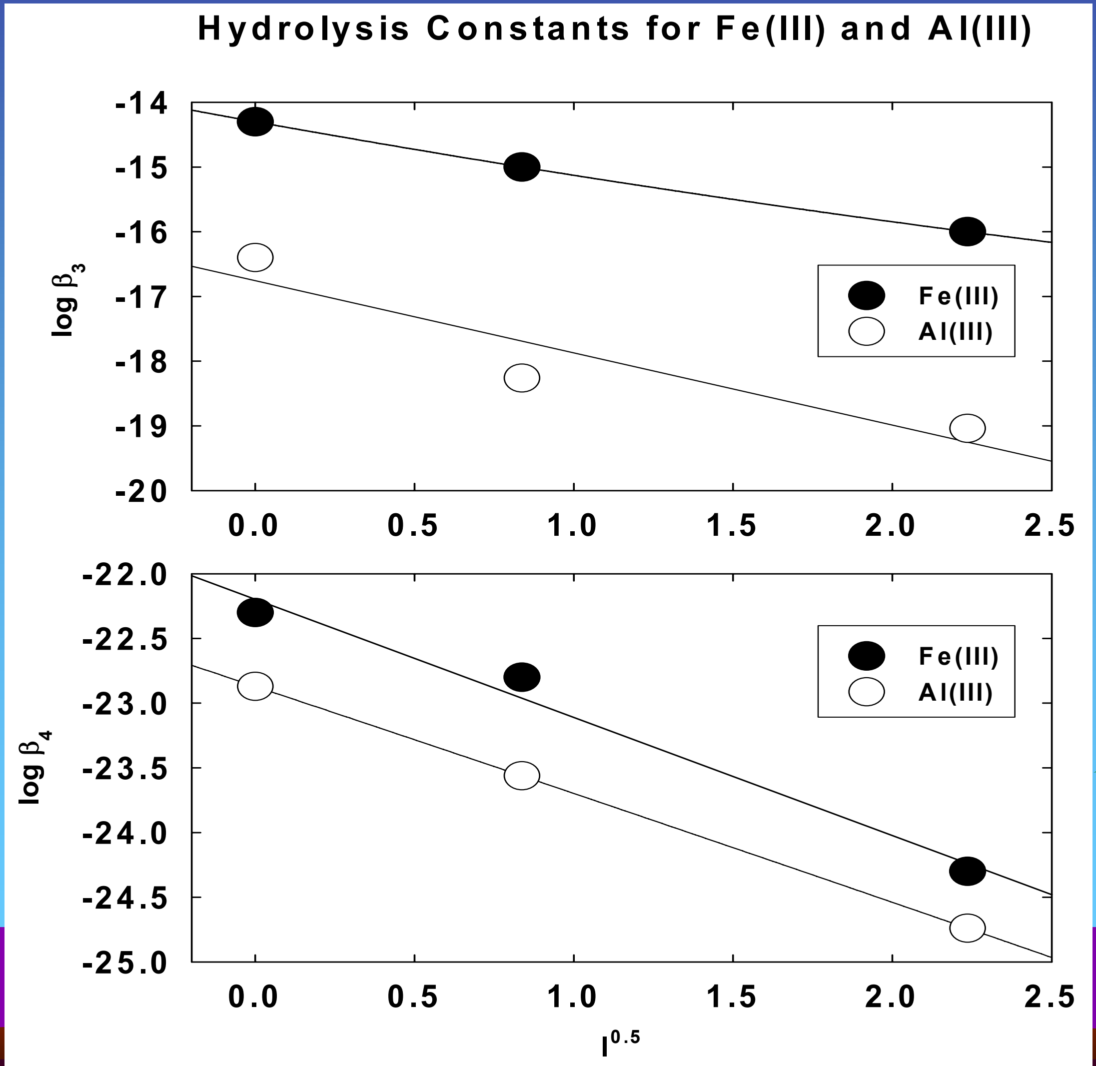
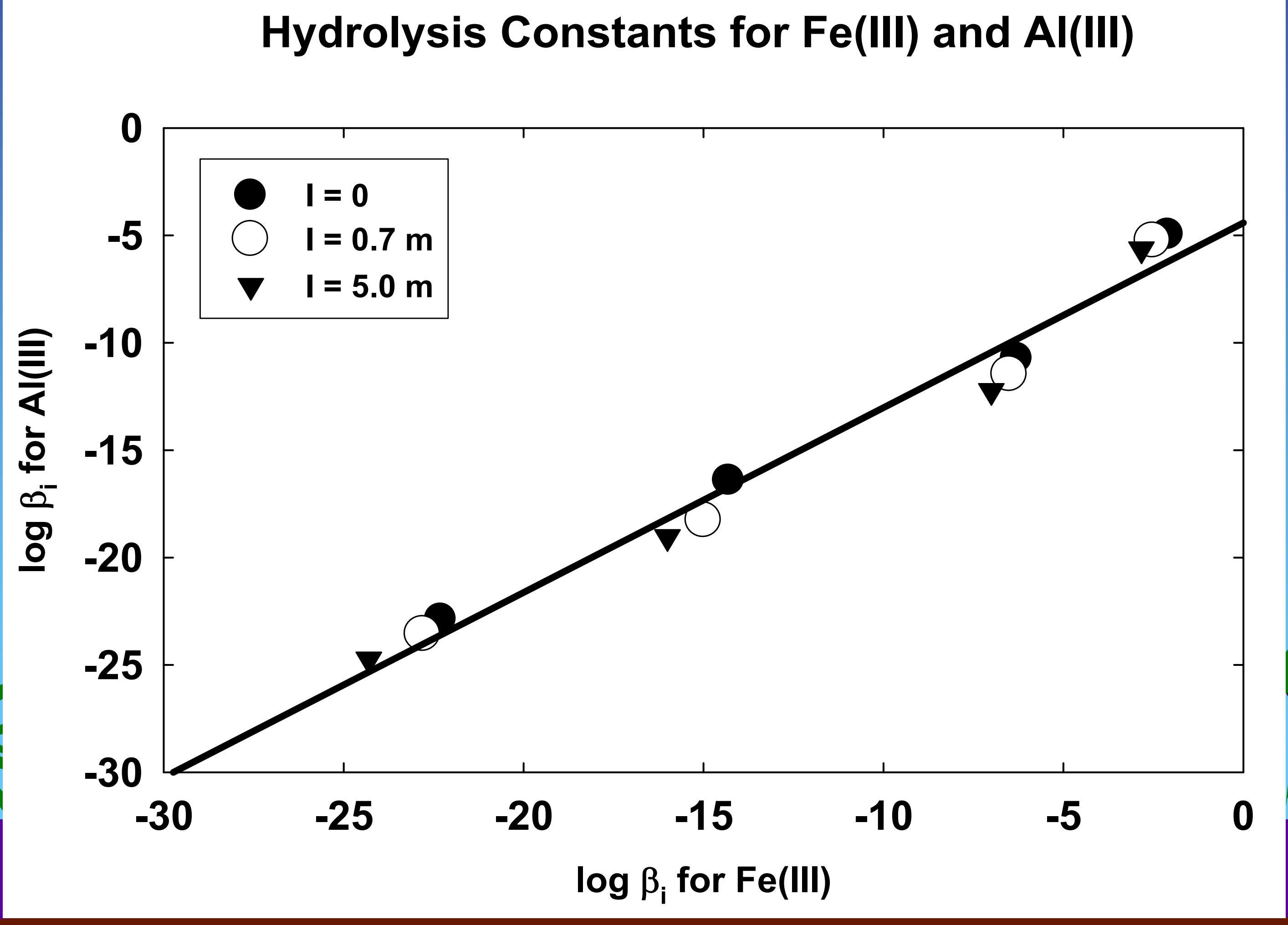


