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A05	53 (1980)	VOL. NO. (YEAR)		-	TABLES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	9	FIGURES
A07	CCA - 1195	OTHER IDENTIFIC.			Conference Paper

WHERE WE ARE IN EXPLANATIONS OF IONIC SOLUBILITY, PRECIPITATION, COAGULATION, AND FLOCCULATION PHENOMENA?

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DESCRIPTORS

Coagulation

critical concentration of,

Colloids

stability/instability of,

Flocculation

action of foreign ions
in,

Precipitation

phenomena of,

A confusion concerning the explanations, concepts and theories in the major sectors of the physics and chemistry of our environment exemplified in the case of real systems of aqueous solutions is pointed out. The much more general, coherent and integrating approaches have failed as it is evidenced by the treatment of phenomena of precipitation, ion-ion and ion-solvent interactions, and colloid stability. In this sense the application of van der Waals cumulative attraction and electrical double layer repulsion for colloid stability/instability (the so-called DLVO-theory) is taken to be a serious hindrance to the progress in this field. The same case is with the indiscriminate use of the solubility product constants. As new supporting collections experimental data three groups of diagrammatical presentations are given:

(1) The 16 basic precipitability-solubility (PS) contours of Precipitation bodies (PB) for fluorescein dyes against cations of silver, barium, lanthanum and thorium salts, and also 3 PS contours for methylene blue B against potassium halides (Figure 1). The discussion emphasizes that the existence of various chemical species, such as simple aquo-complexes, associates of coulombic ion-pairs' type, and the variety of composite complexes are responsible for the colloid stability/instability conditions.

(2) The action of foreign ions or molecules as flocculants for sols *in statu nascendi*.

(3) The discontinuities in transition from homogeneous to heterogeneous electrolytic systems, presented by the discontinuities in linear portions of light scattering during the processes of precipitation-coagulation, and the most expressive linear parts are taken for fundamental relationship between logs of critical time and critical coagulation concentration (Figure 2).

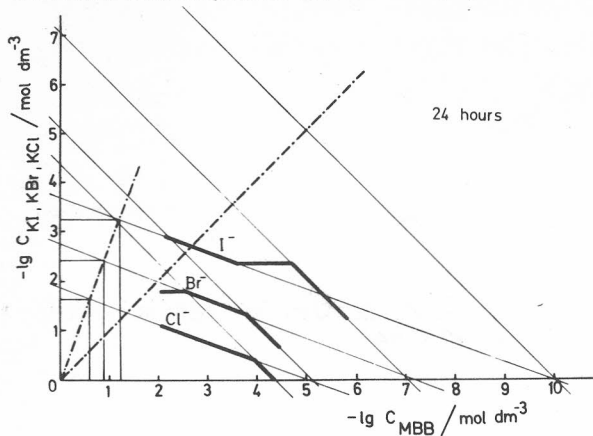


Fig. 1

Precipitability-solubility (PS) contours for methylene blue B (MBB) in aqueous solutions of potassium chloride, bromide and iodide at 293 K, 24 hours after mixing of components. The linear according to the solubility product constants, and the equivalency lines for methylene blue monomer and trimer halide species are constructed.

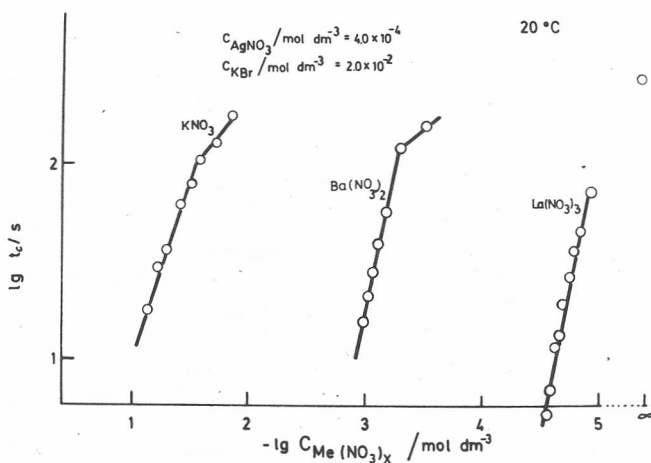


Fig. 2

Plots of logarithm of critical times corresponding coagulation concentrations of potassium, barium and lanthanum nitrate.

The role of the specific species resulting from various short and long range interactions of the ionic and molecular constituents of the system in question is pointed out. Therefore the chemical aspects have to be taken as the basic ones for interpretation of the processes and structures encountered in equilibrated, and much more so in nonequilibrated systems in precipitation, crystallization, coagulation, flocculation, as well as in other kindred phenomena.

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A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	42	REFERENCES
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A05	53 (1980)	VOL. NO. (YEAR)		12	FIGURES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION		Conference Paper
A07	CCA – 1196	OTHER IDENTIFIC.			
A08	THE ELECTRICAL DOUBLE LAYER AT THE SOLID/LIQUID INTERFACE				
A11	<i>Roger Parsons</i>				
A14	Laboratoire d'Electrochimie Interfaciale du C.N.R.S., Meudon-Bellevue, France				

DESCRIPTORS

A review is given on the present state of the theory of the electrical double layer at the solid/liquid interface of metallic electrodes. One of the obstacles to the experimental verification of the theory is in the difficulties of devising adequate ways of preparation of clean surfaces in contact with electrolyte solutions. Simple transfer techniques of Clavilier and Chauvineau (1,2) permit parallel electrochemical and Auger spectroscopic experiments. Applied to noble metal surfaces these experiments demonstrated the power and efficacy of electrochemical techniques of measurement and surface preparation. Examples are given of cyclic voltammograms of clean polycrystalline gold electrodes (Fig. 1) and of the same electrode whose surface has been covered by 1/3 of a monolayer of an adsorbable carbonaceous matter (Fig. 2). Successive cycling shows the reversion of this surface to a clean state. The differential capacity curves (Fig. 3) indicate considerable amounts of fine structure. Experimental evidence and experience such as shown is still scarce, but at present neither the theory is able to predict or explain the different strengths of adsorption on different crystal planes.

Electrodes

metal, cyclic voltammograms of, solid differential capacity of, electric double layer at,

Interface

metal/electrolyte solution,

Voltammetry

cyclic, of metal electrodes,

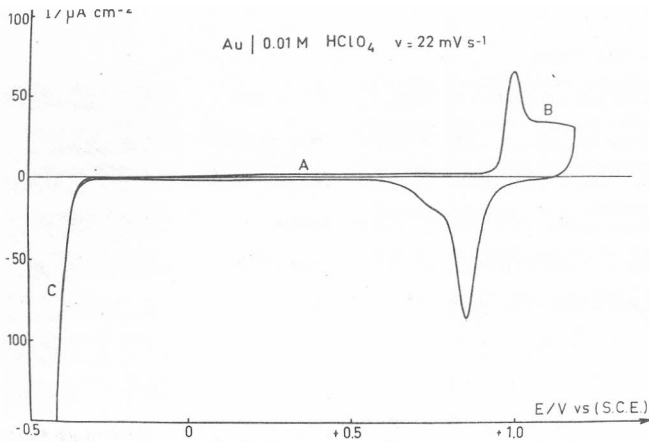


Fig. 1

Cyclic voltammogram for a polycrystalline gold electrode in contact with aqueous 0.01 M HClO_4 at 25 °C. The electrode potential is swept at 22 mV s^{-1} (Data from Clavilier).

