

Surface Complexation Models

91A *Reviews in Mineralogy and Geochemistry* 91A

TABLE OF CONTENTS

1 Solution and Surface Complexation: The European Perspective

Staffan Sjöberg

OBJECTIVES	1
SOLUTION COMPLEXATION	1
Good experimental data.....	3
Literature equilibrium constants.....	3
THE FUTURE	5
SURFACE COMPLEXATION.....	5
The Swiss giants Schindler and Stumm	5
The Dutch group in Wageningen.....	7
The group in Umeå, Sweden	7
Good experimental data.....	8
Specific Surface Area (SSA)	8
Site densities (SD)	9
Equilibration times	9
Reproducibility and reversibility	10
THE FUTURE	10
ACKNOWLEDGMENTS.....	11
REFERENCES	11

2 Development and Modus Operandi relating Surface Structure and Ion Complexation Modeling for Important Metal (Hydr)oxides

Tjisse Hiemstra, Johannes Lützenkirchen

INTRODUCTION AND HISTORICAL NOTE.....	13
ELECTRICAL DOUBLE LAYER.....	14
Concepts	14
Physical–chemical representations of the EDL.....	17
SURFACE CHARGE.....	18
Origin of surface charge	18

Variable charge	18
Electrostatic potential	19
Electrostatic energy corrections	19
Point of zero charge or PZC	20
Physical surface sites	21
Proton affinities	21
SURFACE COMPLEXATION MODELS	23
Thermodynamic nature of surface complexation models.....	23
Towards a mechanistic approach in surface complexation modeling.....	24
Adsorption energy and electrostatic potentials.....	25
Determining electrostatic interfacial potentials.....	26
Interfacial water.....	27
Challenging systems.....	28
Scope and further outline.....	29
ATTRIBUTION OF CHARGE TO SITES.....	30
Quartz and silica.....	30
Gibbsite α -Al(OH) ₃	33
CHARGE–POTENTIAL RELATIONSHIP	37
SURFACE SPECIATION OF SITES	39
Brown bond valence concept.....	39
Surface site speciation of goethite (α -FeOOH)	41
Proton affinity of sites at the α -TiO ₂ (110) surface.....	44
THERMODYNAMIC CONSISTENCY FOR ION ADSORPTION	46
Thermodynamic consistency rule.....	46
Role of solution speciation in the proton co-adsorption of ions.....	47
SURFACE COMPLEXATION OF CATIONS AND ANIONS.....	51
Outersphere complex formation	51
Innersphere complex formation.....	52
Factors influencing the interfacial distribution of charge	53
ELECTRICAL DOUBLE LAYER FEATURES	57
Capacitances of the compact part of the EDL	57
Surface curvature	59
Double layer interactions.....	60
Zeta-potential from electrokinetics.....	60
MODUS OPERANDI FOR A START	62
Case study: Silica	65
Concluding remarks.....	70
ACKNOWLEDGEMENTS	70
REFERENCES	71

3 Impedance Spectroscopy of the Mineral–Electrolyte Interfaces

Youzheng Qi, Yuxin Wu

INTRODUCTION	85
MICRO-SCALE: ELECTRICAL DOUBLE LAYER (EDL) POLARIZATION.....	85
Structure of the EDL	85
Diffuse layer polarization model.....	88
Stern layer polarization model.....	91

Stern and diffuse layer polarization model.....	93
MESO-SCALE: EFFECTIVE MEDIUM MODEL	94
Waxman–Smits and Vinegar–Waxman models.....	95
Three-resistor and Weller–Slater models.....	96
Bruggeman–Hanai–Sen (BHS) model	97
Qi and Wu (2024) model	98
MACRO-SCALE: FROM LABORATORY TO FIELD	99
Laboratory experiments.....	99
Field measurements	100
SUMMARY	102
REFERENCES	102