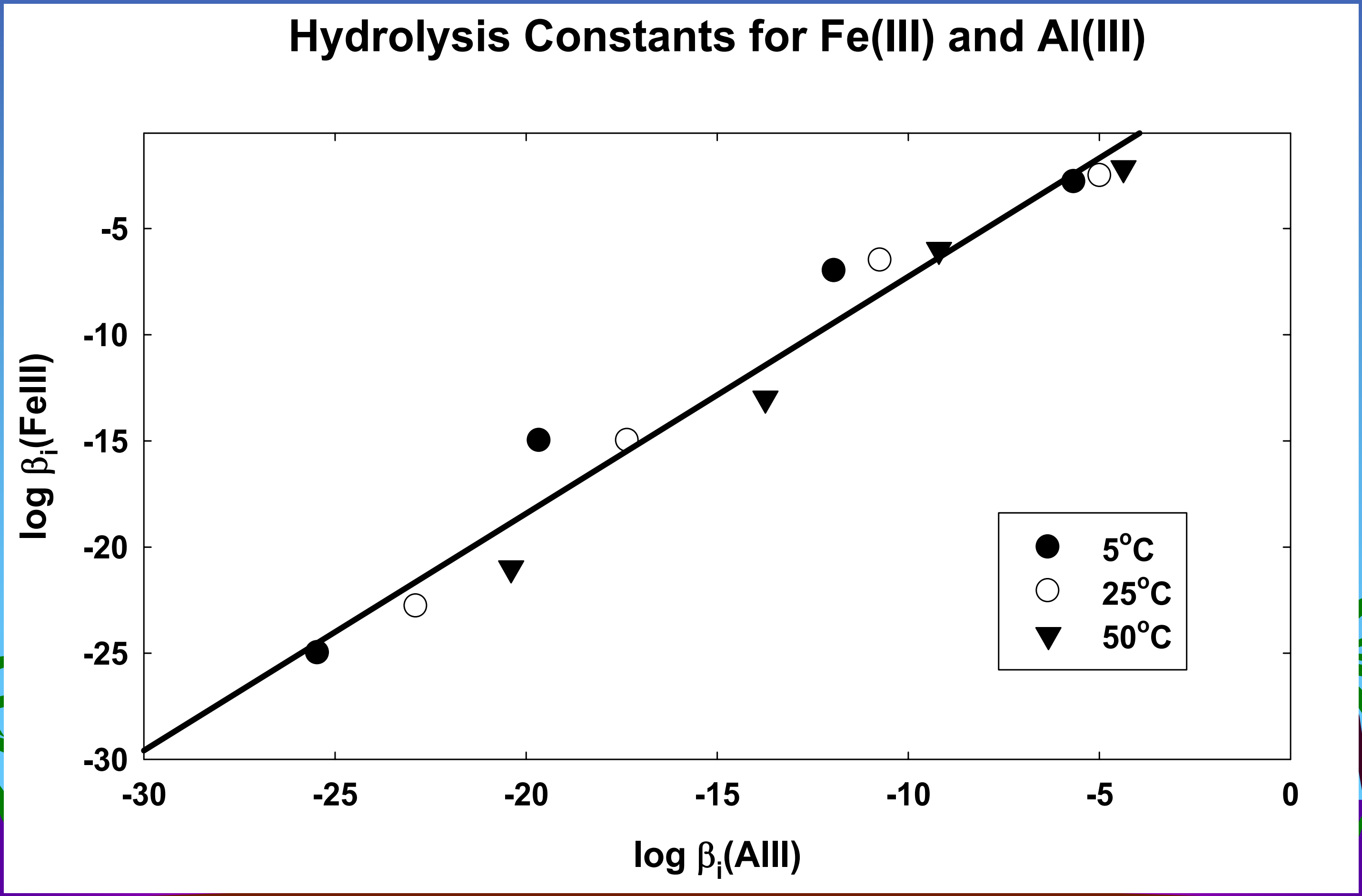
Hydrolysis of Al(III) and Fe(III)



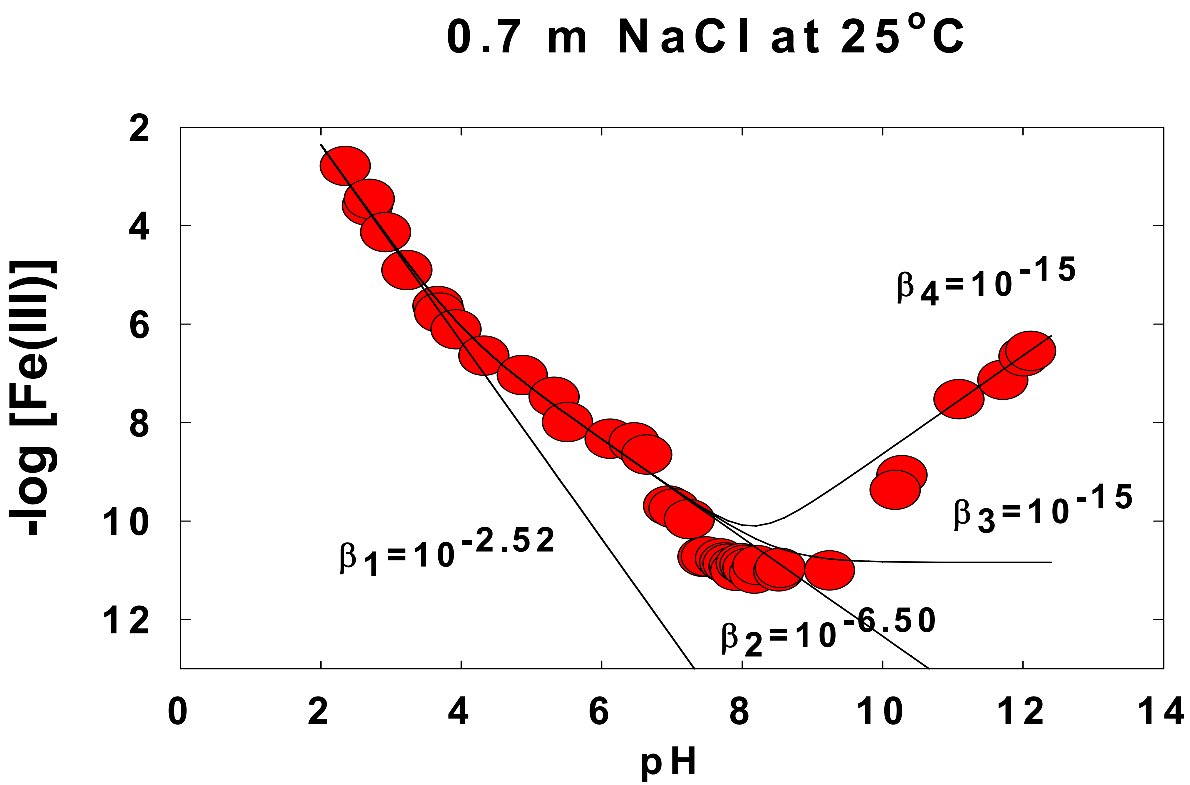
Hydrolysis of Al(III) and Fe(III)