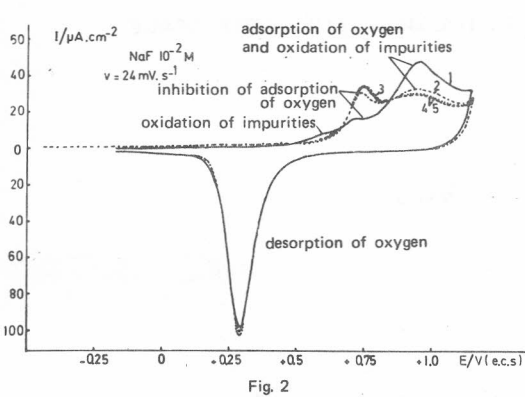


Fig. 2

Cyclic voltammogram for a polycrystalline gold electrode in contact with aqueous 0.01 M NaF at 25 °C. Curve 1 shows an electrode contaminated with about 1/3 of the surface covered with a monolayer of carbonaceous matter. Curves 2, 3, 4 show successive cycles in which these impurities are removed. Curve 5 shows the cycle on a clean electrode (Data from Clavilier).

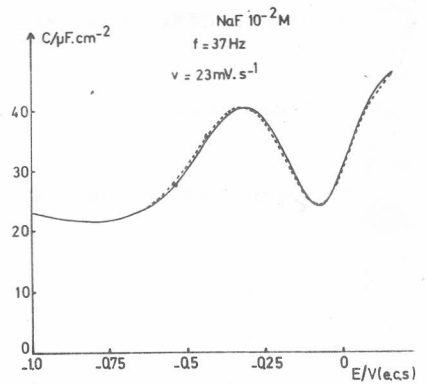


Fig. 3

Differential capacity of a polycrystalline gold electrode in contact with aqueous 0.01 M NaF at 25 °C. Measurement made with a phase sensitive detector and a sweep speed of 23 mV s^{-1} .

REFERENCES

1. J. Clavilier and J.P. Chauvineau, *J. Electroanal. Chem.* 97 (1979) 199.
2. J. Clavilier and J. P. Chauvineau, *J. Electroanal. Chem.* 100 (1979) 461.

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A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	19	REFERENCES
				-	TABLES
A05	53 (1980)	VOL. NO. (YEAR)		8	FIGURES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION		Conference Paper
A07	CCA - 1197	OTHER IDENTIFIC.			
A08	SOME APPLICATIONS OF A USEFUL THEOREM IN DOUBLE LAYER THEORY				
A11	<i>D.G. Hall, H.M. Rendall, and A.L. Smith</i>				
A14	Unilever Research, Port Sunlight Laboratory, Port Sunlight, Wirral, Merseyside L62 4XN, England				

DESCRIPTORS

Adsorption

from ionic solutions,

Electrokinetic potential theory of,

Thermodynamics

of interfacial phenomena,

The paper raises criticism of the conventional approach to the interpretation of potentiometric titration and electrokinetic data for solids in aqueous solutions based on the conventional Grahame model of the double layer (1). It is argued that the expressions used in conjunction with this model, and which relate the amount adsorbed to bulk concentrations lack a firm theoretical basis.

Therefore an alternative thermodynamic approach is presented based on a recently developed theorem (2). The new approach utilises the concept of the outer Stern plane in the same manner as the Grahame model, but no further electrostatic concepts. Beyond the Stern plane and into the bulk of solution the Poisson-Boltzmann equation governs the distribution of ions. The potential in the Stern plane ψ_δ can be identified with the electrokinetic potential ζ . Another assumption is that at least one ionic species, present in the bulk, is absent from the inner regions of the double layer. This assumption, if valid, allows the determination of adsorbed amounts of several species to be made on the basis of electrokinetic data only (3,4). It is also possible to calculate the electrochemical contribution to the total energy of interaction between identical and dissimilar charged plates. For surfaces in a state near to the isoelectric point, and at low

adsorbed amounts Γ_1 , the surface pressure can be expressed as virial expansion of integral powers of Γ_1 .

The approach has been experimentally tested for three different surfaces (nylon, polyester, and AgI), for two surfactants (dodecyltrimethylammonium bromide, and sodium dodecyl sulfate), and at three ionic strengths (10^{-3} , 5×10^{-3} , and 10^{-2} mol/dm³) and found to hold well.

REFERENCES

1. D. C. Grahame, *Chem. Rev.* 41 (1947) 441.
2. D. G. Hall, *J.C.S. Faraday II* 74 (1978) 1757.
3. D. G. Hall, *J.C.S. Faraday II* 73 (1977) 101.
4. D. G. Hall and M. J. Sculley, *J.C.S. Faraday II* 73 (1977) 893.

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A05	53 (1980)	← VOL. NO. (YEAR)		8	← FIGURES
A06	No. 2	← ISSUE NO.	← CAT. OF CONTRIBUTION		Conference Paper
A07	CCA – 1198	← OTHER IDENTIFIC.			
A08	NON-EQUILIBRIUM SURFACE FORCES				
A11	<i>S. S. Dukhin</i>				
A14	Institute of Colloid and Water Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, USSR				

DESCRIPTORS

Colloids
coagulation of,
electric fields in,

Dispersion
surface forces in,

Flotation
theory of,

Surface energy
in disperse systems,

The theory of non-equilibrium double layer and surface forces, developed by the author (1-4) is reviewed. By definition the electric double layer at a solid/liquid interface departs from the equilibrium state whenever external forces cause an electric or hydrodynamic flow in this structure. The problem is exemplified by the polarization of the double layer of a spherical particle by an external stationary field (Fig. 1). This field causes tangential flow of ions in the diffuse part of the layer, changes in concentration, and particle polarization phenomena. Typical examples of practical nature include electrocoagulation, electro-filtration, flotation, and electrodeposition of uncharged molecules (including polymers).

In electrocoagulation an external field (typical values 60 V/cm at $c = 10^{-5} \text{ mol dm}^{-3}$) causes the particle to approach each other by the effect of deepening of the secondary minimum in the potential energy – distance curve. When the field is switched off, no attraction forces remain and the particles disperse again (reversible coagulation). In several cases, with proper combination of the particle size and charge, an avalanche coagulation effect can be observed. The greater is the particle charge, the larger is the decrease in stability of the suspension by the

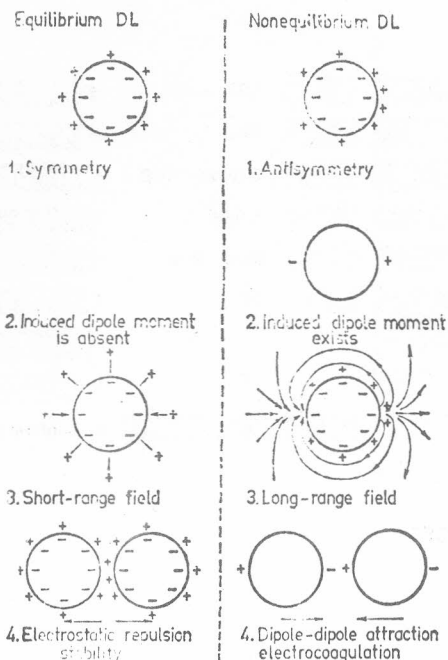


Fig. 1.

The qualitative distinction of the equilibrium and nonequilibrium double layers.

imposed external field. Consequently electrocoagulation is effective when electrolyte coagulation is hampered.

In flotation it is shown that the diffuse electric double layer, resulting from the dynamic adsorption layer of an ionogenic surfactant, controls the particle size which can reach the surface of the bubble and become attached to it. Both electrophoretic and diffusio-phoretic movements effect flotation.

Dielectrophoresis is the motion of particles in the spatially non-uniform electric field caused by the induced dipole moment of the particle.

