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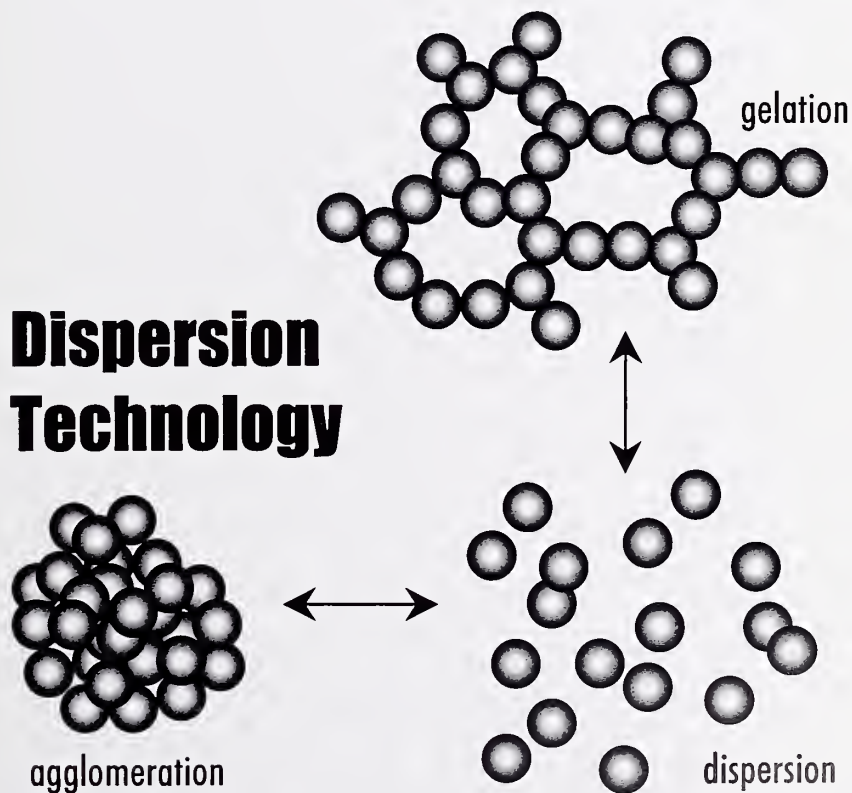
*NIST Special Publication 945*

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# *Guide to the Nomenclature of Particle Dispersion Technology for Ceramic Systems*

*Vincent A. Hackley*

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<sup>2</sup>Some elements at Boulder, CO.

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February 2000



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## Preface

It is generally agreed that measurements and standards play an integral role in the manufacture of ceramic materials. They enhance reliability by providing a basis for quantifying and comparing material properties during each phase of the manufacturing process, from raw materials to the finished product. Equally important is the establishment of a uniform and widely accepted nomenclature to permit the efficient exchange of scientific and technical information, and to provide a sound basis on which to standardize measurement methods and data reporting practices.

In June 1997, NIST established the Ceramic Processing Characterization Council (CPCC)<sup>†</sup> to assist the U.S. ceramics industry in the development of measurements and standards infrastructure. The CPCC is a voluntary, cooperative program among NIST, universities, private companies, other government research laboratories and private sector laboratories. A principal goal of the consortium is to develop guidelines and recommended practices for the implementation of process measurements. Within the CPCC, the Dispersion & Rheology Working Group (DRWG) is responsible for addressing those measurement issues associated with particulates in liquid media. DRWG members quickly recognized the fundamental importance of terminology to any measurement-based strategy, and subsequently initiated a project to develop a uniform nomenclature for dispersion systems.

An ad hoc committee was formed, whose members included J.H. Adair (Penn State), J.A. Casey (IBM), R.A. Condrate (Alfred), M. Frey (3M), V.A. Hackley (NIST), W. Hunt (3M), A. Jilavenkatesa (NIST), M.J. Mayo (Penn State), G.Y. Onoda (NIST), P. Somasundaran (Columbia), and T. Wood (3M). The committee was charged with reviewing the technical content and language of the nomenclature, which I had volunteered to compile. Several revisions were passed through the committee before a draft version was circulated for comment by CPCC members at large. In addition to the committee review, two distinguished authorities in the particle science field, Bob Hunter at the University of Sydney and George Scherer at Princeton, were invited to review the nomenclature and provide input according to their respective areas of expertise. Their help is gratefully acknowledged.