Hydrolysis of Al(III) and Fe(III)

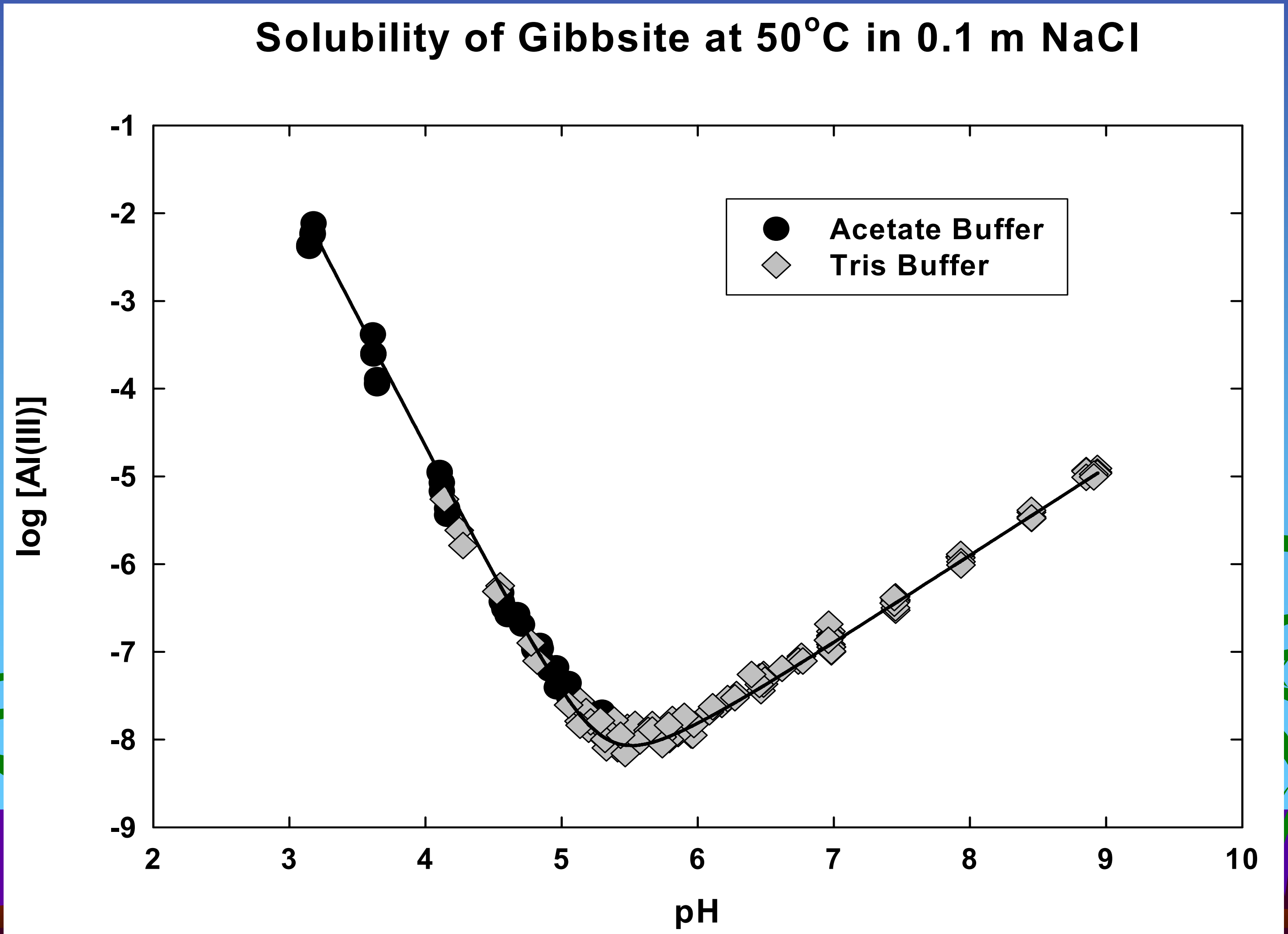


Solubility of Fe(III) in NaCl

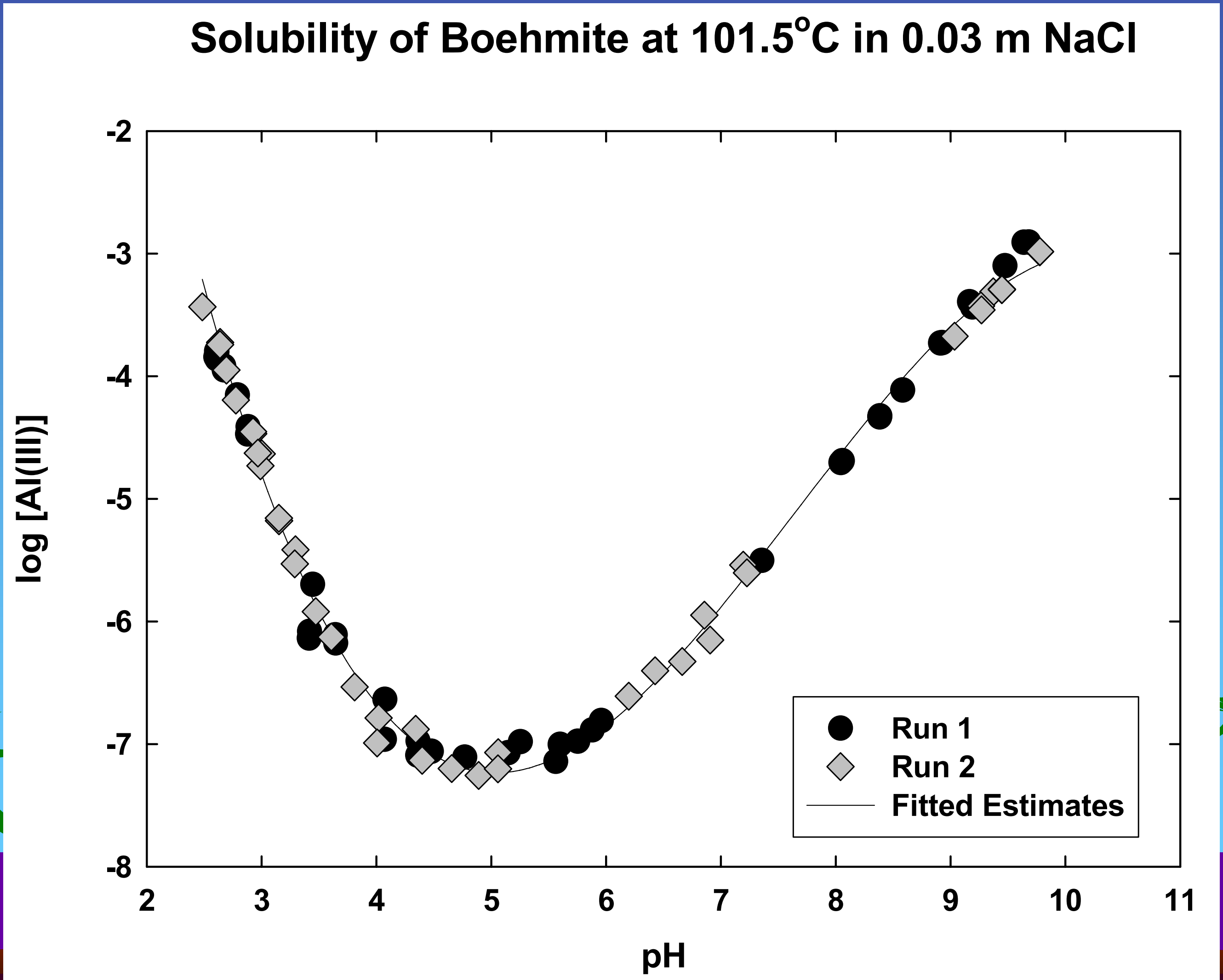


Marine Physical Chemistry

The Effect of pH on the Solubility of Aluminum Oxides



The Effect of pH on the Solubility of Aluminum Oxides



Solubility of Aluminum Oxides

$Al(OH)_3(s) + 3H^+ = Al^{3+} + 3\ H_2O$ $\quad Qs_0$

$Al(OH)_3(s) + 2H+ = Al(OH)_2^+ + 2\ H_2O$ $\quad Q$

$Al(OH)_3(s) + H^+ = Al(OH)^{2+} + 2\ H_2O$ $\quad Qs_2$

$Al(OH)_3(s) = Al(OH)_3$ $\quad Qs_3$

Hydrolysis Constants for Al(III)