REFERENCES

1. S. S. Dukhin and B. V. Derjaguin, *Electrokinetic Phenomena, Surface and Colloid Science*, E. Matijevich (Ed.), Wiley-Interscience, New York, Vol. 7, 1974.
2. S. S. Dukhin, in: *Research in Surface Forces*, New York, 1963, Vol. 1; S. S. Dukhin, in: *Issledovanija v oblasti poverhnostnih sil*, Izdatelstvo Akad. Nauk SSSR, Moscow 1961, p. 197.
3. S. S. Dukhin and V. N. Shilov, *Dielectric Phenomena and Double Layer in Disperse Systems and Polyelectrolytes*, Halsted Press., New York 1974.
4. B. V. Derjaguin and S. S. Dukhin, *Trans.Inst.Mining Met.* 70 (1961) 221.

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A03 <i>Croat. Chem. Acta</i>	SHORT TITLE	A45	21	REFERENCES
A05 53 (1980)	VOL. NO. (YEAR)		-	TABLES
A06 No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	7	FIGURES
A07 CCA – 1199	OTHER IDENTIFIC.			Conference Paper
A08	STATE OF ADSORBED HALIDE IONS AND THEIR COMPETITIVE ADSORPTION AT OXIDIZED Pt ELECTRODES			
A11	<i>B. E. Conway and D. M. Novak</i>			
A14	Chemistry Department, University of Ottawa, Ottawa, Canada			

DESCRIPTORS

Adsorption

isotherms, Frumkin type, on platinum electrodes,

Electrochemistry

adsorption processes in,

Electrodes

platinum, adsorption on,

Halides

adsorption on platinum electrodes,

Sorption

electro-, interaction parameter in,

Experiments are described on the electrochemical study of the adsorption of Cl^- , Br^- , and I^- ions on oxidized Pt electrodes. A micrometer syringe titration technique was used allowing for precise control of electrolyte additions starting from the 10^{-9} to 10^{-7} mol dm $^{-3}$ level. Potentiodynamic sweeps were made of the platinum electrode in H_2SO_4 and HClO_4 solutions between 0.05 and 1.4 V vs. E_{H} at a constant rate of 0.025 V/s.

Isotherms were obtained for competitive adsorption by plotting log concentration of halide vs. the per cent of electrode surface blocked by oxide. It was found that I^- and Br^- loose almost entirely its charge to the metal upon adsorption, whilst Cl^- remains ionic though strongly adsorbed.

Interaction effects are treated using a Frumkin type isotherm (1-3) in the form:

$$\frac{\theta}{1-\theta} = K \exp \frac{VF}{RT} \cdot \exp [-g\theta] \cdot c$$

Here c is the adsorbate concentration, θ the surface fractional coverage, and g is the interaction parameter. Fig 1 shows the graphic method developed to calculate g from the coverage measured at two different concentrations. The values for g (in $RT/\text{kJ mol}^{-1}$) were: Cl^- 35(H_2SO_4) and 57(HClO_4); Br^- 2.7; I^- 1.8.

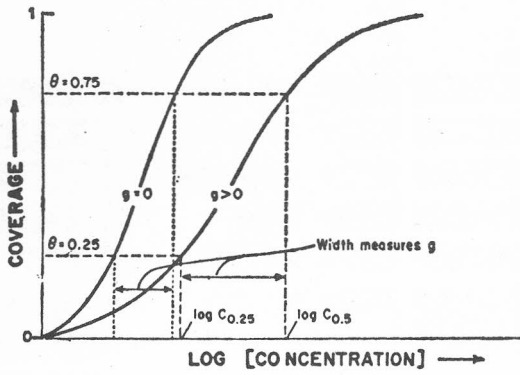


Fig. 1

Illustration of how the coverage attained at two different concentrations (log scale) enables the g factor to be evaluated for ion adsorption involving lateral interactions (schematic).

REFERENCES

1. B. E. Conway, E. Gileadi, and M. D zięciuch, *Electrochim.Acta* 8 (1963) 143.
2. H. Angerstein-Kozłowska, B. E. Conway, and J. Klinger, *J.Electroanal.Chem.* 75 (1977) 45.
3. A. N. Frumkin, *Z.Phys.Chem.* 116 (1925) 466;

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A05	53 (1980)	VOL. NO. (YEAR)		4	FIGURES
A06	No. 2	ISSUE NO.			
A07	CCA - 1200	OTHER IDENTIFIC.			
A08	DE-ADHESION IN THE ORGANIC COATING/METAL INTERFACE IN AQUEOUS MEDIA				
A11	<i>H. Leidheiser, Jr.</i>				
A14	Center for Surface and Coatings Research, Lehigh University, Bethlehem, Pa. 18015, U.S.A.				

DESCRIPTORS

De-adhesion (delamination) of organic coatings at metal surfaces is discussed, and by describing six different possible planes of corrosion attack, and by suggesting methodology and techniques for its study. The techniques should be preferably non-destructive, although the most interesting results were obtained by techniques in which a crack is induced intentionally. Thus the interfacial oxide is non-destructively studied by Mössbauer spectroscopy (1) or optical reflectance spectroscopy. Conductivity and capacitance changes accompany appearance of bulk water aggregation at the metal/coating interface (2). Cathodic polarization and coulometric recording at a surface at which a defect has been induced is another useful tool. The ensuing effect is strongly electrolyte dependent, as shown in Figs. 1 and 2. Full understanding of the strong electrolyte specificity, and of the factors which cause high pH values at the region delaminated by a cathodic process is still absent.

Adhesion
reversal of, in organic coating,

Coating material
organic, on metals,

Corrosion
of metals,

Coulometry
in corrosion studies,

Spectrochemical analysis
Mössbauer, in corrosion studies,

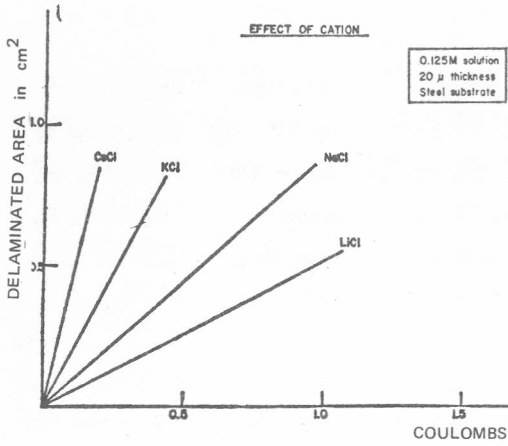


Fig. 1

Delamination of a polybutadiene-coated steel surface when made the cathode in four different electrolytes as a function of the number of coulombs passed through a small defect in the surface. Note that results are a function of the cation.

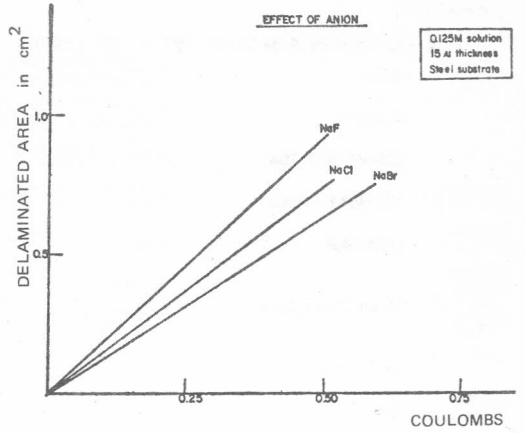


Fig. 2

Delamination of a polybutadiene-coated steel surface when made the cathode in three different electrolytes as a function of the number of coulombs passed through a small defect in the surface. Note that results are a minor function of the anion.

REFERENCES

1. H. Leidheiser, Jr. G. W. Simmons, and E. Kellerman, *J. Electrochem. Soc.* 120 (1973) 1516.
2. H. Leidheiser, Jr. W. Wang, and J. V. Standish, *Polymer News*, in press.