In compiling this nomenclature, every effort was made to maintain a degree of uniformity with existing standards and conventions. To this end, the cooperation of the American Chemical Society and the International Union on Pure and Applied Chemistry (IUPAC) were instrumental.

To help put this nomenclature into practice, I have prepared this special publication. It is my general hope that it will serve as a resource to those working in particle dispersion applications, particularly in the ceramic sciences. It is my further hope that this document will serve to promote the establishment of a commonly recognized system of terminology throughout the ceramics community.

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<sup>†</sup> Formally known as the Ceramic Processing Characterization Consortium.

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# GUIDE TO THE NOMENCLATURE OF PARTICLE DISPERSION TECHNOLOGY FOR CERAMIC SYSTEMS

## 1. INTRODUCTION

The use of nomenclature for identifying dispersed particle systems, along with their associated properties and components, is often inconsistent and subject to misinterpretation in the ceramic and materials science literature. For example, terms for describing the state of association of particles in suspension (e.g., *aggregate* or *agglomerate*) often carry specific connotations that vary among different authors. In an attempt to standardize usage of dispersion terminology, and as a resource for researchers, engineers and students, an internally consistent system of nomenclature has been developed. In compiling definitions, a variety of sources were examined, including IUPAC<sup>1</sup> recommendations, current and draft ASTM<sup>2</sup> and ISO<sup>3</sup> standards, and published materials drawn from both the ceramic and the more general colloid and interface science literature (*see the bibliography for a complete list of primary and secondary sources*).

Definitions have been written first and foremost to serve those people in the ceramics field, but should be of equal utility to those involved in a broad range of dispersion-based non-ceramic applications. This is not, nor is it intended to be, an exhaustive compilation. Rather, this document focuses on commonly encountered terms, and endeavors to provide a consistent

framework for improved technical communication.

The terms are organized into five subsections, each dealing with a specific aspect of dispersion: (1) physical description of dispersed systems; (2) states of subdivision; (3) association and disassociation processes; (4) dispersion stability; and (5) interfacial and electrokinetic properties. Acceptable alternative expressions and common abbreviations are shown in parentheses adjacent to the defined term. In general, the American Chemical Society's formalism for abbreviations has been adopted here.<sup>4</sup>

In some cases, a definition may have two parts; one more general in context and the other more specific to ceramic applications. Recommendations are also provided, for instance, regarding the discontinuance of terms deemed ambiguous or obsolete, and are presented at the end of each subsection. Within each definition, separately defined terms are identified in *italics* at their first occurrence. In addition, an alphabetized index to defined terms is provided.

## 2. DEFINITIONS

### 2.1 Physical Description of Dispersed Systems

#### *Aerosol*

*Droplets* or *particles* dispersed in a gaseous phase.

<sup>1</sup> International Union on Pure and Applied Chemistry

<sup>2</sup> American Society for Testing and Materials

<sup>3</sup> International Organization for Standardization

<sup>4</sup> The ACS Style Guide, 2<sup>nd</sup> Edition, 1997.



**Continuous Phase**

Constituting the *dispersion* medium, a phase that exhibits continuity throughout the dispersion; e.g., the liquid in a *suspension*.

**Dispersed Phase (Discontinuous Phase)**

In a *dispersion*, the phase that is distributed in the form of discrete discontinuities (*particles*, *droplets* or bubbles), in a second immiscible phase that is continuous.

**Dispersion**

In general, a two-phase system in which discontinuities of any kind (solid, liquid, gas) are dispersed in a *continuous phase* of a different composition or state; more specifically in the field of ceramics, the term dispersion is used to describe a *suspension* of solid *particles* in a liquid medium.

**Emulsion**

A *dispersion* consisting of two or more liquid phases.

**Hydrosol**

A *sol* in which water forms the *dispersion* medium.

**Liquid Phase**

Consisting of a condensed fluid; e.g., the *dispersion* medium in a *suspension*.

**Organosol**

A *sol* in which an organic liquid forms the *dispersion* medium.