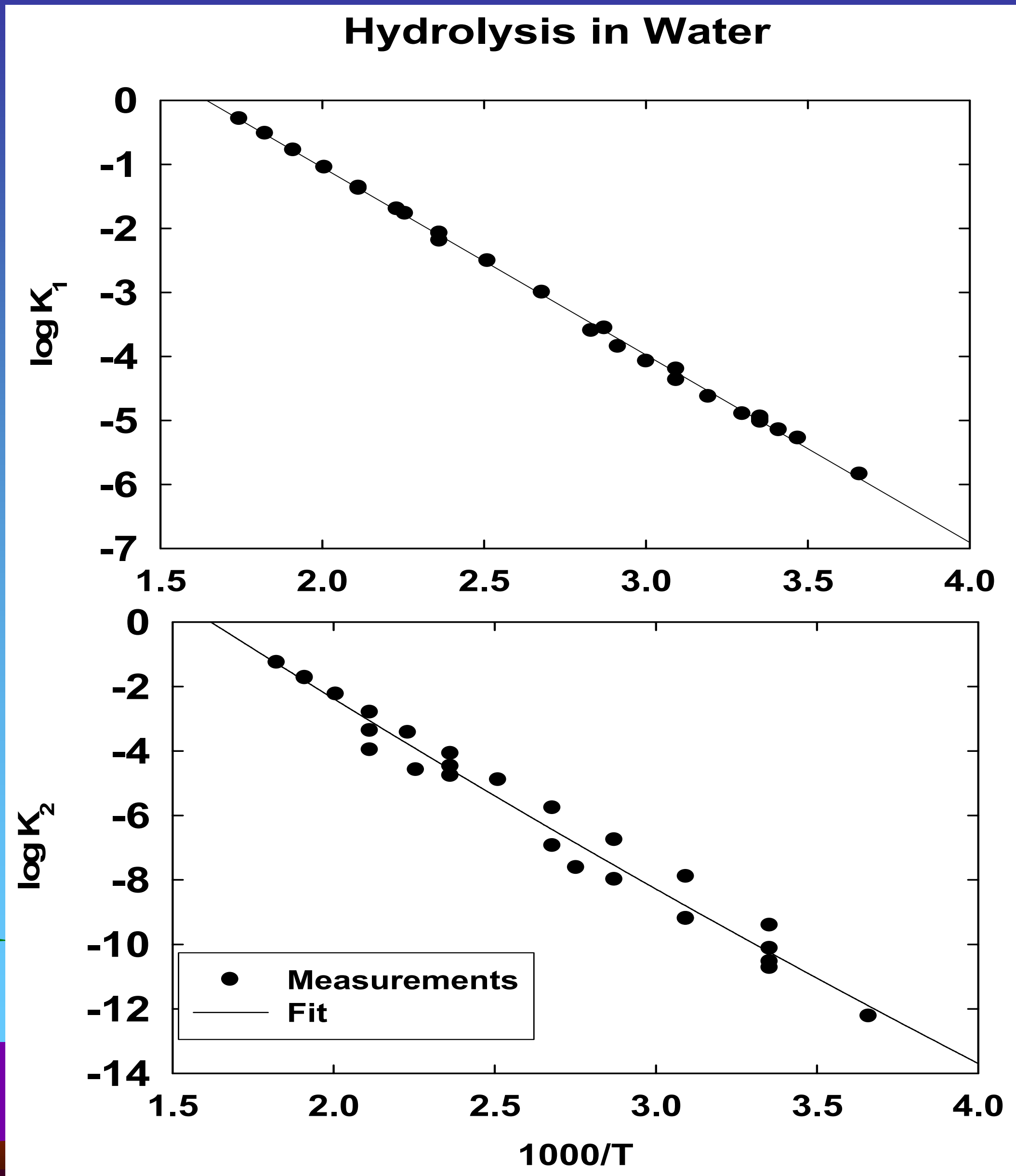
$$\beta_1 = Qs_1 / Qs_0$$

$$\beta_2 = Qs_2 / Qs_0$$

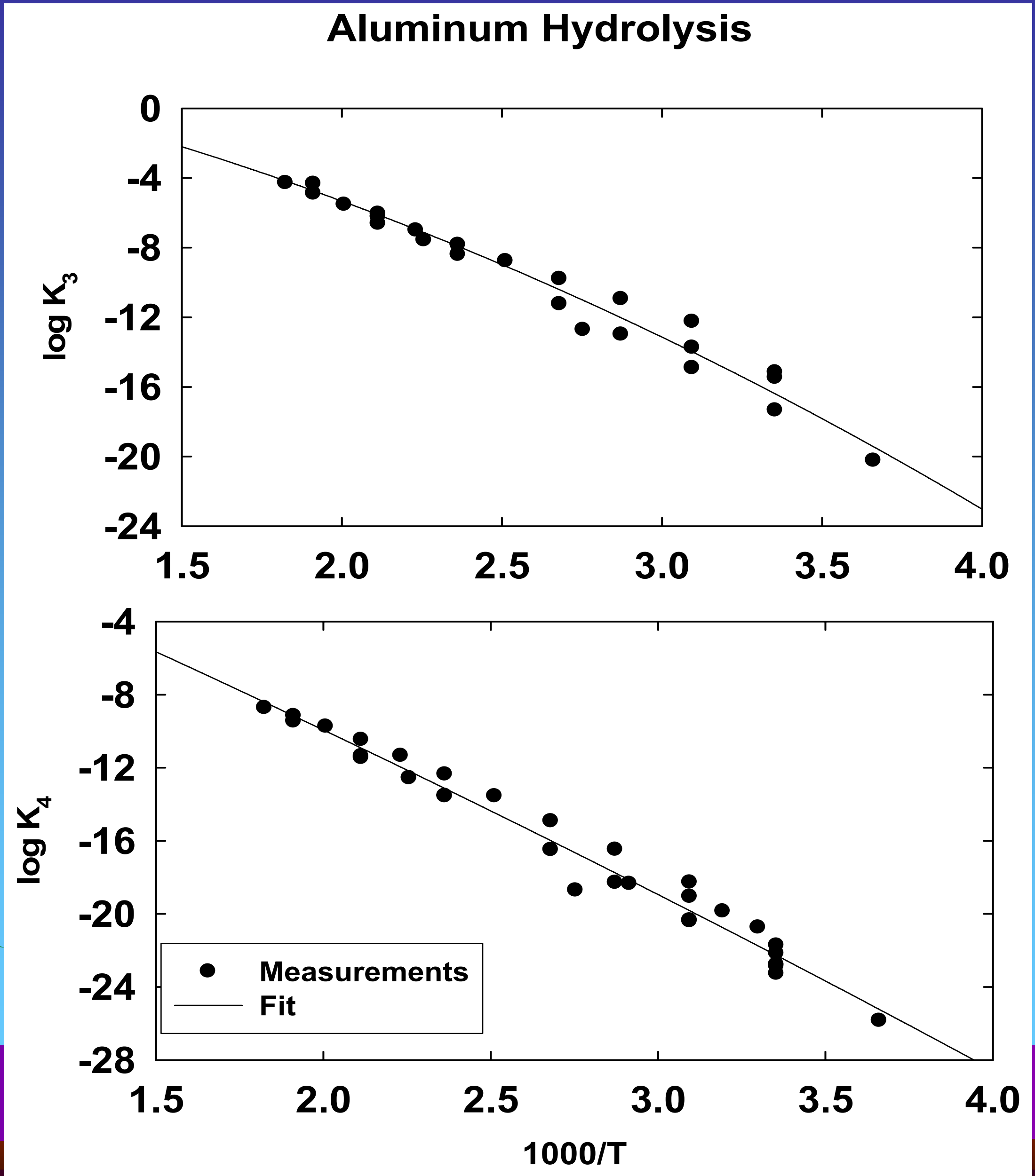
$$\beta_3 = Qs_3 / Qs_0$$

$$\beta_4 = Qs_4 / Qs_0$$

Hydrolysis Constants from 0 to 300°C



Hydrolysis Constants from 0 to 300°C



Hydrolysis of Al(III)

$$\alpha_{Al} = [Al^{3+}]/[Al(III)] = 1/(1 + \sum \beta^*_j [H^+]^{-n})$$

