

The Colloid and Surface Chemistry of Clays in Natural Waters

*Ivan Sondi and Velimir Pravdić**

*Laboratory of Electrochemistry and Surface Phenomena, Center for Marine
Research, Ruđer Bošković Institute, Zagreb, Croatia*

Received February 12, 1998; accepted September 9, 1998

The colloid and surface chemistry of clays is discussed based on recent work of the authors. The aim is to test the predictability of the role and fate of suspended matter in natural waters, transforming a reductionistic approach into a holistic picture. Most of the information is based on model substances and model clay minerals, for which electrokinetic properties, ion exchange capacities, and enthalpies of wetting were measured. It has been shown that mimicking the disintegration of particles, accomplished by milling, new positively charged surfaces can be created. Beidellite, a model smectite mineral, is the prevailing type of clay minerals by its large specific surface area, large ammonia saturation indexes, and high specific enthalpies of wetting, however with little contribution to new amphoteric surfaces as a result of milling. In ripidolite, a chlorite, all these values are much lower, however the creation of amphoteric surfaces through milling is strongly expressed. Indeed, ripidolite is a unique example of clays that can exhibit positively charged surfaces. Adsorption of fulvic acid, a widespread detrital organic, obscures the differences by producing commonly observed negatively charged surfaces of natural suspended matter and sediments.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

* Author to whom correspondence should be addressed.

INTRODUCTION

Clay minerals are the main component of suspended solid material in natural waters, responsible for the transport of inorganic and organic contaminants.¹⁻⁴ Clays surpass carbonates and many metal oxides in their chemical persistence, colloid stability and adsorption capacities. Geochemical processes that govern the land/sea interaction occur in rivers and effectively regulate the adsorption and deposition phenomena in estuaries, in the transition between soft river water and seawater.⁵⁻⁹

Natural waters – rivers, estuaries and the sea – are complex systems of electrolytes, dissolved and particulate organic matter, and inorganic particulates, comprised of clays, quartz, carbonates, and a variety of metal oxides (most frequently Al, Fe and Mn). Research into the physical and colloid chemistry designed to reveal single processes is difficult, or nearly impossible. As a way out of these problems, model minerals and simple electrolyte solutions were used in carefully designed experiments.¹⁰⁻¹⁵

Clays have been studied extensively from various aspects and for various purposes. The overwhelming diversity of clays, their chemical composition, structural properties, ionic exchange capacities and the related surface charge phenomena are responsible for their role in the transport of microconstituents of the aquatic phase.^{3,5,17,18}

As a physical model, clay minerals attract attention due to heterogeneity of their surfaces. One of the most important characteristics is colloid stability of clay mineral particles in the aquatic environment. Several factors determine this interaction: density relationship between the particles, the aquatic environment and hydrodynamic conditions,^{11,19,20} their mineralogical, chemical and surface properties. The electrolyte concentration, pH,^{3,12,21} and the presence of organic matter^{6,8,9,16} provide for the interaction with the environment.

The leading idea of our research in clays was a reductionistic approach: is it possible, by investigating individual clay minerals, their properties and changes induced by mechanical disintegration, to predict, with a fair degree of confidence, the processes in natural aquatic systems? Such predictions would provide a scientifically based estimate of an ecosystem's carrying and receiving capacities for contaminants. This would enable the scientist to predict the impact of some human activities on the state of the riverine, estuarine, and marine environments. This leading idea was followed in a number of studies of real-life conditions in the environmentally strained small estuaries of the Adriatic coast.^{11,17,22,23} These are in themselves models for large global estuaries.²⁴

The paper summarizes the most important facts that have been learned.

EXPERIMENTAL

Materials

Samples were taken of suspended particulates and sediments in the region. Analyses have shown that two types of clays prevail, chlorites and smectites, and that, by studying carefully chosen models, useful information could be obtained.

Minerals, used as models in this work, belonged to the two mentioned groups.^{1,2} These are frequent components of most natural clays. Montmorillonite, beidellite and saponite belong to the smectite group of swelling clay minerals; ripidolite and kaolinite belong to the chlorite and kaolinite groups, respectively, and are non-swelling clay minerals. Some experiments were done also on kukeit and illite.