4 Molecular Controls on Complexation Reactions and Electrostatic Potential Development at Mineral Surfaces

Jean-François Boily

INTRODUCTION	105
SURFACE SITE IDENTITY AND REACTIVITY.....	107
Spatial distributions of sites on ideal vs. real particles.....	108
Spectroscopic markers for site identity	111
Case example: OH groups on iron (oxy)(hydr)oxide nanoparticles.....	113
Spectroscopic markers for protonation.....	115
Spectroscopic markers for site-specific binding.....	115
Spectroscopic markers for site-specific hydration.....	117
THE HYDRATED INTERFACE.....	119
Hydration controls on protonation constants.....	121
Loadings and interfacial distributions of electrolyte ions	124
THE CHARGED INTERFACE.....	125
Multi-face complexation modeling	126
The framework for a face-specific SCM	127
The Variable Capacitance Model.....	132
THE ELECTROCHEMICAL INTERFACE	135
SUMMARY	139
ACKNOWLEDGMENTS.....	139
REFERENCES	139

5 Surface Complexation at Charged Organic Surfaces

Maryam Salehi

INTRODUCTION	149
Objectives	150
CHARGED ORGANIC SURFACES AND THEIR CHARACTERISTICS.....	150
Microbial matter	150
Biochar	151
Natural organic matter (NOM).....	155
Other types of organic surfaces	157

TYPES OF SURFACE COMPLEXES AT CHARGED ORGANIC SURFACES AND SCMS	160
Metal complexation with microbial matter	160
Metal complexation with biochar	163
Metal complexation with natural organic matter (NOM).....	165
Metal complexation with other organic matter.....	166
MAJOR FACTORS INFLUENCE METAL COMPLEXATION WITH ORGANICS	168
SUMMARY	169
ACKNOWLEDGMENT.....	170
REFERENCES	170

6 Surface Complexation and Reactivity of Ferrihydrite in Relation to its Surface and Mineral Structure, with Applications to Natural Systems

Tjisse Hiemstra, Annette Hofmann, Juan C. Mendez, Yilina Bai

INTRODUCTION AND HISTORICAL NOTE.....	175
MINERAL STRUCTURE OF FERRIHYDRITE	177
Ferrihydrite family.....	177
SURFACE AREA OF FERRIHYDRITE AND ITS DYNAMICS	182
Specific surface area.....	182
VARIABLE PROTON CHARGE OF FERRIHYDRITE.....	187
Reactive sites of ferrihydrite.....	187
PRIMARY CHARGE AND ION PAIR FORMATION OF FERRIHYDRITE.....	188
Double layer structure	190
SURFACE COMPLEXATION OF IONS BY FERRIHYDRITE	193
Experimental approaches.....	193
Charge distribution model	193
Monocomponent adsorption.....	194
Competitive ion–ion interactions.....	197
Cooperative ion–ion interactions.....	200
Ion adsorption and co-precipitation.....	204
APPLICATION OF SURFACE COMPLEXATION MODELS TO SOIL	205
Reactive surface area	205
Organo-oxide interaction.....	209
NOM-CD model.....	211
Application of the NOM-CD model approach	213
Reactivity of organo-oxide nanoaggregates	216
Reactivity of DOC.....	220
ACKNOWLEDGMENT.....	222
REFERENCES	222

7 Ligand and Charge Distribution Modeling of Natural Organic Matter Adsorption on Metal (Hydr)oxides: State-of-the-art

Yun Xu, Yilina Bai, Tjisse Hiemstra, Liping Weng

INTRODUCTION	229
THEORETICAL BACKGROUND OF THE MODELING APPROACH	232

Heterogeneous adsorption model for HNP.....	232
APPLICATION AND PRACTICAL IMPLICATIONS	242
HNPs in natural soil systems.....	242
Understanding competitive interactions of oxyanions with NOM.....	243
OUTLOOK	246
Size fractionation.....	246
Variability of NOM materials.....	247
Competitive interaction of FA and HA.....	247
NOM-oxide coprecipitates	247
REFERENCES	247