**Particulate Phase (Solid Phase)**

The particles in a *suspension*, *gel*, or *aerosol*.

**Slip**

A term that refers to a *suspension* prepared for the expressed purpose of

consolidating the *solid phase* (e.g., by slip-casting, tape-casting, or spray drying).

**Slurry**

A concentrated ceramic particulate *suspension*.

**Sol**

A liquid *dispersion* containing particles of *colloidal* dimensions.

**Suspension**

A liquid in which solid particles are dispersed.

**Related Terms**

**Heterodisperse**

Describes a *polydisperse* particulate system in which more than one discrete size distribution mode occurs; e.g., bimodal, trimodal, etc.

**Monodisperse**

Realistically, all *dispersions* exhibit a finite spread in their *particle* size distribution. In practice, the term monodisperse can be used to identify a dispersed system in which all particles are of nearly the same size, forming a narrow (unimodal) distribution about an average value. Numerically, a dispersion may be considered monodisperse if 90% of the distribution ( $1.645\sigma$ , where  $\sigma$  is the standard deviation of the size distribution) lies within  $\pm 5\%$  of the average size,  $\langle d \rangle$ :

$$\frac{1.645\sigma}{\langle d \rangle} \leq 0.05$$

**Polydisperse**

Describes a dispersed system in which many *particle* sizes occur. In practice, a system may be considered polydisperse if



less than 90% of the size distribution ( $1.645\sigma$ , where  $\sigma$  is the standard deviation of the size distribution) lies within  $\pm 5\%$  of the average size,  $\langle d \rangle$ :

$$\frac{1.645\sigma}{\langle d \rangle} > 0.05$$

### ***Well-Dispersed***

A term used to describe a *stable suspension* in which the *minimum particle size* has been achieved.

## **Recommendations**

### ***Relative Concentration Terms***

It is recommended that relative descriptive terms relating to particle concentration in *suspension* (e.g., dilute or concentrated) be defined in such a manner that the reader has a clear understanding of their relevance to the measurement or application at hand. For instance, in a light scattering measurement, "dilute" may infer the absence of multiple scattering, whereas in an ultrasonic measurement this term may imply a linear response with concentration. These conditions may vary by several orders of magnitude with respect to particle concentration. Concentration can also be defined on a more fundamental basis, taking into consideration the relative dominance of thermal, hydrodynamic, or surface forces in controlling suspension properties.

## **2.2 States of Subdivision (Dispersed Phase)**

### **Definitions Based on Size**

#### ***Nanosize (Nanophase)***

A special state of subdivision implying that the *particles* (or atomic clusters) have average dimensions smaller than

roughly 100 nm, and exhibit properties not normally associated with the bulk phase (e.g., quantum optical effects).

#### ***Colloid***

State of subdivision implying that the *particles* have at least in one direction a dimension roughly between 1 nm and 1  $\mu\text{m}$ . Colloids are significantly affected by *Brownian motion* when suspended in a liquid.

#### ***Ultrafine***

State of subdivision implying that the *particles* have in any given direction a maximum dimension lying roughly between 1  $\mu\text{m}$  and 10  $\mu\text{m}$ .

#### ***Fine (Subsieve Range)***

State of subdivision implying that the *particles* have in any given direction a maximum dimension less than roughly 37  $\mu\text{m}$ .

#### ***Coarse (Sieve Range)***

State of subdivision implying that the *particles* have in any given direction a dimension greater than roughly 37  $\mu\text{m}$ .

#### ***Granule***

State of subdivision generally referring to dry particulates with dimensions lying roughly in the 50  $\mu\text{m}$  to 200  $\mu\text{m}$  range; typically, granules are *aggregates* of finer particles produced by spray-drying. Granulation is performed for ease of handling during subsequent consolidation operations.

### **Definitions Based on Structure**

#### ***Particle***

Any condensed-phase tridimensional discontinuity in a dispersed system may generally be considered a particle; e.g., *droplets* in an *emulsion* or solids

dispersed in a liquid. The term is normally used in reference to solid materials. An *aggregate* may also be regarded as a particle.

***Droplet***

Liquid-phase *particle* in an *emulsion* or *aerosol*.

***Particulate***

Composed of distinct *particles*.