Ripidolite (CCa-1, Flagstaff Hill, El Dorado Country, California, USA), beidellite (SBCa-1, California, USA), saponite (Ballarat, USA) and montmorillonite (SCa-3, type »Otay«, San Diego Country, California, USA), kukeit (North Little Rock, Arkansas) and illite (Silver Hill, Montana, USA) were obtained as standard reference minerals by courtesy of Professor W. D. Jons of The Clay Minerals Society, Source Clay Minerals Repository, University of Missouri-Columbia, USA. They were chemically and structurally characterized as reported earlier.²⁵

Amorphous SiO₂ (Aldrich Chem. Comp., specific surface area, SSA = 69 m² g⁻¹) was used as the model of a nonpolar hydrophobic surface. γ -Al₂O₃ (Aluminium oxide C, Degussa AG, Germany, a nonporous solid, with an average particle size of 20 nm, and a SSA of 100 ± 15 m² g⁻¹), and gibbsite, γ -Al(OH)₃ (commercial sample from J. T. Baker Co. USA), were used as models for polar, hydrophilic, and charged mineral surfaces as reported previously.^{26,27} These materials were used as received.

Fulvic acid (FA) (Aldrich Chem. Comp., USA) used in all of our work was declared as an extract from peat. It was characterized according to Ochs:²⁶ N/C = 0.02; H/C = 1.3; O/C = 0.6; elementary analysis (mass fractions, without ash): C = 50.17; H = 5.43; N = 0.88; S = 3.26; O = 41.0. The molar absorption coefficient ratio at 465 and 665 nm was 6.3, indicating a low degree of condensation. Its low molecular mass (1000–5000), indicates that such FA would correspond to substances found in riverine waters.

Measurement Techniques

Samples of ripidolite were prepared for the experiment by ultrasonication of a piece of rock. The part that disintegrated from the rock (mostly particles sized from 8 to 16 μ m) was extracted by centrifugation and dried at 80 °C. Samples of beidellite were suspended in water, suspensions were centrifuged, and particles smaller than 2 μ m were extracted by centrifugation and dried at 80 °C. The samples were next treated with diluted, sodium acetate buffered H₂O₂ (at pH = 5) to remove residual organic matter from the surfaces. After this treatment, samples were treated with a citrate-bicarbonate-dithionate solution to remove surface adsorbed crystalline and amorphous iron oxides and oxyhydroxides. The monoionic (Na-form) samples of ripidolite and beidellite were prepared following the method of Karen and Shainberg.²⁸ An estimate was made that particle sizes used in the measurements ranged from 20 nm to 0.5 μ m.

Mineral composition and purity of clays were checked using a Philips 1070 P.W. X-ray diffractometer. The X-ray diffraction pattern (Cu-K α radiation) of oriented clay minerals showed that the < 2 mm fraction contained impurities, if any, below the limit of detection.

Particle disintegration was done manually in an agate mortar (for purity reasons).

Specific surface areas (SSA) of particles were determined by single point nitrogen adsorption, using a Micromeritics FlowSorb II 2300 instrument. Prior to the measurements, the samples were outgassed for 24 hours at 80 °C. In the case of montmorillonite, this technique gave only the outer surface area, the magnitudes considered in this paper.*

Electrophoretic mobility (EPM) measurements were made using an automated electrophoresis instrument (type S3000, PenKem, Bedford Hills, NY). This is an instrument with automated focusing capability, very high sensitivity and precision. The software calculated automatically the electrokinetic potential using Henry's equation,²⁹ and the limiting value for $f(a) = 3/2$. The electrokinetic potential was calculated as: $\zeta = 12.8 \times 10^8 \mu_e$, where the electrokinetic potential is in mV if the mobility, μ_e , is in $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$. An integral part of the PenKem electrophoretic measuring system was a Radiometer automatic burette titration system, adjusting the pH of the sample suspension to preprogrammed values, and to selected rates of titration. In this way, identification of the isoelectric points (IEP) was possible with commensurate precision.

Cation exchange capacities – the ammonia saturation indexes (ASI) were determined using ammonia exchange monitored by an ammonia-specific electrode.³⁰ The composition of exchanged ions (Na⁺, K⁺, Ca²⁺ and Mg²⁺) for montmorillonite was determined by atomic absorption spectrometry (Jarrell Ash, Waltham, MA, USA).

Heats of wetting were measured in a microcalorimeter built around a commercial HAAKE R/N4 thermostat (Karlsruhe, Germany), controlled to 0.02 °C. The heat sensor was a thermistor in a Wheatstone bridge, balanced with precision resistances and measured by the recorder output of a microvolt nullmeter. Samples were heated and evacuated during 24 hours in small glass bulbs, then sealed under vacuum and brought into the microcalorimeter. The heat measured, evolved by bulb breaking in water in the microcalorimeter cell, was recalculated into the specific enthalpy of wetting.