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A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION		Conference Paper
A07	CCA – 1201	OTHER IDENTIFIC.			
A08	ELECTROCHEMICAL STUDIES ON DIFFERENT GLASSY CARBON ELECTRODES. II. CORROSION AND DOUBLE LAYER CHARACTERISTICS				
A11	<i>L. Bjelica, R. Parsons, and R. M. Reeves</i>				
A14	Department of Physical Chemistry, University of Bristol, Bristol BS8 1TS, England				

DESCRIPTORS

The properties of glassy carbon electrodes from three different sources, subject to high temperature treatment (HTT) in the range between 600 and 3000°C were studied by electrochemical kinetic and double layer capacitance methods. The physical appearance of the surface was observed by scanning electron microscope and analysed by ESCA.

The electrochemical characteristics were tested by measuring the rates (1) of redox reactions. The rate of the $\text{Fe}(\text{CN})_6^{4-} / \text{Fe}(\text{CN})_6^{3-}$ (Fig. 1) is accelerated by HTT and surface oxidation, as are the $\text{Fe}^{+2} / \text{Fe}^{+3}$ and the quinone/hydroquinone couples. Rates of redox reactions like the hexachloroirridate, ferrocene, and nickelocene couples remains unaffected by surface oxidation of the glassy carbon electrode, and close to those measured at platinum electrodes. It is concluded that the 'oxidation' of the surface is not a process similar to metal oxidation (2-4), but rather one of incorporation of an oxygenated film both on and in the surface layer of carbon.

Corrosion

of glassy carbon electrodes,

Electrodes

glassy carbon, electrochemical reactions at,

Oxidation

high temperature, of glassy carbon,

Surface structure

scanning electron microscope studies of,

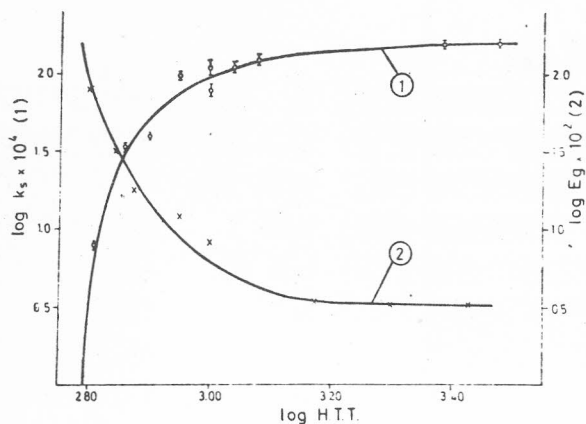


Fig. 1

Dependence of (1) standard rate constant for $\text{Fe}(\text{CN})_6^{-4/-3}$ and (2) energy band gap on H.T.T. of glassy carbon electrodes.

REFERENCES

1. L. Bjelica, R. Parsons, and R. M. Reeves, *Proc. Third Symposium on Electrode Processes, Electrochem. Soc.* 1979, p.196.
2. D. Laser and M. Ariel, *J. Electroanal. Chem.* 52 (1974) 291.
3. J. P. Randin and E. Yeager *J. Electroanal. Chem.* 58 (1975) 313.
4. R. E. Panzer and P. J. Elwing, *Electrochim. Acta* 20 (1975) 635.

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A05	53 (1980)	VOL. NO. (YEAR)		1	TABLES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	6	FIGURES
A07	CCA - 1204	OTHER IDENTIFIC.			Conference Paper
A08	INVESTIGATIONS OF COMPLEX PRECIPITATION SYSTEMS				
A11	<i>H. Füredi-Milhofer</i>				
A14	Laboratory for Precipitation Processes, 'Ruder Bošković' Institute, P.O.Box 1016, 41001 Zagreb, Croatia, Yugoslavia				

DESCRIPTORS

Calcium oxalate
precipitation of,
Crystal growth
in aqueous solutions,
Precipitation
from electrolyte solutions,

A review is presented on the experimental techniques, methodologies of studies, and graphical presentation of results on the precipitation of salts from aqueous electrolyte solutions. The original methodology has been described by Težak (1) in 1935, developed in studies of a large number of systems, culminating in recent studies of the kinetics of the precipitation processes and the determination of its rate controlling steps. The techniques most frequently used were light scattering, particle size determination with a Coulter Counter, and potentiometry with ion-specific electrodes.

The methodology is exemplified by a study of the precipitation of calcium oxalate in the concentration region of spontaneous heterogeneous nucleation (2,3) (Fig. 1).

It has been shown that the precipitate is characterized by conditions of supersaturation and of the reactant concentration regions of heterogeneous nucleation from those of homogeneous. In the latter one hydrophobic precipitates form colloidal dispersions.

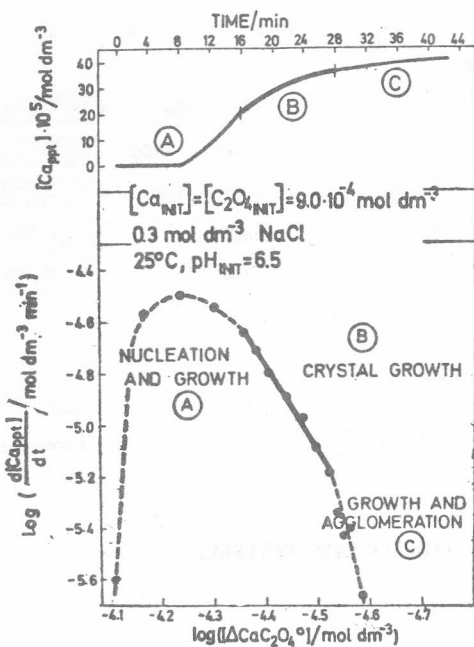


Fig. 1

Kinetics of precipitation of calcium oxalate in the region of spontaneous heterogeneous nucleation. Upper diagram: the amount of precipitated calcium as a function of time. Lower diagram: the rate of the reaction as a function of supersaturation, expressed in terms of the stable neutral complex, CaC_2O_4^0 . Regions A and C are corresponding in time. The prevalent precipitation processes are indicated.

REFERENCES

1. B. Težak, *Z. Phys. Chem.* A175 (1935) 219.
2. M. Marković and Lj. Komunjer, *J. Cryst. Growth* 46 (1979) 701.
3. M. Marković, Lj. Komunjer, and H. Füredi-Milhofer, *Investigations of Precipitation Processes by Particle Size Analysis* in: *Industrial Crystallization 78*, E. D. Jong and S. J. Jančić, (Eds.), North Holland Publ. Co., New York 1979, 65.

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A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	17	REFERENCES
A05	53 (1980)	VOL. NO. (YEAR)		11	TABLES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION		FIGURES
A07	CCA – 1205	OTHER IDENTIFIC.			Conference Paper
A08	TRANSPORT CONTROL IN CRYSTAL GROWTH FROM SOLUTION				
A11	<i>A. E. Nielsen</i>				
A14	Medicinsk-Kemisk Institut, University of Copenhagen, Copenhagen, Denmark				

DESCRIPTORS

Transport processes involved in crystal growth or dissolution in solutions are analysed mathematically. It is shown that solution matter has to pass through a diffusion field, resulting in diffusion control of crystal growth and dissolution in most cases. This applies strictly to stationary crystals, which means mostly those of diameter less than 1 μm . For larger crystals convection has to be considered. Mathematical treatment is presented for the cases of pure diffusion control, for the various cases of convection transport, for the cases of seeding, and for the method of controlled hydrodynamics by the rotating disc (1). Solutions are offered for both stoichiometric and nonstoichiometric solution composition. Appended to the main body of paper is a discussion on diffusion coefficients of ions and of electrolytes, and a nomogram for obtaining numerical values of parameters in the diffusion controlled dissolution experiments (2). A general rule is advanced that small crystals are more suitable for studies of surface processes and for experiments with low supersaturation. For diffusion studies with large crystals high supersaturations have to be used, since convection cannot be neglected.