***Primary Particle***

Smallest identifiable subdivision in a *particulate* system. Primary particles may also be subunits of *aggregates*.

***Microsphere***

Refers to a spherical *particle* in the micrometer size range.

***Aggregate***

A cohesive mass consisting of *particulate* subunits.

***Hard-Aggregate***

An *aggregate* that cannot be easily redispersed by the application of moderate mechanical agitation (shaking, stirring, or ultrasonication) and/or mild chemical treatment. Hard-aggregates consist of subunits that have been chemically bonded or *fused*.

***Agglomerate***

In a *suspension*, an *aggregate* held together by physical or electrostatic forces.

***Coagulate (Coagulum)***

In a *suspension*, an *aggregate* formed by the addition of electrolyte.

***Floc***

In a *suspension*, an *aggregate* formed by the addition of a polymer. Floccs are

generally characterized by a loose structure (low density).

***Powder***

A relatively dry, undispersed accumulation of *particulate* matter with a macroscopic consistency.

***Gel***

Bicontinuous structure with a solid and a liquid component. The solid network may consist of *particles* or polymers, held together by covalent, ionic, or dispersion (physical) forces. The network may be elastic, viscoelastic, or plastic. The scale of the mesh of the network (distance between cross links) is of *colloidal* dimensions.

***Aerogel***

A porous solid produced from a *gel* in such a way that very little shrinkage occurs. Typically, the term refers to materials made by supercritical extraction of the solvent, although structurally equivalent materials can be made under ambient conditions by increasing network stiffness and/or elastic recovery, and by reducing interfacial tension.

***Alcogel***

A *gel* containing an alcoholic liquid phase.

***Hydrogel***

A *gel* containing an aqueous liquid phase.

***Xerogel***

Porous solid made by drying a *gel* under subcritical conditions.

**Related Terms**

***Average Agglomeration Number (AAN)***

An estimate of the degree of *agglomeration* in a *suspension*. AAN is

the average number of *primary particles* contained within an *agglomerate*. AAN is calculated from the ratio of the median particle size, as determined by, for example, light scattering, *sedimentation* or electrical zone sensing techniques, to the average equivalent spherical volume ( $V_{\text{BET}}$ ) given by the BET gas adsorption method, such that:

$$\text{AAN} = \frac{V_{50}}{V_{\text{BET}}} = \left( \frac{D_{50} \cdot \text{SSA} \cdot \rho}{6} \right)^3$$

where  $V_{50}$  is the equivalent spherical volume calculated from the median diameter,  $D_{50}$  in  $\mu\text{m}$ , SSA is the specific surface area in  $\text{m}^2/\text{g}$  and  $\rho$  is the particle density in  $\text{g}/\text{cm}^3$ .

#### ***Equivalent Spherical Diameter***

The diameter of a sedimenting particle determined from Stokes' law and assuming a spherical shape. The term is sometimes used in conjunction with other measurement techniques and theoretical constructs, where spherical geometry is assumed.

#### ***Fractal***

A structure that has an irregular geometry under all scales of observation (i.e., it is non-Euclidian). The fractal dimension of a species,  $D_f$ , is the exponent to which a characteristic length scale must be raised to obtain proportionality with the overall size of the species. Destabilized suspensions tend to form aggregates with fractal structures. In this case,  $D_f$  has a value lying between 1 and 3, where  $D_f=3$  is a fully dense object.

#### ***Minimum Particle Size (MPS)***

An experimental quantity operationally defined as the minimum *particle size* that can be achieved by a particular *dispersion* process as determined by an appropriate measurement technique. The

characteristic dimension used in determining the MPS should be clearly noted (e.g., mean size, median size, modal size, etc.).

#### ***Ultimate Working Unit***

An individual *particle* or group of particles that retains its structure throughout a *dispersion* process and subsequent application. See also *minimum particle size*.

### **Recommendations**

#### ***Floccule***

It is recommended that this term not be used in the ceramic literature. (see *Floc*)

#### **Hard, Soft**

With the exception of the defined term *hard-aggregate*, it is recommended that such adjectives be avoided in the context of dispersed phase structure. If their use is deemed necessary to convey material-specific information, then the author should make a clear statement that defines the meaning and extent of usage.