RESULTS

The following results describe the most important findings that have been obtained in recent studies of model clay minerals in aqueous media.^{11–15} These are based on electrokinetic investigations, on the particle

* It is well known²¹ that the internal surface areas of smectites can reach up to several hundreds of m^2/g , an order of magnitude higher than data obtained by the described treatment of samples, and accessed by single point nitrogen adsorption measurements. The present results have been found to best represent the interaction of particles with the natural aquatic environment.

size and specific surface area determination, and on the microcalorimetric measurements of wetting enthalpies. The results also show the effects of milling, a process mimicking the erosion of clay minerals in natural waters. These minerals have also been studied using high resolution transmission electron microscopy (HRTEM), where some fine details have been found that substantiate the results discussed here. For details, the reader is referred to previous papers.^{13,14}

Figure 1 shows the electrokinetic potential of chlorite in electrolyte solutions at close to pH of 6.5 ± 0.2 , adjusted by HCl/NaOH titration to a 10^{-3} mol/dm³ NaCl solution. These experiments were done to study the influence of major, naturally present, cations on the electrokinetic potential of clays. It is indicative that only CaCl₂ produces an isoelectric point (IEP) at a concentration close to 10^{-3} mol/dm³. Chlorites are common clay minerals and the critical concentration of Ca²⁺ is almost always present in riverine and seawaters above this limit.

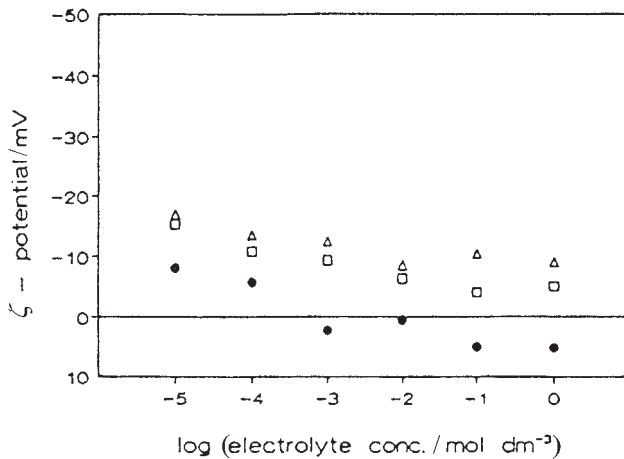


Figure 1. The electrokinetic potential of chlorite in various electrolyte solutions: (Δ) NaCl, (●) CaCl₂, (□) MgCl₂ at pH = 6.5 ± 0.2 (reproduced by permission from Ref. 12).

Very important information is the response of clay surfaces to the change of the medium pH. Therefore, Figure 2 shows experiments with smectite clays along the pH gradient. The electrokinetic potential is unaffected in the whole range, retaining its negative values.

Figure 3 shows the same experiments done with chlorite (ripidolite) and kaolinite minerals. Though the influence of pH is manifested by a decrease of the electrokinetic potential, it does not produce any changes of the charge sign.

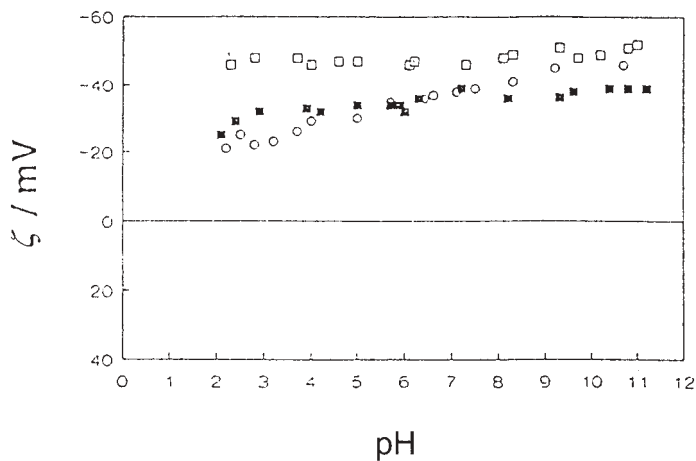


Figure 2. The electrokinetic potential of smectite clay minerals suspended in 1×10^{-3} mol/dm³ NaCl solution as a function of pH: (□) saponite, (●) beidellite, (■) Otay montmorillonite (reproduced by permission from Ref. 14).

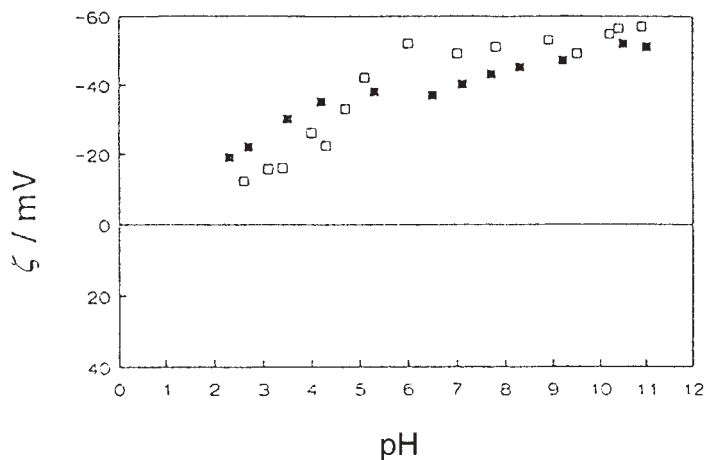


Figure 3. The electrokinetic potential of ripidolite (□) and kaolinite (■) suspended in 1×10^{-3} mol/dm³ NaCl solution as a function of pH (reproduced by permission from Ref. 14).