Crystal growth
convection control in,
from solutions,

Diffusion
in crystal growth,

Transport process
in electrolyte solutions,

REFERENCES

1. V. G. Levich, *Physicochemical Hydrodynamics*, Prentice Hall, London 1962.
2. A. E. Nielsen, *Kinetics of Precipitation*, Pergamon Press, Oxford 1964.

Abstractor: V. P r a v d i ć

published in

Croatica Chemica Acta 53 (2) 281 - 289 (1980)

	Serial	LITERATURE TYPE	A20	281 - 289	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Dec. 11, 1979	RECEIPT DATE
	548.52:546.41:546.161	UDC	A22	October 1980	PUBLICAT. DATE
A01	YU 0011-1643	ISSN	A23	English	TEXT LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY LANG
A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	17	REFERENCES
A05	53 (1980)	VOL. NO. (YEAR)		2	TABLES
A06	No. 2	ISSUE NO.		5	FIGURES
A07	CCA - 1206	OTHER IDENTIFIC.			CAT OF CONTRIBUTION
					Conference Paper

THE KINETICS OF CRYSTALLIZATION OF CALCIUM FLUORIDE. A NEW CONSTANT COMPOSITION METHOD

L. J. Shyu and G. H. Nancollas

Chemistry Department, State University of New York at Buffalo, Buffalo, New York, 14214, U.S.A.

DESCRIPTORS

Calcium fluoride
 crystal growth of,
Crystal growth
 inhibition of by ions,
 kinetics of,
Precipitation
 of calcium fluoride,

A new method of constant solution composition to study the kinetics of crystallization was developed and is described. In the conventional seeded crystal growth experiments (1) the rate is determined by measuring the concentration of lattice ions as a function of time. Small errors in measured concentration preclude differentiation between the possible solid phases which can form (2). The constant solution composition method avoids these problems enabling macro amounts of an insoluble precipitate to be formed at low solution supersaturation.

The method was tested in experiments of CaF₂ precipitation. The concentration of lattice ions was maintained constant by simultaneous additions of CaCl₂ and NaF from mechanically coupled burettes, and by monitoring the F⁻ concentration with a fluoride specific electrode. It is shown that the rate, R, of crystal growth follows the relation:

$$R = k s \Delta^n$$

where *k* is rate coefficient, *s* is a function of the surface area, and Δ is given by the relation:

$$\Delta = ([Ca^{+2}][F^{-}]^2)^{1/3} \cdot \gamma_{\pm} - K_{so}^{1/3}$$

Here γ_{\pm} is the mean activity coefficient, and K_{so} is the thermodynamic solubility product. The effective reaction order, n , was found to be 3 for relative supersaturations, S , of less than 0.75, and 2 for S between 0.75 and 2.0. The relative supersaturation is defined as

$$S = \frac{[Ca^{+2}] - [Ca^{+2}]_0}{[Ca^{+2}]_0}$$

where $[Ca^{+2}]_0$ is the equilibrium concentration.

The method is highly suitable for studies of inhibitor effects, of which PO_4^{3-} has been studied in detail (Fig. 1).

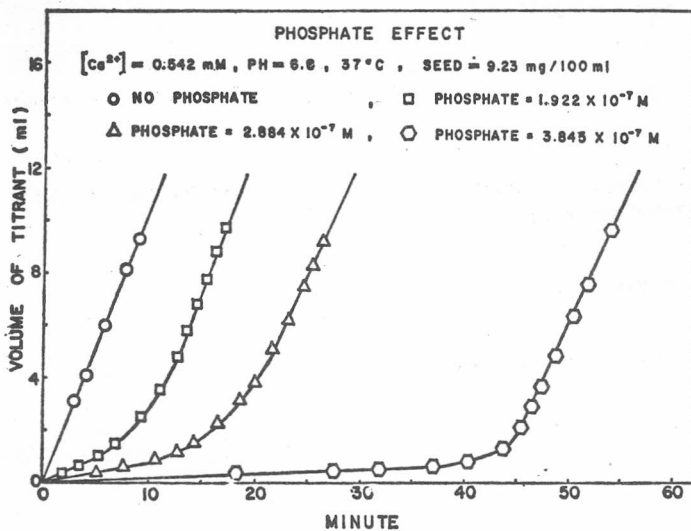


Fig. 1

Influence of phosphate ion. Plots of titrant volume against time. ($[Ca^{+2}] = 0.542$ mmol dm⁻³; 23 mg seed; 37°C). ○, no phosphate; □, 1.922×10^{-7} mol dm⁻³ phosphate; △, 2.884×10^{-7} mol dm⁻³; ◇, 3.845×10^{-7} mol dm⁻³.

REFERENCES

1. G. H. Nancollas and N. Purdie, *Q.Rev.Chem.Soc.* 18 (1964) 1.
2. G. L. Gardner and G. H. Nancollas, *J.Dent.Res.* 55 (1976) 342.

Abstractor: V. Pravić

published in

Croatica Chemica Acta 53 (2) 291 – 312 (1980)

	Serial	LITERATURE TYPE	A20	291 – 312	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Sept. 24, 1979	RECEIPT
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A01	YU 0011–1643	ISSN	A23	English	TEXT
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	25	REFERENCES
				4	TABLES
A05	53 (1980)	VOL. NO. (YEAR)		14	FIGURES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION		Conference Paper
A07	CCA – 1207	OTHER IDENTIFIC.			

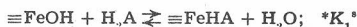
A08 **A LIGAND EXCHANGE MODEL FOR THE ADSORPTION OF INORGANIC AND ORGANIC LIGANDS AT HYDROUS OXIDE INTERFACES**

A11 *W. Stumm, R. Kummert, and Laura Sigg*

A14 Institute of Aquatic Sciences, Swiss Federal Institute of Technology, Zürich, Switzerland

DESCRIPTORS

A model is presented for the adsorption of weak acids and anions on the surfaces of hydrous oxides by virtue of a ligand exchange equilibrium. The model assumes the specifically adsorbed species to be inner sphere complexes. The tendency of ligands to form surface complexes at the oxide/water interface (1):



is strongly correlated with that to form corresponding metal complexes in solution:



The correlation is shown for some ligand anions in Fig. 1.

The principles involved in developing the model are exemplified by the acidity determination of α -FeOOH, by surface coordination of F⁻ on α -FeOOH, and of phthalic acid on γ -Al₂O₃ (2,3).

The validity of the ligand exchange equilibrium model is limited by inaccuracies in determination of intrinsic equilibrium constants, by the difficulties encountered in experimental determination of the charge dependence of these constants and by often sluggish approach to a true surface equilibrium. Thus metastable states are often taken as equilibria.

Adsorption

on metal oxide surfaces,
specific, of anions,

Alumina

adsorption on,

Formation Constants and Stability Constants

of complexes
heterogeneous,
homogeneous,

Iron oxides

adsorption on,

Ligands

exchange of, in adsorption,

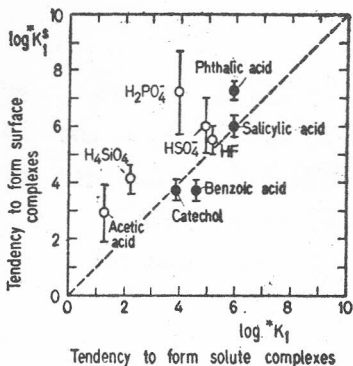


Fig. 1
Comparison of the tendency to form surface complexes ($\log K_1^s$, Eq. 1) with that to form solute complexes (K_1 , Eq. 2).