$$\overset{\beta^*_1}{}$$

$$Al^{3+} + H_2O = Al(OH)^{2}+ + H^+$$

$$\overset{\beta^*_2}{}$$

$$Al^{3+} + 2H_2O = Al(OH)^{2}+ + 2H^+$$

$$\overset{\beta^*_3}{}$$

$$Al^{3+} + 3H_2O = Al(OH)_3^{0} + 3H^+$$

$$\overset{\beta^*_4}{}$$

$$Al^{3+} + 4H_2O = Al(OH)_4^{-} + 4H^+$$

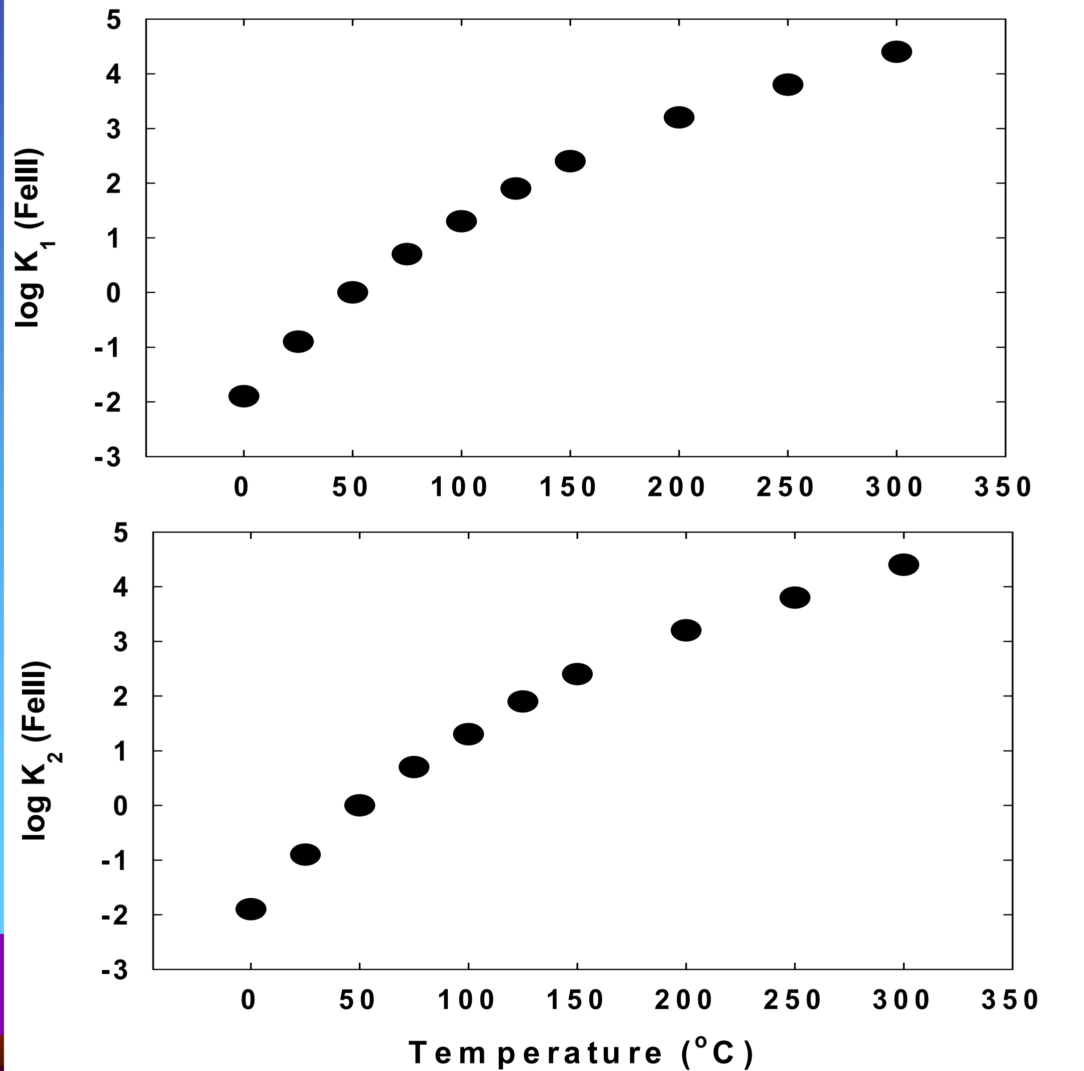
Fits of βi for Hydrolysis of Al(III)