The influence of particle disintegration was studied by milling the minerals in an agate mortar. Figure 4 shows the electrokinetic potentials of the »original« and milled beidellite, the model mineral of the smectite group. The milled sample, exhibiting new edge surfaces shows an IEP at a very low pH, between 3 and 2.

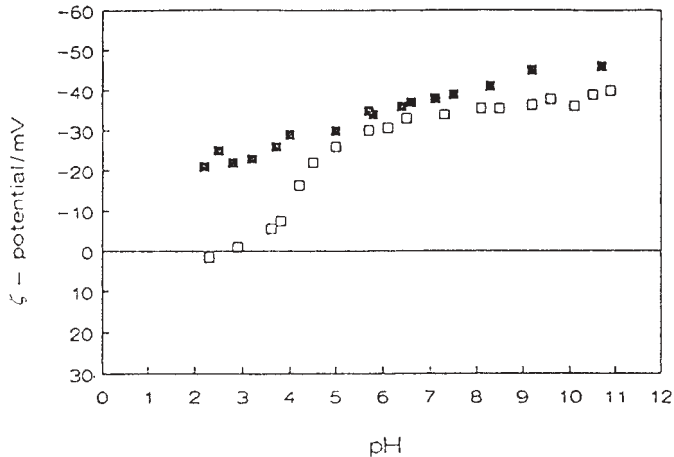


Figure 4. The electrokinetic potential of beidellite suspended in 1×10^{-3} mol/dm³ NaCl solution as a function of pH: (■) natural and (□) milled samples (reproduced by permission from Ref. 13).

The same pH dependence is shown in Figure 5 for ripidolite, the model mineral of the chlorite group. The change in the electrokinetic potential is much larger, and the IEP is observed already at $\text{pH} = 6 \pm 0.5$.

The nature of the new surfaces, created by milling, was studied using the models of amorphous silica, gibbsite $\gamma\text{-Al}(\text{OH})_3$ and aluminium oxide,

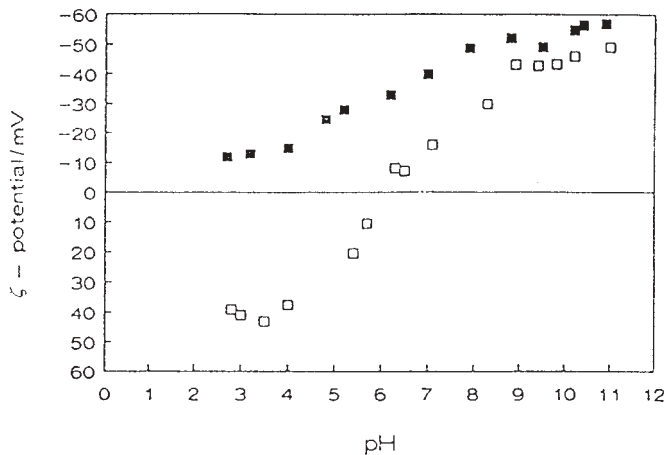


Figure 5. The electrokinetic potential of ripidolite in 1×10^{-3} mol/dm³ NaCl solution as a function of pH: (■) natural and (□) milled samples (reproduced by permission from Ref. 13).

$\gamma\text{-Al}_2\text{O}_3$. These minerals are models for the types of clay surfaces. Silica is the type of siloxane surfaces prevailing in clays, to 99% in *e.g.* smectites. Alumina and aluminium hydroxide are models for amphoteric surfaces. Figure 6 shows the electrokinetic potential *vs.* pH for these three minerals.