(○) with $\alpha\text{-FeOOH}$ and FeOH^{+2} , respectively;
(●) with $\gamma\text{-Al}_2\text{O}_3$ and AlOH^{+2} , respectively.

A more refined approach will have to take into account surface energy heterogeneities originating from surface defects and edge effects and from differences in crystal faces. The present model neglects the changes in the acidity constants of OH groups with increasing coverage by a charged adsorbate.

In its present form the ligand exchange model has been successfully used to predict the extent of adsorption of an anionic adsorbate, the surface charge as a function of pH and of solution variables, the concentration domains of colloidal stability of oxides, and the speciation of $\alpha\text{-FeOOH}$ surfaces in natural lake waters.

REFERENCES

1. L. Sigg, *Ph.D. Thesis* Nr. 6417, ETH, Zürich 1979.
2. R. Kummert, *Ph.D. Thesis* Nr. 6371, ETH Zürich 1979.
3. R. Kummert and W. Stumm, *J. Colloid Interface Sci.* 75 (1980) 373.

Abstractor: V. Pravić

published in

Croatia Chemica Acta 53 (2) 313 - 318 (1980)

	Serial	LITERATURE TYPE	A20	313 - 318	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Nov. 22, 1979	RECEIPT DATE
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A01	YU 0011-1643	ISSN	A23	English	TEXT LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	18	REFERENCES
A05	53 (1980)	VOL. NO. (YEAR)		1	TABLES
A06	No. 2	ISSUE NO.		3	FIGURES
A07	CCA - 1208	OTHER IDENTIFIC.			CAT. OF CONTRIBUTION
					Conference Paper

SURFACE REACTIONS OF SOME AQUEOUS SILVER HALIDE DISPERSIONS

A. H. Herz

Research Laboratories, Eastman Kodak Co., Rochester, N.Y. 14650, U.S.A.

DESCRIPTORS

Surface effects are described in silver halides dissolution and particle growth processes in the presence of various surfactants of polarographic interest (gelatine, cyanine dyes, alkyl-aryl-amines). It is shown that the initial rates of dissolution depend on the concentration of excess halide and on the charge of the ligand. It has been also observed that cationic surfactants destabilize silver halide/halide solution interfaces. *N*-Dodecyl pyridinium causes well defined cubic AgBr to recrystallize into spherical particles (1). The acceleration of AgBr recrystallization and ripening by organic cations, which themselves are not Ag⁺ ligands, was interpreted in terms of Br⁻ coadsorption with the cationic surfactant. Thus, the counterion adsorption (2) enriches the Br⁻ concentration in the double layer to produce enough AgBr₂⁻ for accelerated recrystallization.

The paper addresses itself to the question on whether proof exists on the influence of silver halide crystal habitus on the rate of surface reactions. The answer is negative for the process of dissolution in sulfite solutions and for the adsorption of gelatine. Also for the reversible adsorption of anionic thiocarbocyanine the free energies, enthalpies, and entropies of adsorption are nearly equal for cubic and octahedral AgBr, although the optical spectra of adsorbed dyes are strikingly varied (3). The

Adsorption

of constituent ions on silver bromide,
of surfactants on silver bromide,

Crystal growth

of silver halides,

Silver halides

adsorption of surfactants on,

Surfactants

adsorption of, on silver halides,

question posed above should be answered affirmatively for Br⁻ adsorption on AgBr, though the limiting areas per molecule of Br⁻ (1.21 and 0.80 nm² for the cubic and octahedral habits, respectively) demonstrate that only a small fraction of the geometrically available surface is involved in Br⁻ adsorption.

REFERENCES

1. L. Oppenheimer, T. James, and A. Herz, in *Particle Growth in Suspensions*, A. L. Smith, Ed., Academic Press, London, 1973, p. 159-178.
2. A. Herz and J. Helling, *J. Colloid Interface Sci.* 22 (1966) 391.
3. W. Gardner, D. Wrathall, and A. Herz, *Photogr.Sci.Eng.* 21 (1977) 325.

Abstractor: V. P r a v d i ć

published in

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	Serial	LITERATURE TYPE	A20	319 - 331	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Jan. 15, 1980	RECEIPT DATE
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A01	YU 0011-1643	ISSN	A23	English	TEXT LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY LANG
A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	25	REFERENCES
A05	53 (1980)	VOL. NO. (YEAR)		5	TABLES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	4	FIGURES
A07	CCA - 1209	OTHER IDENTIFIC.			Conference Paper

A08 SORPTION OF WATER AND POLAR-NONPOLAR ORGANIC VAPORS ON MICROPOROUS CHROMIA

A11 A. C. Zettlemoyer, M. Siddiq, P. Kovacs, and F. J. Micalé

A14 Center for Surface and Coatings Research, Lehigh University, Bethlehem, Pa. 18015, U.S.A.

DESCRIPTORS

Adsorbents

metal oxides as, characteri-
zation of,

Adsorption

of gases and vapours on
chromia,
on microporous adsorbents,

Porosity

meso-, in metal oxide par-
ticles,
micro-, in metal oxide par-
ticles, determination of,

The adsorption was studied of water, methanol, isopropanol, and of butane, isobutane, neopentane and heptane on microporous chromia of narrow particle size distribution. Chromia was prepared by a process devised by Matijević (1). It contained 0.5% of sulfur as sulfate, had a mean particle size of 0.41 μm , and a BET (argon) surface area of 14.4 m^2/g .

Microporosity volumes were determined from the intercepts of the a_s -plots (2) shown in Fig. 1. The slopes in the same Fig. yield external surface areas. The multilayer portion of the isotherms in Fig. 2 were analysed on mesoporosity, and it was found that the definition of these includes cylindrical pore diameters up to 2 nm. Calculations were made using Brunauer's corrected modelles method (3). The micropore volumes were determined by subtraction of the mesopore volumes and of the monolayer volumes of a standard non-porous chromia sample, from the total observed sorption capacity as measured at the relative pressure $p/p_0 = 0.98$. It is shown that the Matijević method of preparation of hydrous oxides yields microporous material of narrow pore sizes of about 1.2 nm. The molecular probes, in the form of the mentioned small molecule adsorbates, are the most direct method of size and geometry evaluation of an adsorbent yielding information on both micro and meso porosity.

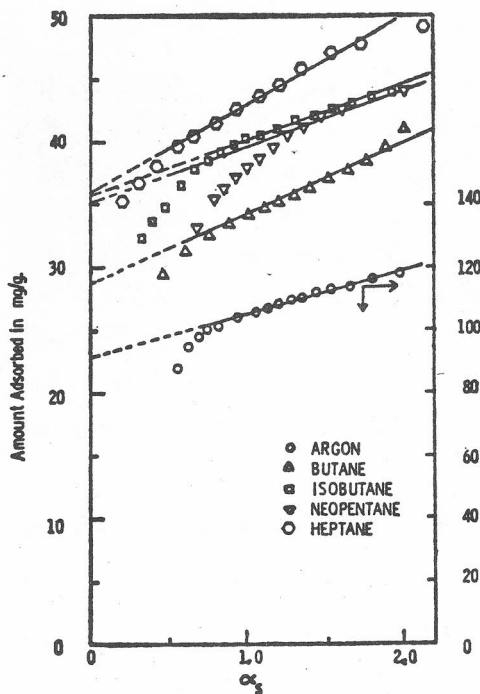


Fig. 1

α_s -Plots of the sorption isotherms shown in Fig. 2.