$$\log K_i = A + B/T + C \log T + D\,T$$

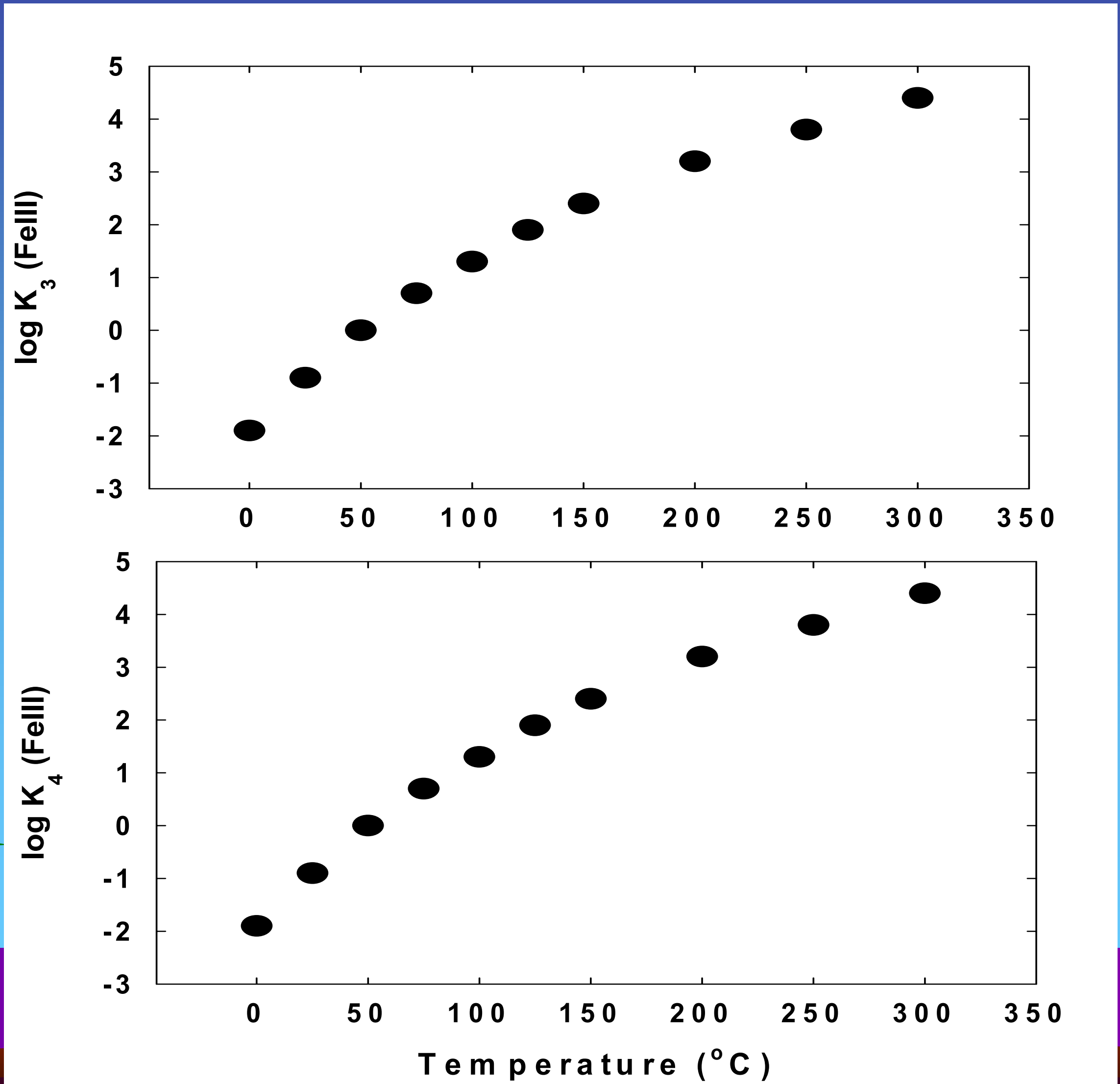
$$\log \beta_i - \log K_i = a_0\, I^{0.5} + a_1\, I^{0.5}/T + a_2\, I + a_3\, I/T + a_4\, I^2$$

σ = 0.05 from 0 to 100°C

K_i for Hydrolysis of Fe(III)



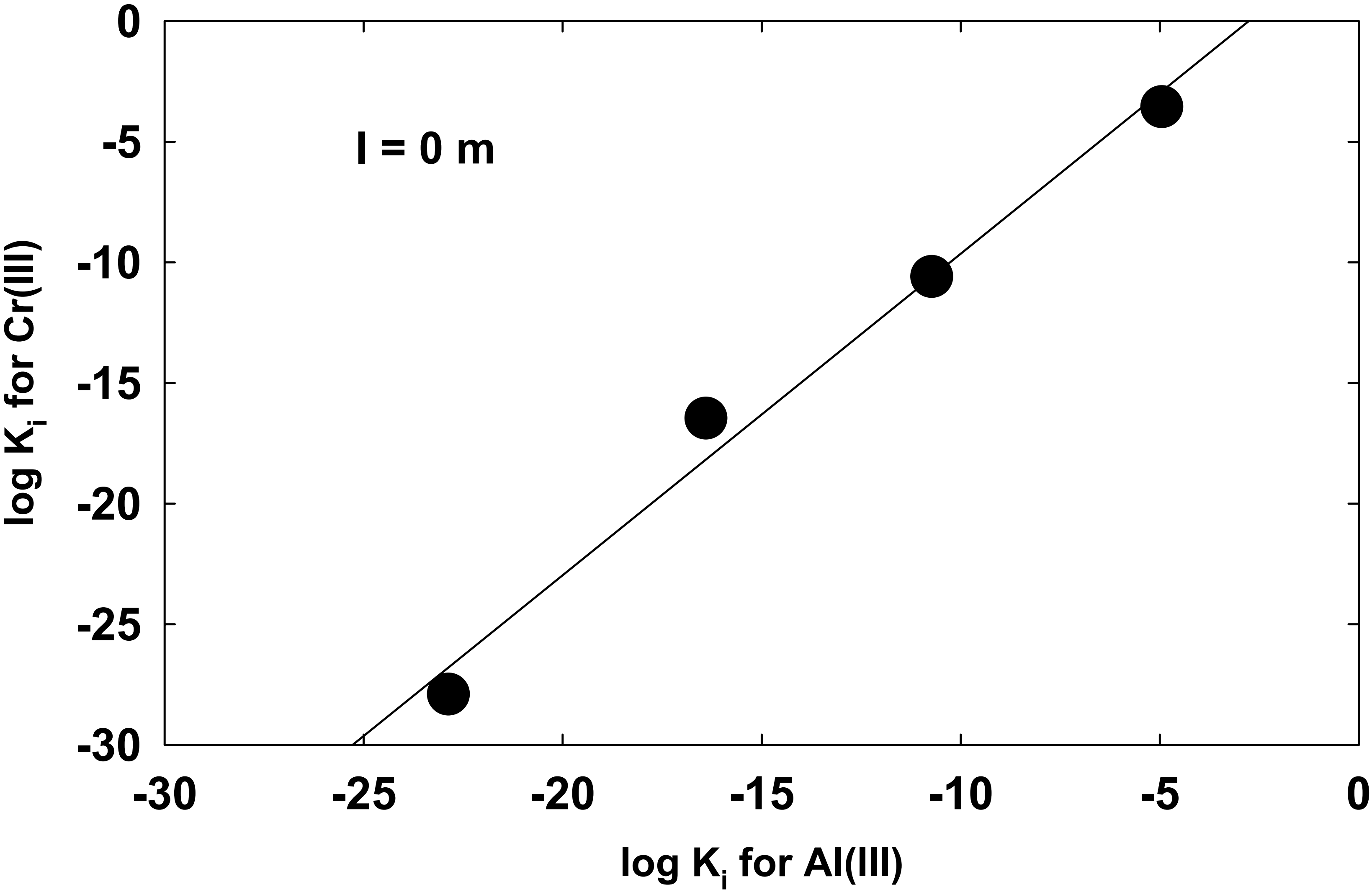
K_i for Hydrolysis of Fe(III)