### **2.3 Association and Dissociation Processes**

#### **Association Processes**

##### ***Aggregation***

A general term defined as any process by which particles collect to form a cohesive mass or cluster; the resulting structure is called an *aggregate*.

##### ***Agglomeration***

Formation of *aggregates* in a *suspension* through physical (van der Waals, hydrophobic) or electrostatic forces. The resulting structure is called an *agglomerate*.



### ***Coagulation***

A specific type of *agglomeration* in which formation of *aggregates* is induced by the addition of electrolyte to a *suspension*. The resulting structure is termed the *coagulate* or *coagulum*, while the electrolyte additive is termed the *coagulant*.

### ***Flocculation***

Formation of *aggregates* in a *suspension* mediated by polymeric species, that are either attached to the particles or exist freely in the suspending medium. The resulting structure is called a *floc*, while the polymer additive is termed a *flocculant*. Polymer bridging is a flocculation process.

### ***Gelation***

Formation of a continuous (space-filling) solid network characterized by a finite static shear modulus (stress/strain ratio); results from percolation of bonds between particles or polymers. The resulting structure is termed a *gel*.

### ***Fusion***

Process by which *particles* form irreversibly bonded structures; often characterized by the appearance of interparticle necks. (see also *hard-aggregates*)

### ***Heteroagglomeration, Heterocoagulation, Heteroflocculation***

Generally refers to the *aggregation* of dissimilar *particles*; in ceramic applications, the formation of *aggregates* by the cohesion between particles of different materials (e.g., alumina and silica).

### ***Orthokinetic Aggregation***

The process of *aggregation* induced by hydrodynamic motions, such as stirring,

*sedimentation*, or convection.

### ***Perikinetic Aggregation***

The process of *aggregation* induced by *Brownian motion*.

### ***Sol-gel***

Process for making a *gel* from *colloidal* or molecular precursors.

## **Dissociation Processes**

### ***Deagglomeration***

Reversal of *agglomeration*, i.e., the dispersion of *agglomerates* to form a *suspension*.

### ***Deflocculation***

Reversal of *flocculation*, i.e., the dispersion of *flocs* to form a *suspension*.

### ***Comminution***

Breaking down large pieces to the required size; term commonly used in association with milling of ceramic *slurries*.

### ***Peptization***

Refers to the reversal of *agglomeration* by the addition of a strong acid or strong base, such as HCl or NaOH.

## **Related Terms**

### ***Diffusion-Limited Rate***

Refers to a rate of *aggregation* corresponding to the frequency of encounter (collision rate) of the *particles*. Each collision results in particle adherence (i.e., a sticking probability equal to 1). The rate of encounter is controlled by the diffusion rate, which depends on the viscosity of the medium, the dimensions of the particles, and the concentration of the particles.



***Reaction-Limited Rate***

Refers to a rate of *aggregation* that is controlled by the reactivity of the *particles* (i.e., the frequency of collisions resulting in particle sticking). Usually characterized by a sticking probability much less than 1. A low sticking probability results from the presence of an energy barrier.

***Syneresis***

Spontaneous shrinking of a gel with exudation of liquid.

***Ultrasonication***

Application of high-energy, high-frequency sound to a *suspension* in order to disperse *aggregates*. Dispersion is thought to arise from the energy released during fluid cavitation.

**Recommendations**

***Sonication, Sonification***

It is recommended that these terms not be used in the ceramic literature. (see *Ultrasonication*)

**2.4 Dispersion Stability**

**States of Stability**

***Colloidal Stability***

A physical state that characterizes the relative ability of *colloids* to remain dispersed in a liquid; *suspensions* that do not *aggregate* at a significant rate are said to be colloiddally stable. The precise connotation depends on the time frame under consideration. Colloidal stability is a form of *kinetic stability*, and is therefore considered a metastable thermodynamic state. From this perspective, *aggregation* may be described as a transition from a metastable to a stable state, occurring at

rates that depend on the magnitude of the activation energy barrier that separates them.

***Kinetic Stability***

Most dispersed systems are thermodynamically unstable, relative to their separate bulk phases; however, a dispersion may exist for an appreciable length of time and therefore exhibit kinetic stability. The term may be used in reference to various destabilizing processes, e.g., *aggregation*, coalescence, or *sedimentation*.