8

Ion-Dependent Calcium Carbonate Cohesion: Insights from Surface Forces Measured between Calcite Surfaces

Joanna Dziadkowiec, Anja Røyne

INTRODUCTION	251
COHESION IN CALCIUM CARBONATE ROCKS.....	252
Cohesion in relation to textures of calcium carbonates.....	252
Effect of water on carbonate cohesion	254
THEORETICAL ASPECTS OF SURFACE FORCES IN BRIEF.....	257
Physicochemical effects and disjoining pressure	257
DLVO theory	258
Other forces	260
Roughness and reactivity.....	261
EXPERIMENTAL MEASUREMENTS OF CALCIUM CARBONATE MECHANICAL STRENGTH.....	262
Carbonate cohesion in salt solutions	262
EXPERIMENTAL MEASUREMENTS OF INTERACTIONS BETWEEN CALCITE SURFACES.....	270
Direct force measurements between two calcite surfaces	272
Direct force measurements in asymmetrical surface configurations.....	274
Summarized effects of main salt ions on surface forces between calcite surfaces....	277
INTERACTIONS OF SALT IONS WITH CALCIUM CARBONATE SURFACES	279
Rheological behavior of calcium carbonate	279
Zeta potential of calcium carbonate	280
Calcium carbonate/electrolyte interface	283
CONCLUSIONS.....	284
ACKNOWLEDGMENTS.....	285
REFERENCES	285

9

Measurements of the Electrostatic Potential at the Mineral/Electrolyte Interface

*Tin Klačić, Jozefina Katić, Davor Kovačević, Danijel Namjesnik,
Ahmed Abdelmonem, Tajana Begović*

INTRODUCTION	295
INTERFACIAL POTENTIALS WITHIN THE ELECTRICAL INTERFACIAL LAYER	295

TYPES OF INTERFACIAL POTENTIALS	299
Inner surface potential	299
Diffuse layer potential	300
Electrokinetic ζ -potential.....	301
The potential drop.....	301
METHODS FOR THE MEASUREMENTS OF INTERFACIAL POTENTIALS	301
Electrochemically based methods for determination of the inner surface potential .	303
Non-linear optical spectroscopy	309
X-ray photoelectron spectroscopy	311
Atomic force microscopy	312
Methods for measuring electrokinetic potential	315
A CASE: INTERFACIAL POTENTIALS AT THE	
SiO ₂ /AQUEOUS ELECTROLYTE INTERFACE	317
Measurements by single crystal electrodes and OCP technique	318
Electrokinetic and AFM measurements.....	322
Measurements by electrochemically based techniques and XPS	324
Measurements by non-linear optical methods	326
CONCLUSIONS.....	328
ACKNOWLEDGMENTS.....	329
REFERENCES	329

10 Surface Complexation Reactions in Oxide Nanopores

Anastasia G. Ilgen

INTRODUCTION	337
SOLUTION STRUCTURE AND DIELECTRIC PROPERTIES IN NANOPORES	339
Triple layer model of solution structures at interfaces	339
Dielectric properties, capacitance, and surface potentials in nanopores	340
NANOCONFINEMENT EFFECTS ON ADSORPTION COMPLEXES	341
Speciation of adsorbed cations in nanopores.....	341
NANOCONFINEMENT EFFECTS ON EQUILIBRIUM CONSTANTS	346
Solvation of nanoconfined aqueous species	346
Nanoconfinement effects on adsorption equilibrium constants.....	346
Equilibrium constants for surface (de)protonation and (de)hydroxylation reactions	348
Case study: SCM for cation adsorption in silica nanopores.....	349
CONCLUSIONS.....	349
ACKNOWLEDGEMENTS	349
REFERENCES	350