Summary

1. The physical chemical properties of estuarine waters can be estimate from diluted seawater to the same S_A
2. Models are available to determine the activity coefficient and speciation of metals from I = 0 to 6m and 0 to 50^{o}C

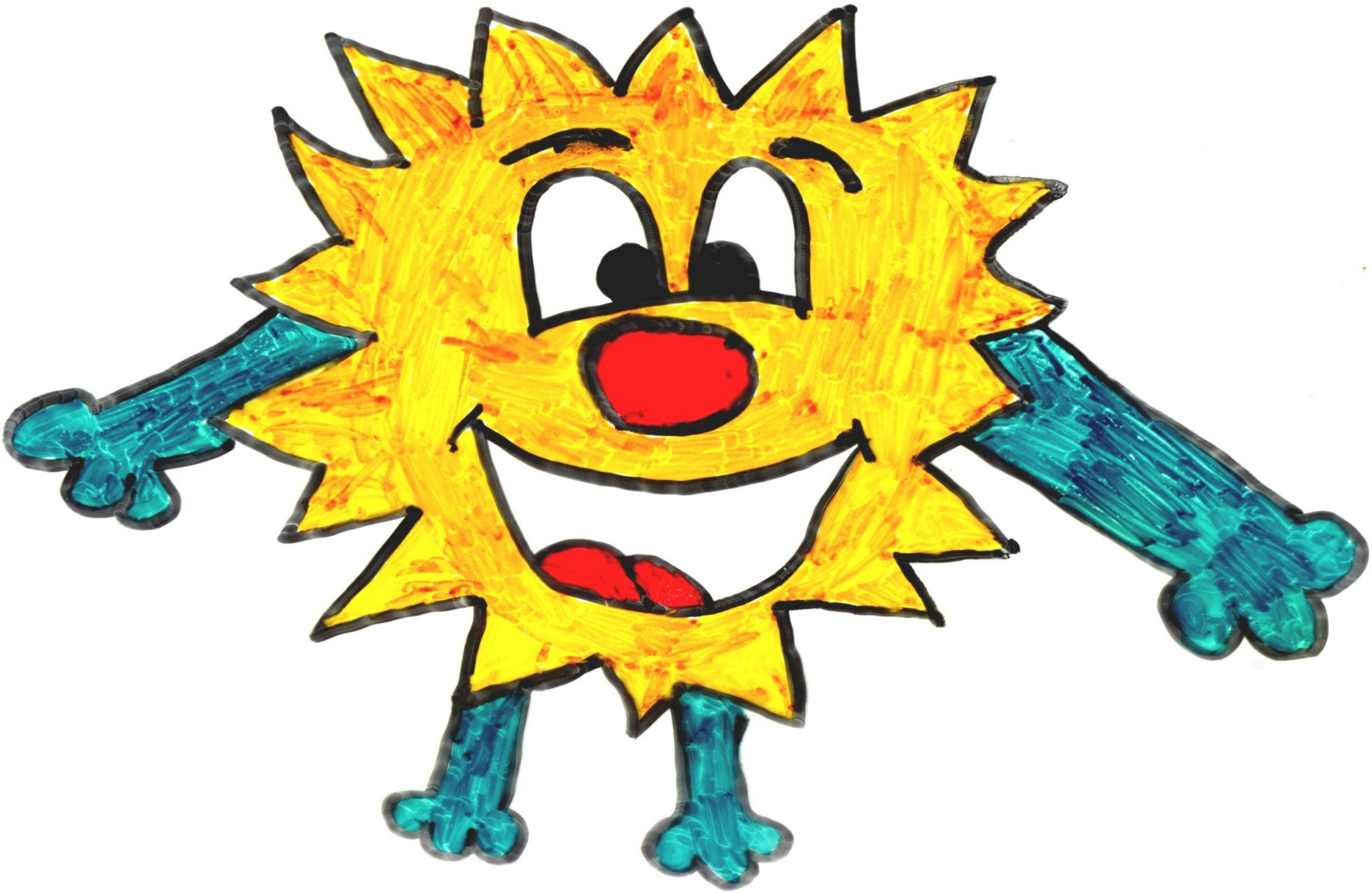
Hydrolysis of Al(III) and Cr(III)