***Stable Suspension***

A *suspension* that has sufficient *kinetic stability* to prevent the occurrence of significant *aggregation* as measured over a relevant time frame. Stability may be ascertained by suitable experimental means, such as *particle size*, turbidity, or *sedimentation* measurements.

***Unstable Suspension***

A *suspension* that lacks *kinetic stability* as measured over a relevant time frame; a highly unstable suspension is one that is subject to rapid (*diffusion-limited*) *aggregation*.

**Stability Mechanisms**

***Electrostatic Stabilization***

Mechanism in which *aggregation* is inhibited by the presence of a mutually repulsive electrostatic potential that surrounds each *particle*.

***Steric Stabilization***

Mechanism in which *aggregation* is inhibited by the presence of an adsorbed polymer layer that is firmly anchored to the *particle* surface so as not to desorb during collisions. In general, a *steric stabilizing* agent has one portion of its

structure that exhibits low solubility in the *dispersion* medium and/or high affinity for the particle surface, and the other portion is soluble in the medium.

#### ***Electrosteric Stabilization***

Mechanism in which *aggregation* is inhibited by the combined effects of *electrostatic* and *steric stabilization*. Usually associated with the *adsorption* of *polyelectrolytes* onto the *particle* surface.

#### ***Depletion Stabilization***

Mechanism in which *aggregation* is inhibited by the presence of free (non-adsorbed) polymer due to the creation of high-energy depletion zones (i.e., depleted of polymer compared to the bulk solution) between closely interacting *particle* surfaces.

### **Interaction Terms**

#### ***DLVO***

An abbreviation for a theory of the stability of *colloidal dispersions* describing the pair-wise interaction between charged *particles* in a dielectric medium. The theory, derived independently by Derjaguin and Landau, and by Verwey and Overbeek, calculates the opposing effects of attractive van der Waals forces and repulsive electrostatic forces on the *interaction potential*.

#### ***Interaction Potential***

The potential free energy between two surfaces, typically presented as a function of separation distance. By convention, a positive potential is mutually repulsive and a negative potential is mutually attractive.

#### ***Primary Maximum***

The first appearance of a maximum in the *interaction potential energy* curve with

increasing separation distance. The primary maximum results from the fact that repulsive and attractive forces decay at different rates as a function of separation distance. In *DLVO* theory, a large primary maximum acts as an energy barrier, preventing *aggregation* of *particles* into the *primary minimum*.

#### ***Primary Minimum***

The first appearance of a minimum in the *interaction potential* curve with increasing separation distance. The primary minimum results from the fact that repulsive and attractive forces decay at different rates as a function of separation distance. In *DLVO* theory, a deep (negative) primary minimum acts as an energy well, allowing *particles* to adhere and resulting in a loss of *colloidal stability*.

#### ***Secondary Minimum***

A shallow energy minimum (usually of the order of a few  $kT$ ) in the *interaction potential* curve occurring at relatively large separation distances beyond that of the *primary maximum*. In the presence of such an energy well, secondary minimum *aggregation* may occur. Because of the shallow nature of the secondary minimum, the *aggregates* formed are held together weakly and as such tend to be *unstable* toward rather small energy inputs such as stirring.

#### ***Born (Hard Core) Repulsion***

As two surfaces are brought into close contact, the attractive van der Waals force between them increases continuously. At some point in their approach, the electron clouds of the two surfaces begin to overlap, giving rise to a repulsive force termed the Born or hard core repulsion. This results in a steep increase in the *interaction potential* curve

at very small interatomic separation distances, becoming effectively infinite when interpenetration occurs.

***Solvation (Structural) Forces***

Non-DLVO forces that occur at extremely small separation distances (typically a few molecular diameters) when *particles* interact through an intervening fluid medium. These forces arise whenever liquid molecules are induced to order into quasi-discrete layers between surfaces, and can result in a monotonically increasing (repulsive), monotonically decreasing (attractive), or oscillatory *interaction potential*. In aqueous solvents these forces may be referred to as hydration forces.