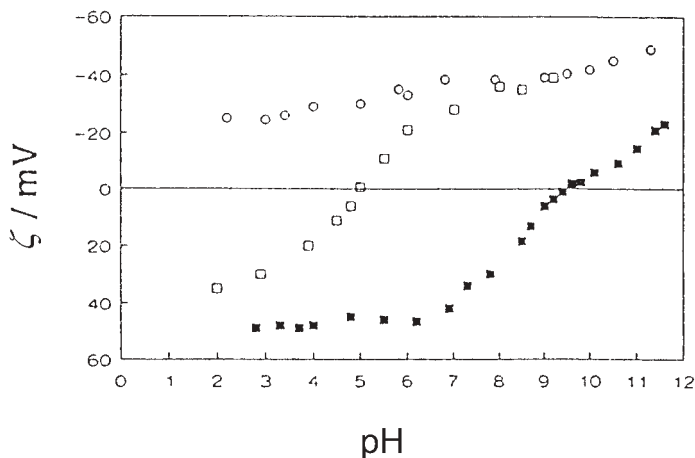


Figure 6. The electrokinetic potential of amorphous silica (●); gibbsite, $\gamma\text{-Al}(\text{OH})_3$ (□); and $\gamma\text{-Al}_2\text{O}_3$ (■) suspended in 1×10^{-3} mol/dm³ NaCl as a function of pH (reproduced by permission from Ref. 14).

The results indicate that silica surfaces do not show an IEP down to a very low pH. Gibbsite and aluminium oxide do, the former at a pH close to 5, the latter at pH between 9 and 10. In natural waters, buffered by a natural $\text{CO}_2/\text{HCO}_3^-$ buffer, aluminium oxide should, thus, be positively charged.

Experiments with fulvic acid, a model for humic acids, the most frequent natural organic compounds, show its predominant influence. Figure 7 shows the results of measurements of the electrokinetic potential along the gradient of fulvic acid concentration. The experiments with milled clay mineral samples are intended for studies of an increased fraction of amphoteric surfaces. Again, both the natural and the milled samples show distinctly negative surface charges throughout the investigated concentration range, although the two samples differ in the magnitude of the electrokinetic potential.

The interaction of FA with other model surfaces is indicative of why only negative values are observed for suspended matter consisting mostly of clays. Figure 8 shows the electrokinetic potential of silica, gibbsite and $\gamma\text{-Al}_2\text{O}_3$ along the concentration gradient of FA. At concentrations above 3 mg/dm³ there is no surface with a positive charge.

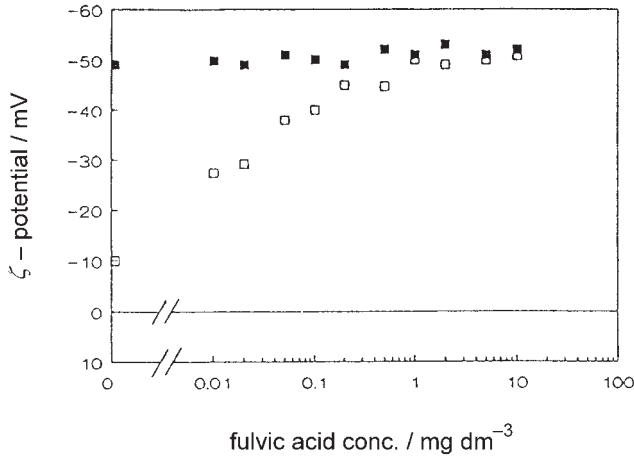


Figure 7. The electrokinetic potential of ripidolite in dependence on the concentration of fulvic acid in 1×10^{-3} mol/dm³ NaCl solution at pH = 6.5 ± 0.5 : (■) natural and (□) milled samples (reproduced by permission from Ref. 13).

Other clay characteristics: specific surface area, ammonia saturation index, and the enthalpy of wetting.

The results of measurements done on natural clays are summarized in Table I.

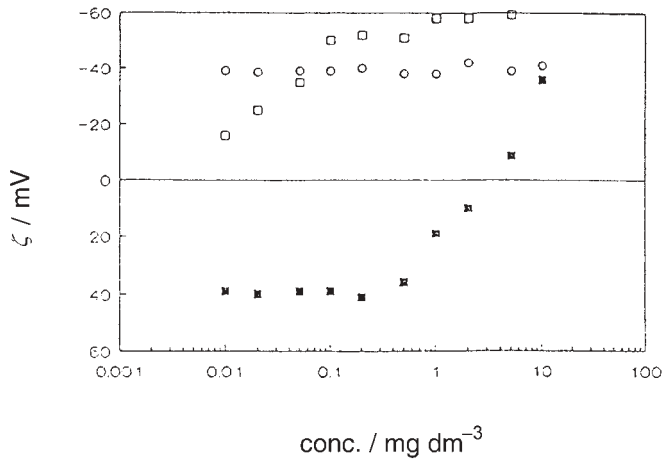


Figure 8. The electrokinetic potential of amorphous SiO₂ (●); gibbsite, γ -Al(OH)₃ (□); and γ -Al₂O₃ (■); suspended in 1×10^{-3} mol/dm³ NaCl as a function of the FA concentration, at pH = 6.5 ± 0.2 (reproduced by permission from Ref. 14).