Summary

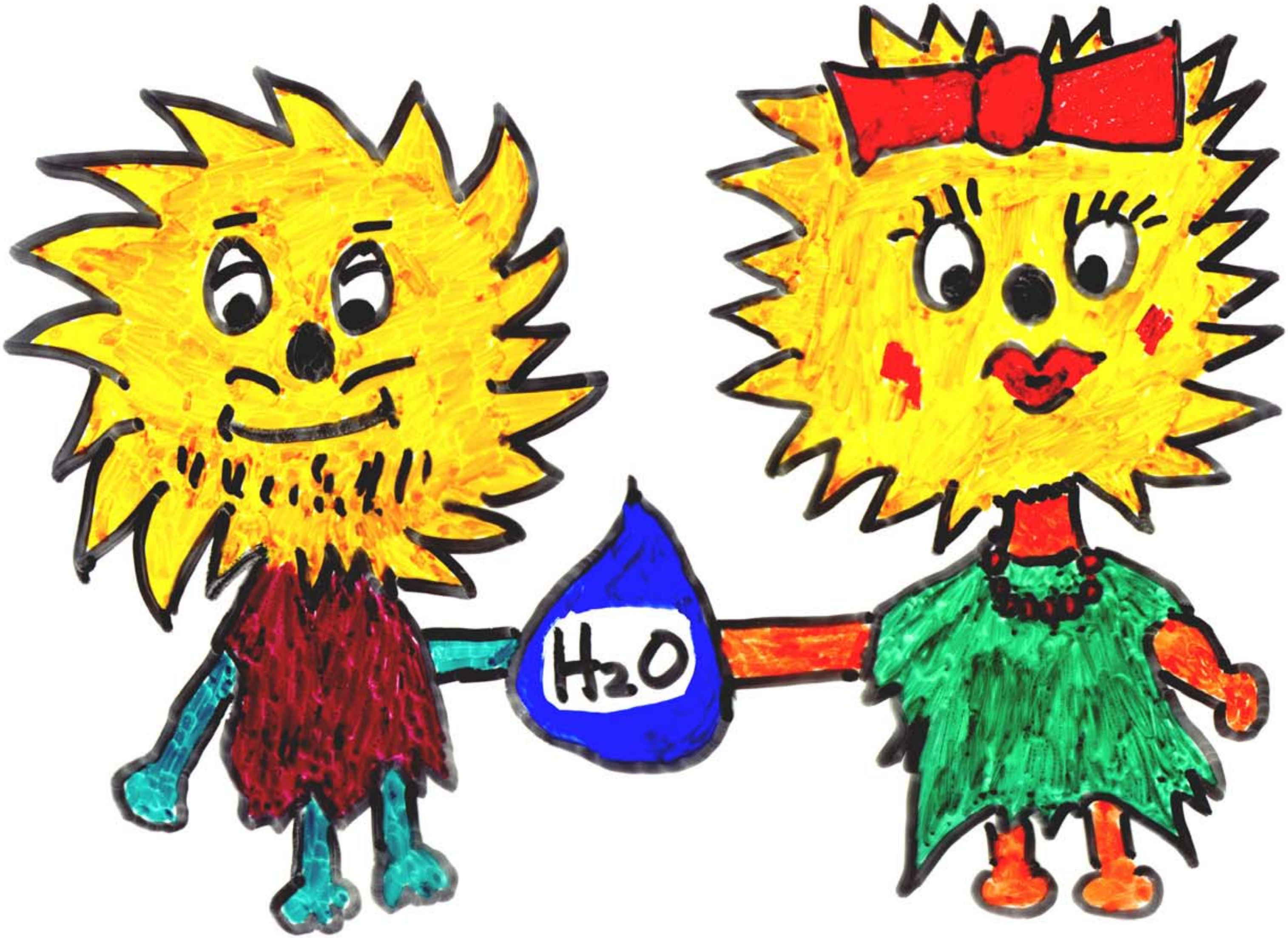
3. One can use correlations of the hydrolysis constants of Al(III) and Fe(III) to estimate the Fe(III) values over a wide range of temperature and ionic strength in NaCl brines

Free Ion

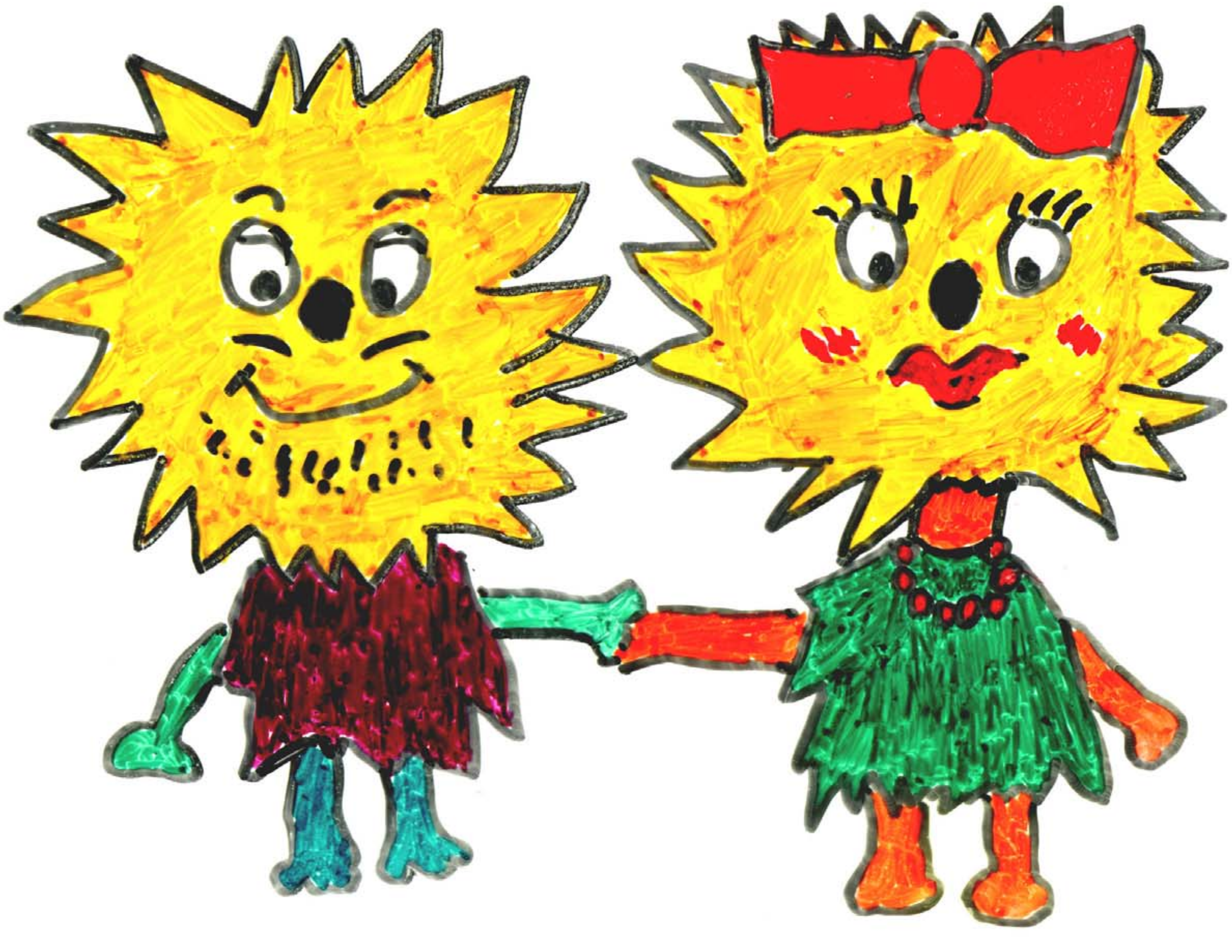


Solvent Separated Ion Pair

Solvent Shared Ion Pair



Contact Ion Pair



Covalent Ion Pair

Questions