***Hamaker Constant***

In the case of *particle* interactions, a material constant that measures the relative strength of the attractive van der Waals forces between two surfaces. Particles interacting through an intervening fluid medium will experience a reduced attractive potential due to the presence of the third component.

***Hard Sphere Interaction***

A largely theoretical construct in which the *interaction potential* between approaching *particles* is assumed to equal zero, except upon contact where it goes abruptly to infinity (i.e., no interpenetration occurs).

***Noninteracting***

If no barrier to *particle* approach, contact and adherence exists, the particles are said to be noninteracting. If the *primary minimum* is sufficiently deep, every collision will result in particles sticking together. The rate of *aggregation* will then be kinetically controlled (*diffusion-limited rate*).

**Related Terms**

***Critical Coagulation Concentration (ccc)***

The molar concentration of electrolyte,  $C_0$ , necessary to induce rapid (*diffusion-limited*) *aggregation*. Experimentally determined by extrapolation of  $\ln W$  versus  $\ln C_0$  to  $\ln W=0$ , where  $W$  is the *stability ratio*.

***Coagulant***

An electrolyte additive that induces *coagulation* in a *suspension*.

***Schulze-Hardy Rule***

An empirical rule summarizing the general tendency of the *critical coagulation concentration* to vary inversely with the sixth power of the *counterion* charge number of added electrolyte.

***Lyotropic Series***

An ordered series of ions indicating, in decreasing order, their effectiveness in influencing the behavior of *colloidal dispersions*. Typically associated with an ion's relative propensity to *coagulate* a dispersion.

***Stability Ratio***

Ratio of the *diffusion-limited* to *reaction-limited rate* constants for *aggregation*. A large ratio indicates a high degree of *colloidal stability*, whereas a ratio of unity indicates that diffusion-limited conditions prevail and the system is *colloidally unstable*. The rate constants are determined experimentally from the initial rates of aggregation. Usually denoted by the symbol,  $W$ .



***Defoaming (Antifoaming) Agent***

A *surfactant* that when present in small amounts prevents the formation of a foam or aides in the coalescence of bubbles.

***Dispersing Agent (Stabilizing Agent, Dispersant)***

A substance that when present in small amounts facilitates the dispersion of *aggregates* and improves the *kinetic stability* of *particles*. For example, *polyelectrolytes* are often used as dispersing agents in ceramic processing.

***Surface Active Agent (Surfactant)***

A substance that lowers the interfacial tension between the solution in which it is dissolved, and other phases which are present (e.g., solid *particles* in a *suspension*), and, accordingly, is positively adsorbed at the *interface*.

***Polyelectrolyte***

A macromolecular substance that, on dissolving in water or other ionizing solvent, dissociates to give polyions (polycations or polyanions) – multiply charged ions – together with an equivalent amount of *counter ions*. A polyelectrolyte can be a polyacid, a polybase, a polysalt, or a polyampholyte. Frequently used as *dispersing agents* in ceramic *slurries*.

***Sedimentation***

The settling of suspended *particles* or *droplets* due to the influence of gravity or an applied centrifugal field.

***Sedimentation Volume***

The volume of *particulate* sediment formed in a *suspension*. If the sediment is formed in a centrifugal field, the strength of this field should be explicitly indicated, otherwise normal gravity is understood.

***Brownian (Thermal) Motion***

Random fluctuations in the density of molecules in a liquid, due to thermal energy, cause other molecules and small dispersed *particles* to move along random pathways. This random motion is termed Brownian motion, and is most noticeable for *colloidal* particles.

***Coacervation***

When a *colloidal suspension* loses stability, a separation into two liquid phases may occur. This process is termed coacervation. The phase that is more concentrated in the colloid is the coacervate, and the other phase is the equilibrium solution.

**Recommendations**

***Deflocculant, Dispersing Aid***

It is recommended that these terms not be used in the ceramic literature. (see *Dispersing Agent*)

**2.5 Interfacial and Electrokinetic Properties**

**The Interface**

***Interface***

A boundary between two immiscible phases, at least one of which is condensed. Experimentally, the portion of the sample through which the first derivative of any concentration versus location plot has a measurable departure from zero. In a *suspension*, the region of contact between the *particle* surface and the suspending medium.

***Interfacial Region (Interphase)***

The region that exists between two phases where the properties vary from those in the bulk.