TABLE I
Specific surface areas (SSA), ammonia saturation indexes (ASI), and
specific enthalpies of wetting, $\Delta_w H^*$

Clay sample	SSA/(m ² /g)	ASI/(meq/100g)	$\Delta_w H$ /(J/g)	$\Delta_w H$ /(J/m ²)
Kukeit	6.7	4.0	1.7	0.12
Ripidolite	2.6	1.5	1.4	0.11
Bedellite	61.0	107.1	101.3	3.06
Montmorillonite	71.1	142.3	147.0	1.59
Illite	44.3	24.6	28.7	0.66
Kaolinite	11.7	12.0	3.0	0.26

* Taken from Ref. 31.

Results in Table I. indicate large SAA, capacities of smectites for ion exchange, and their large heats of wetting. Ripidolite (a chlorite) and kaolinite have considerably lower values, and they only show the IEP in milled samples (Table II). Beidellite and montmorillonite show more than an order of magnitude higher enthalpies of wetting than the chlorites and kaolinite. An assumption is made that any polar binding of atoms or molecules at these surfaces is directly proportional to the enthalpies of wetting.

The studies of the effects of milling on ripidolite and beidellite have also produced some interesting data. These are shown in Table II.

TABLE II
Specific surface areas (SSA), ammonia saturation indexes (ASI), and enthalpies
of wetting ($\Delta_w H$), of natural and milled ripidolite and beidellite*

Sample	SSA/(m ² /g)		ASI/(meq/100g)		$\Delta_w H$ (J/g)		$\Delta_w H$ (J/m ²)	
	natural	milled	natural	milled	natural	milled	natural	milled
Ripidolite	2.6	32	1.5	4.3	1.4	31.4	0.11	0.85
Beidellite	61.0	92	107	132	101	79.6	3.06	0.86

* Taken from Ref. 31.

The difference shows that smectites have much higher values of SSA, of ASI, and of $\Delta_w H$. However, the disintegration of particles, exemplified by milling, equalizes these differences, at least in the specific enthalpy of wetting. The last value indicates that disintegration has its limits and that prolonged milling causes a blocking of the surface, probably by particle-particle adhesion.³²

DISCUSSION

As stated, the aim of this paper was to answer the question: do the techniques and the methodology used in our work provide adequate information on the interaction of clay with its aquatic environment? Does this information contribute to the ultimate goal of understanding the role of clays and particulate matter in assessing the processes that govern the exchange of matter in natural aquatic environments? The answers are to some degree positive.

The answers are sought in applied colloid and surface chemistry. The basic knowledge of structure and function, revealed through the contemporary level of experimental techniques, provides pieces of necessary information. From the reductionistic point of view, such information is easily collected. Whether a synthesis is possible with the aim of predicting the impact of solid matter in the holistic approach on the land/sea interaction is still ambiguous. We are fully aware that a rigorous discussion in line with the knowledge developed in basic colloid and surface chemistry^{21,34} would reveal shortcomings of the present approach. This pertains specifically to the internal surfaces of swelling clays. The incorporation of such studies would be the subject matter of a paper with different aims.

Colloid chemistry has taught us that the interaction of a surface with its aquatic environment is twofold: one part governed by coulombic forces, the other part by forces of specific (noncoulombic) interaction.³³ In the research described here, we have used electrokinetic measurements and ion exchange to unveil the coulombic interaction; measurements of specific surface areas and of the enthalpies of wetting provide an insight into the state of the surface effected by non-coulombic forces.

What have we learned by electrokinetic measurements? The answer is in the understanding of the electrification of interfaces. A change produced by breaking up surfaces and creating new mineral surfaces was found. The theory goes back to van Olphen² who initiated what later became to be known as the Constant Basal Surface Charge model. It was a model of clay surfaces elaborated on a kaolinite model, supported and advanced further in many subsequent, and also recent investigations.³⁴⁻³⁷ The basal surface (siloxane surface) of a clay mineral carries a constant negative charge, which is attributed to the isomorphous substitution of Si^{4+} by Al^{3+} and which is pH independent. In contrast, the charge of broken bonds (edges) depends on pH and shows an amphoteric character: it can be exemplified by the model of Al_2O_3 . The hydroxyl groups at the edges are the major reactive sites³⁸ in clay surfaces. The fraction of edge surfaces depends on the type of the clay mineral. For kaolinite this fraction is 12 to 14%,^{39,40} which is also expected for chlorite minerals on the basis of structural similarity, although there are no experimental data in literature. For smectites, this fraction is close to 1%.⁴¹ Milling of minerals, a process by which surface bonds are broken, ex-

poses new (edge) surfaces, which are amphoteric. At low pH, protolytic equilibria then produce positively charged surfaces. Such edge sites are considered to be the most reactive sites, and those which preferably bind anionic species. These surfaces are also adsorption sites, primarily for organic polymers, humic and fulvic acids.