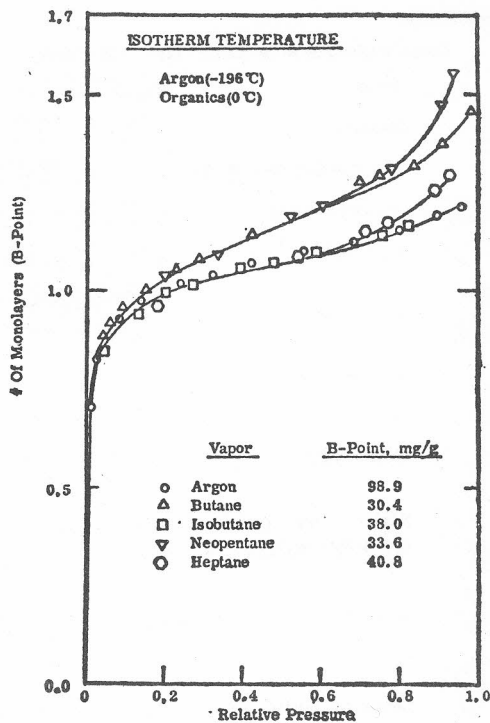


Fig. 2

Sorption isotherms of argon and four selected hydrocarbons on microporous B_3 obtained by activation of hydrous chromia at 450°C in 100 Torr argon.

REFERENCES

1. A. Bell and E. Matijević, *J.Inorg.Nucl.Chem.* 37 (1975) 907.
2. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London 1969.
3. S. Brunauer, R. Sh. Mikhail, and E. E. Boder, *J.Colloid Interface Sci.* 24 (1967) 451.

Abstractor: V. Pravić

published in

Croatia Chemica Acta 53 (2) 333 - 339 (1980)

Serial	LITERATURE TYPE	A20	333 - 339	PAGES	
Analytic	BIBLIOGR. LEVEL	A21	October 15, 1979	RECEIPT DATE	
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A01	YU 0011-1643	ISSN	A23	English	TEXT
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	22	REFERENCES
A05	53 (1980)	VOL. NO. (YEAR)	-	-	TABLES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION		Figures
A07	CCA - 1210	OTHER IDENTIFIC.	Conference Paper		
A08	THE ROLE OF THE SURFACE IN THE BEHAVIOUR OF TITANIUM DIOXIDE PIGMENTS				
A11	<i>G. D. Parfitt</i>				
A14	Tioxide International Ltd. Billingham, Cleveland, U.K.				

DESCRIPTORS

Catalysts and Catalysis
photo-, of oxidation,

Dispersion
of pigments into liquids,

Pigments
stability of,

Surface
of pigment coatings,

Titanium dioxide
alumina coated surfaces,
silica coated surfaces,
use of as pigment,

A review is presented on the relevance of the surface properties in pigment behaviour. Titanium dioxide, widely used as a white pigment in paints and coatings, plastics and fibers, is often applied in the form of particles of typically 0.2 μm dia. Such particles have surface areas of the order of 10 m^2/g , but the surface itself is not TiO_2 , rather SiO_2 or Al_2O_3 coated (1). Adsorptive properties of these surfaces have been widely studied (2,3).

Dispersion of these pigments into a liquid medium, for application as paint or for further processing, is a problem of high technological importance. The resulting dispersion should exhibit high colloidal stability (4,5). In applicative cases the stability of coating is impaired by photocatalytic oxidation, flocculation and aggregation. The knowledge of basic chemical and physical processes, involved in all these categories, is necessary if high quality coatings are desired.

REFERENCES

1. R. E. Day, *Prog. Org. Coatings* 2 (1973/4) 269.
2. R. E. Day, G. D. Parfitt, and J. Peacock, *J. Colloid Interface Sci.* 70 (1979) 130.

3. G. D. Parfitt, *Progress in Surface and Membrane Science*, Ed. D. A. Cadenhead and J. F. Danielli, Academic Press, New York, 11 (1976) 181.
4. D. N. L. McGown and G. D. Parfitt, *Kolloid Z.-Z.Polym.* 220 (1967) 56.
5. G. D. Parfitt and J. Peacock, *Surface and Colloid Science*, Ed. E. Matijević, Plenum Press, New York, 10 (1978) 163.

Abstractor: V. P r a v d i ć

published in

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Serial	LITERATURE TYPE	A20	341 – 351	PAGES
Analytic	BIBLIOGR. LEVEL	A21	Dec. 10, 1979	RECEIPT DATE
541.18:539.61: 532.691	UDC	A22	October 1980	PUBLICAT. DATE
A01 YU 0011–1643	ISSN	A23	English	TEXT LANG
A02 CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03 <i>Croat. Chem. Acta</i>	SHORT TITLE	A45	19	REFERENCES
A05 53 (1980)	VOL. NO. (YEAR)		–	TABLES
A06 No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	9	FIGURES
A07 CCA – 1211	OTHER IDENTIFIC.			Conference Paper
A08	EFFECT OF SURFACTANT UPON CAPILLARY ADHESION IN FOUR-PHASE SYSTEMS			
A11	<i>E. Wolfram and J. Pinter</i>			
A14	Department of Colloid Science, Lorand Eötvös University, P.O.Box 328, Budapest, Hungary			

DESCRIPTORS

Capillary adhesion between polytetrafluoroethylene and pyrex glass surfaces, bridged by a liquid film of an aqueous sodium dodecylsulfate (SDS) solution and an immiscible liquid, has been experimentally investigated. The mechanical (Laplace) properties (1) of such a double-bridge four-phase system of two liquids and two solid surfaces, have been investigated by plate-sphere geometry device (2,3) shown in Fig. 1.

Adhesion
capillary phenomena in,
Films
liquid, stability of,
Surfactants
liquid films of,

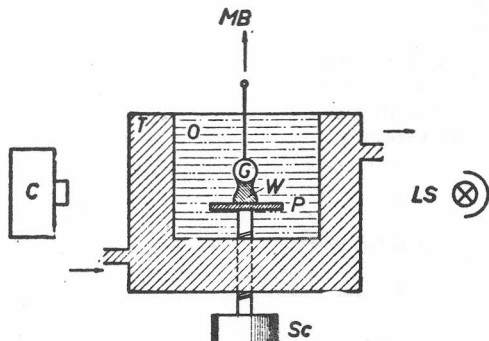


Fig. 1

Measuring cell, W water bridge, O octane, P Teflon plate, G glass sphere, MB microbalance, Sc fine screw, T thermostat, C camera, LS light source

The mechanical stability of the systems studied is characterized by bridge distribution isotherms. These are obtained by plotting the transferred mass of liquid against the total mass of the bridge liquid. A critical total mass is determined by a break in the isotherm above which the bridge collapses. In these experiments also an inverse exponential dependence of the critical mass vs. the bulk concentration of SDS has been found. Hysteresis of the measured force of adhesion, F , has been observed when experiments of cyclically increasing and decreasing the relative bridge height, d/h_0 , were performed (d is separation distance of the solid surfaces, h_0 is the original drop height). A typical result is shown in Fig. 2. The hysteresis effects are more pronounced at lower surfactant concentrations, but decrease in subsequent cycles. The phenomenon is accompanied by the ejection of a minute satellite droplet at the breakdown point of the bridge. This droplet has a lifetime of seconds before coalescence occurs.

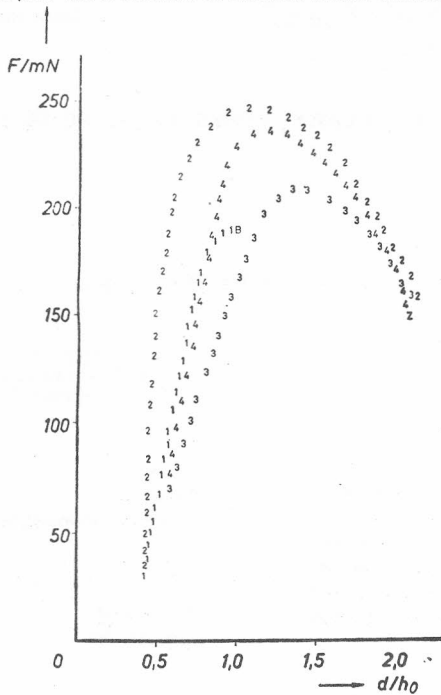


Fig. 2

Force vs. separation curves, $V = 100 \text{ mm}^3$; $c = 0.1 \text{ c}_M$ 1 first compression; 2 first expansion; 3 second compression; 4 second expansion; B bridge formed, Z bridge disrupted.