11 Transport and Surface Complexation in Subsurface Flow-through Systems

Massimo Rolle, Lucien Stolze, Jacopo Cogorno, Muhammad Muniruzzaman

INTRODUCTION	353
SCALES FOR TRANSPORT AND SURFACE COMPLEXATION.....	355
Laboratory scale	355
Field scale.....	357

Reactive transport modeling	359
A CLOSER LOOK AT SURFACE COMPLEXATION IN FLOW-THROUGH SYSTEMS: COUPLING OF PHYSICAL AND CHEMICAL PROCESSES	360
Reactive transport system.....	361
pH front propagation in 1D columns.....	364
Impact of flow velocity and incomplete mixing.....	365
Dimensionality effects.....	368
Transport in physically, chemically and electrostatically heterogeneous media.....	370
CONCLUSIONS AND OUTLOOK.....	374
REFERENCES	376

12

History, Algorithms, Model Uncertainty, and Common Pitfalls of Traditional SCM Fitting Procedures

Norbert Jordan, Frank Heberling, Jeffrey Kelling, Johannes Lützenkirchen

INTRODUCTION	383
NUMERICAL APPROACHES TO SURFACE COMPLEXATION AND PARAMETER OPTIMIZATION	384
History	384
Numerical approaches	385
Law of mass action and Gibbs energy minimization	386
Parameterization of SCM	390
DESCRIPTION OF THE ALGORITHMS USED IN FITTING PROCEDURES.....	390
Newton–Raphson	390
Levenberg–Marquardt	393
The Downhill Simplex method.....	395
A BRIEF SURVEY OF PARAMETER STATISTICS AND MODEL UNCERTAINTY	396
Data uncertainty.....	396
Goodness of fit.....	396
Parameter uncertainty	397
Model uncertainties	398
COMMON ISSUES IN SURFACE COMPLEXATION MODELING.....	399
COMPARISON OF TRADITIONAL FITTING PROCEDURES	403
CONCLUSIONS.....	406
REFERENCES	407

13

Practical Application of Surface Complexation Models: Evolution, Approaches, and Examples

David A. Dzombak, Jerry D. Allison, Ted P. Lillys, Jason Mills

INTRODUCTION	413
SURFACE COMPLEXATION MODELS: DEVELOPMENT AND BASICS	415
CHALLENGES FOR APPLICATION OF SURFACE COMPLEXATION MODELS IN SOIL, SEDIMENT AND AQUIFER SYSTEMS	418
Identifying dominant sorbents.....	419
Determining accessible surface areas.....	420
Accounting for NOM	422

APPROACHES FOR PRACTICAL APPLICATION OF	
SURFACE COMPLEXATION MODELS	424
Multisurface approach	424
Single-surface/surrogate approach	427
Generalized composite approach.....	429
SURFACE COMPLEXATION MODELS AND DISTRIBUTION (K_b) COEFFICIENTS:	
COMPARISONS AND COMPLEMENTARITY	433
EXAMPLE SCM PRACTICAL APPLICATION: DEVELOPMENT OF	
CONTAMINANT K_d VALUES FOR COAL COMBUSTION RESIDUALS	
FOR USE IN PROBABILISTIC GROUNDWATER FATE AND	
TRANSPORT MODELING	435
Description of MINTEQA2.....	436
Contaminants of interest.....	437
Modeling approach.....	438
Characterization of model groundwater systems	439
Model groundwater compositions	439
Model sorbents	440
MINTEQA2 modeling procedure.....	443
Results	444
Further develop SCM databases	447
Further test multisurface SCMs.....	447
Perform uncertainty analyses	447
Advance models for clays	448
Advance models for NOM	448
Further develop standard protocols for parameterizing models	448
Develop efficient and standard protocols for generalized composite	
SCM modeling	448
Develop standard protocols for reduced-order K_d models.....	449
SUMMARY AND CONCLUSIONS.....	449
ACKNOWLEDGEMENTS	450
REFERENCES	450