Electrokinetic phenomena are closely related to the ion exchange capacities, as measured by the ammonia exchange index. The indication is that the measured sign of charge is the indicator of the dominant type of ionic adsorption. It has been long known that the net surface charge is just the excess charge at the surface. The steady-state phenomenon of negative signs in all clay minerals, and indeed of particulate matter of mixed origin of clays, silica, and carbonates, even of metal oxides such as iron and manganese, carries little significance for the interaction with anions. Some microconstituents of aquatic media are in the anionic form; this is the final form of most complexes, either hydroxylated or mediated by organic ligands. Among these, humic acid adducts are the most common. The conclusion is that anions are carried by adsorption on particulates.

Comparison of SSA and ASI of clays shows the importance of smectites, beidellite in particular. The differences between beidellite and ripidolite in SSA, ASI and the enthalpies per unit surface are almost two orders of magnitude. While in chlorites, *e.g.* ripidolite, new amphoteric edge surfaces increase the SSA rather more than in smectites, the differences are gradually decreased by prolonged milling. Indeed, the enthalpies of wetting converge to the same value of less than 1 Joule per m².

A corollary question is: does the information obtained give enough insight into the contribution of electric and nonelectric surface forces to the overall surface energy?

Many investigations of the surface properties and colloid stability of clays were concerned only with the chemical and mineral purity of samples, and most of these studies dealt with aggregation, or flocculation of particles. Few, if any, have studied the reverse process. Our recent studies have proven that the properties of clay surfaces depend also on the physical wear of the source clay minerals.

Several additional parameters can be calculated and have been used in studies of the surface chemistry of sediments. It has been shown that only clays produce small particles with large specific surface areas but not silica or carbonates. In the context of interacting with the environment, clays are by far the most important vehicle for the transport of microconstituents, and consequently of pollutants. Using average numbers in this data domain and by assessing the amounts of solid minerals transported, one can obtain a fair measure of the receiving capacity of an aquatic ecosystem for pollutants.

One aspect has been missed, not neglected, but escaped meaningful experimentation. This is the rate at which adsorption occurs at newly created surfaces. In short terms, the double layer at a positively charged surface is compensated by chloride, sulfate or carbonate anions, and then, probably, by a host of carboxylic acids and their adducts. The information on how fast this exchange is for larger anions, e.g. fatty or humic acids, and whether these are bound by stronger bonds is still an unanswered question.

Acknowledgments. – Appreciation is expressed to the anonymous referees whose comments served for further improvement of the manuscript. Research, reviewed here, was supported by Contracts with the Ministry of Science and Technology of the Republic of Croatia. Purchases of the laboratory instruments were made possible through the support of the Commission of European Community, Directorate General for Science Research and Development (Project CI1-01100, 1989–1993).

REFERENCES

1. B. Velde, *Origin and Mineralogy of Clays*, Springer, Berlin, Heidelberg, New York, 1995.
2. H. van Olphen, in: A. C. D. Newman (Ed.), *Chemistry of Clay and Clay Minerals*, Wiley, New York, 1987.
3. W. Stumm, *Chemistry of the Solid – Water Interface*, Wiley-Interscience, New York, 1992.
4. R. E. Grim, *Clay mineralogy*, McGraw-Hill Book Co., New York, 1968.
5. D. Eisma, *Suspended Matter as a Carrier for Pollutants in Estuaries and the Sea*, in: R. A. Geyer (Ed.), *Marine Environment Pollution*, Elsevier, Amsterdam, 1981.
6. J. I. Hedges, *Geochim. Cosmochim. Acta* **41**(1977) 1119–1123.
7. R. J. Gibbs, *J. Sediment. Petrol.* **41** (1977) 237–243.
8. R. Beckett and N. P. Le, *Colloids Surf.* **44** (1990) 35–49.
9. C. O'Melia, *Colloids Surf.* **39** (1989) 255–271.
10. M. Juračić and V. Pravdić, *Chemistry and Ecology* **5** (1991) 241–248.
11. I. Sondi, M. Juračić, and V. Pravdić *Sedimentology* **42** (1995) 769–783.
12. I. Sondi, J. Bišćan, and V. Pravdić, *J. Colloid Interface Sci.* **178** (1996) 514–522.
13. I. Sondi and V. Pravdić, *J. Colloid Interface Sci.* **181** (1996) 463–469.
14. I. Sondi, O. Milat, and V. Pravdić, *J. Colloid Interface Sci.* **189** (1997) 66–73.
15. I. Sondi, M. Stubičar, and V. Pravdić, *Colloids Surf.* **127** (1997) 141–149.
16. R. J. Gibbs, *J. Sediment. Petrol.* **53** (1983) 1193–1203.
17. M. Juračić, L. M. Vitturi, S. Rabitti, and G. Rampazzo, *Sci. Total Environ.* **55** (1986) 243–249.
18. M. Juračić and V. Pravdić, *Chemistry and Ecology* **5** (1991) 241–248.
19. K. Kranck, *Sedimentology* **28** (1981) 107–114.
20. J. P. M. Syvitski, in: R. H. Bennett, W. R. Bryant, and M. H. Hulbert (Ed.), *Microstructure of fine-grained sediments: from mud to shell*, Springer-Verlag, New York, 1991.
21. H. H. Hahn and W. Stumm, *Am. J. Sci.* **268** (1970) 354–368.
22. A. Boldrin, M. Juračić, L. Menegazzo-Vitturi, S. Rabitti, and G. Rampazzo, *Marine Geology* **103** (1992) 473–485.