Importance of these phenomena, which can be quantitatively interpreted, are not only of basic science interests, but of prime importance in powder technology, printing, enhanced petroleum recovery, and in understanding the behaviour of porous adsorbents.

REFERENCES

1. D. H. Everett and J. M. Haynes, *Z.Phys.Chem.(N.F.)* 82 (1972) 36, *ibid.* 97 (1975) 301.
2. T. Gilanyi, Chr. Stergiopolus, and E. Wolfram, *Colloid Polymer Sci.* 254 (1976) 1018.
3. E. Wolfram and R. Faust, in *Wetting, Spreading and Adhesion* (ed. J. F. Padday), Pergamon Press, London 1978, p. 212.

Abstractor: V. Pravić

published in

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Serial	LITERATURE TYPE	A20	353 – 362	PAGES
Analytic	BIBLIOGR. LEVEL	A21	Oct. 30, 1979	RECEIPT
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A01 YU 0011–1643	ISSN	A23	English	TEXT
A02 CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03 <i>Croat. Chem. Acta</i>	SHORT TITLE	A45	12	REFERENCES
A05 53 (1980)	VOL. NO. (YEAR)		–	TABLES
A06 No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	5	FIGURES
A07 CCA – 1212	OTHER IDENTIFIC.			Conference Paper
A08	ON SOME PECULIARITIES IN THE ADSORPTION OF NATURAL AND SYNTHETIC MACROMOLECULES			
A11	<i>J. Lyklema</i>			
A14	Laboratory for Physical and Colloid Chemistry, Agricultural University, Wageningen, The Netherlands			

DESCRIPTORS

Adsorbents

polystyrene latex as,

Adsorption

enthalpy of polymers,
entropy of polymers,
of macromolecules,
of synthetic polymers,

Polymers

polystyrene latex as ad-
sorbent,

Adsorption of a macromolecular substance, human serum albumin (HPA) on a polystyrene latex is described, focussing on the observation that the negatively charged protein adsorbs spontaneously on negatively charged surfaces. The adsorbed amount increases with increasing negative charge of the latex. The enthalpy of adsorption is, in many cases, still negative, exothermal (1), contradicting general experience that work has to be done on the system to counteract electrostatic repulsion (Fig. 1). The explanation of this phenomenon is found, primarily, in the entropy contribution which is positive for hydrophobic bonding. Another contribution to the positive entropy changes originates from the electric field overlap. Also, only a fractional increase in the degrees of freedom of the constituent aminoacids of HPA suffices to overcome the loss of translational and rotational entropy of the molecule on adsorption.

The negative sign of the enthalpy of adsorption (exothermal) is due to the coadsorption of simple cations (1,2), which in turn depends on the concentration and the nature of the electrolyte.

The paper also deals with the problem of the reversibility of adsorption of natural and synthetic macromolecules. While upon dilution no adsorption is observed, tracer experiments have shown that adsorbed and dissolved HPA exchange readily (3).

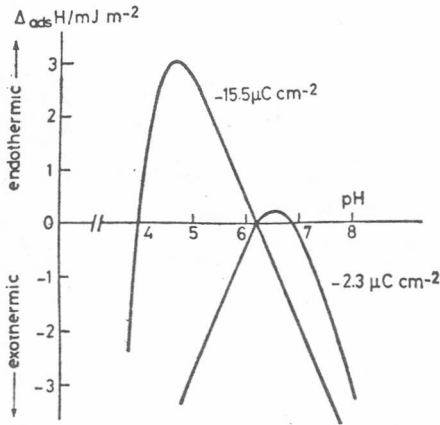


Fig. 1

Adsorption enthalpies for the adsorption of HPA on polystyrene latex.

• Fine resolution analysis of adsorption isotherms finds the plateau slightly inclined instead of horizontal. This means that for desorption extremely low solution concentrations are required. For molecular weight $M = 2500$ the desorption concentration should be less than $10^{-6} \text{ g dm}^{-3}$. Another reason for adsorption reversibility is the heterodispersity of the polymer. At low concentrations of the adsorbate high and low molecular weight molecules adsorb proportional to their bulk concentrations. Increasing the bulk concentration, low molecular weight molecules are exchanged for those of high. In desorption, again the low molecular weight molecules desorb preferentially and are displaced by the high molecular weight ones. Experimentally this has been verified by observing 'kinks' in the adsorption isotherms of binodal and trimodal mixtures (4,5).

REFERENCES

1. W. Norde and J. Lyklema, *J. Colloid Interface Sci.* 71 (1979) 350.
2. W. Norde and J. Lyklema, *J. Colloid Interface Sci.* 66 (1978) 257, 266, 277, 285, 295.
3. J. L. Brash and Q. M. Samak, *J. Colloid Interface Sci.* 65 (1978) 495.
4. M. A. Cohen Stuart, J. M. H. M. Scheutjens, and G. J. Fleer, *J. Polymer. Sci. Part B* 18 (1980) 559.
5. V. Hlady, G. J. Fleer, and J. Lyklema, to be published.

Abstractor: V. P r a v d i 6

published in

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	Serial	LITERATURE TYPE	A20	363 - 372	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Sept. 9, 1979	RECEIPT
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A01	YU 0011-1643	ISSN	A23	English	TEXT
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03	<i>Croat. Chem. Acta</i>	SHORT TITLE	A45	21	REFERENCES
A05	53 (1980)	VOL. NO. (YEAR)		5	TABLES
A06	No. 2	ISSUE NO.	CAT. OF CONTRIBUTION	4	FIGURES
A07	CCA - 1213	OTHER IDENTIFIC.			Conference Paper
A08	BEHAVIOR OF PROTEINS AT INTERFACES				
A11	<i>A. G. Walton and M. E. Soderquist</i>				
A14	Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.				

DESCRIPTORS

A theory is developed and described on the adsorption of proteins on biopolymer surfaces. The initial stages of adsorption are reversible, and only a time dependent conformational change of the adsorbed molecule leads to irreversible long term adsorption. Most of the experimental information is obtained by the technique of circular dichroism (1), the only one giving information on conformational changes.

The polymer adsorbent used was a random copolypeptide synthesized by copolymerizing two or more amino acids (2). The adsorption and structural changes for three adsorbates - blood proteins - are described: albumin, γ -globulin, and fibrinogen. The theory also goes on assuming that the 'body' prefers surfaces that do not damage proteins. This implies that surfaces which are more hydrophobic and do not bind proteins tightly, are more desirable since less damage is done to the protein upon adsorption. Since proteins vary in their stability in the adsorbed state adsorption is selective. Sensitive enzymes are most likely to be effective if covalently bound to highly hydrated substrates. Stable enzymes may be appropriately bound to solid particulates by physical adsorption.

Adsorption

of proteins,

Polymers

biological,
random copolypeptide, as
adsorbent,

Proteins

adsorption of,
conformational changes of
upon adsorption,

REFERENCES

1. C. R. McMillin and A. G. Walton, *J. Colloid Interface Sci.* 48 (1974) 346.
2. C. R. McMillin, H. Saito, O. D. Ratnoff, and A. G. Walton, *J. Clin. Invest.* 54 (1974) 1312.

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and of the International Symposium
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