23. M. Juračić, I. Sondi, E. Prohić, and V. Pravdić, *Sedimentation in a Microtidal, Rock-Bounded Estuary*, Proc. of Littoral '94., Lisbon, Portugal, 1994.
24. E. Olausson and I. Cato (Eds.), *Chemistry and Biogeochemistry of Estuaries*, Wiley, New York, 1980.
25. A. C. D. Newman and G. Brown, in: A. C. D. Newman (Ed.), *Chemistry of clays and clay minerals*, Longman Sci., London, 1987, p.1.
26. M. Ochs, B. Čosović, and W. Stumm, *Geochim. Cosmochim. Acta* **58** (1994) 639–650.
27. M. Plavšić, B. Čosović, and S. Rodić, *Colloid Polym. Sci.* **274** (1996) 548–554.
28. R. Karen and I. Shainberg, *Clays Clay Miner.* **27** (1979) 145–151.
29. R. J. Hunter, *Zeta Potential in Colloid Science*, Academic Press, London, 1981. p. 71.
30. E. Busenberg and C. V. Clemency, *Clays Clay Miner.* **21** (1973) 213–217.
31. I. Sondi, Ph.D. Thesis, University of Zagreb, 1995.
32. C. Kosanović, J. Bronić, B. Subotić, M. Stubičar, I. Šmit, A. Tonejc, and T. Yamamoto, *Zeolites* **13** (1993) 261–268.
33. J. Lyklema, *Fundamentals of Interface and Colloid Science: Vol II. Solid – Liquid Interfaces*, Academic Press, London 1995.
34. R. K. Schofield and H. R. Samson, *Faraday Discuss. Chem. Soc.* **18** (1954) 135–145.
35. D. J. A. Williams, and K. P. Williams *J. Colloid Interface Sci.* **65** (1978) 79–87.
36. G. M. Beene, R. Bryant, and D. J. A. Williams, *J. Colloid Interface Sci.* **147** (1991) 358–369.
37. Z. Zhou, and W. D. Gunter, *Clays Clay Miner.* **40** (1992) 365–368.
38. H. D. Morris, B. Shelton, and P. D. Ellis, *J. Phys. Chem.* **94** (1990) 3121.
39. R. S. Dyal and S. B. Hendricks, *Soil Sci.* **69** (1950) 421–432.
40. S. Yariv and H. Cross, *Geochemistry of Colloid Systems*, Springer Verlag, Berlin, 1979.
41. G. Sposito, *The surface chemistry of soils*, Oxford University Press, New York, 1984.

SAŽETAK

Koloidna i površinska kemija glina u prirodnim vodama

Ivan Sondi i Velimir Pravdić

Prikazani su najvažniji rezultati nedavnih istraživanja nekih svojstava glinenih minerala s osvrtom na njihovo značenje za adsorpciju zagađivala u prirodnim vodama. Za proučavanje izabrani su kao modeli dobro poznati, čisti minerali glina. Elektrokinetičkim mjerenjima, određivanjem amonijeva saturacijskog indeksa, te toplina kvašenja, pokazano je da su minerali smektitne grupe (npr. beidelit) najvažnija komponenta prirodnih vodenih sustava. Kod minerala tipa klorita (npr. ripidolit) sve su te veličine i do dva reda veličine manje. Ipak, samo kloriti pokazuju izoelektričnu točku pozitivnog naboja. Usitnjavanjem čestica, koje imitira trošenje minerala u prirodnim uvjetima, pokazane su posljedice stvaranja novih rubnih površina. Promatranjem čestica u prirodnim uvjetima te se razlike ne primjećuju zbog kinetički brze adsorpcije humusnih materijala, općeprisutnih u svima prirodnim vodama.