### **Surface Region**

The tridimensional region, extending from the free surface of a condensed phase towards the interior, where the properties differ from the bulk.

### **Electrical Double Layer (EDL)**

The term describes the non-random array of ions at an *interface* in which two oppositely charged layers coexist. For particles dispersed in a fluid, the EDL consists of the surface charge and the solution charge. The solution charge may be further subdivided into *Stern* and *diffuse* layers, which is often referred to as the triple layer model.

### **Double Layer Thickness**

Length characterizing the decrease of potential with distance from a charged *interface*. Typically defined as  $1/\kappa$ , where  $\kappa$  is the *Debye-Hückel parameter*. For low potentials it represents the distance over which the potential falls to  $1/e$ , or about one third, of the value of the surface potential.

### **Diffuse Layer**

The region surrounding a suspended *particle* in which non-specifically adsorbed ions are accumulated and distributed by the opposing action of the electric field and *thermal motion*.

### **Stern Layer (Compact Layer)**

*Counter* and *co-ions* in immediate contact with a surface are said to reside in the Stern layer, and form with the fixed surface charge a molecular capacitor. Often equated with the immobile portion of the *electrical double-layer* that exists inside the *shear plane*.

### **Inner Helmholtz Plane (IHP)**

At a charged interface, an imaginary plane representing the distance of closest

approach of desolvated ions to the surface, and containing the ions or molecules that are specifically adsorbed.

### **Outer Helmholtz Plane (OHP)**

At a charged interface, an imaginary plane representing the distance of closest approach of solvated (hydrated) ions to the surface. Often equated with the position of the *shear plane*.

### **Shear Plane (Plane of Shear, Surface of Shear)**

In calculating the *electrokinetic potential* from electrokinetic phenomena it is often assumed that a sharp plane separates the liquid adhering to the solid surface from the mobile liquid. This imaginary plane is considered to lie close to the solid surface.

## **Adsorption Processes**

### **Adsorption**

The process by which a substance is accumulated at an *interface* or in an *interfacial region*. Should not be confused with absorption, which denotes accumulation inside a material or phase.

### **Adsorbate**

A substance that is adsorbed at the *interface* or into the *interfacial region* of a substrate material, or *adsorbent*.

### **Adsorbent**

The substrate material onto which a substance is adsorbed.

### **Adsorption Isotherm**

The relationship between the equilibrium quantity of a substance adsorbed and the composition of the bulk phase, at constant temperature.

### ***Specific Adsorption***

Ions are specifically adsorbed when they are present in the *Stern layer* in amounts that exceed those expected from simple electrostatic considerations. Empirically, ions that are specifically adsorbed have a noticeable effect on the *isoelectric point*.

### ***Non-Specific Adsorption***

Ions are non-specifically adsorbed when they are kept in the *interphase* only by long-range coulombic interactions. They are believed to retain their solvation shell and in the position of closest approach to the interface they are separated from it by one or more solvent molecular layers. Empirically, ions that are non-specific (*indifferent*) have no measurable effect on the value of the *isoelectric point*.

### ***Chemical Adsorption (Chemisorption)***

Molecules are chemically adsorbed when they exist within the *Stern layer* and form bonds with the surface groups, which have a significant valence contribution. Empirically, ions that are chemically adsorbed have a noticeable effect on the *isoelectric point* of a *suspension* and exhibit a significant enthalpy (heat of adsorption).

### ***Physical Adsorption (Physisorption)***

*Adsorption* in which the forces involved are intermolecular (i.e., van der Waals, hydrogen bonding) of the same kind as those responsible for the non-ideality of real gases and the condensation of vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved.

### ***Monolayer Adsorption***

*Adsorption* in which only a single layer of molecules becomes adsorbed at an *interface*. In monolayer adsorption, all

adsorbed molecules are in the position of closest approach to the substrate surface.

### ***Multilayer Adsorption***

Adsorption in which more than a single layer of molecules is adsorbed at the *interface*. Molecules adsorbed in excess of *monolayer adsorption* are not in the position of closest approach to the substrate surface.

### ***Coadsorption***

The simultaneous *adsorption* of two or more species.

### ***Desorption***

The process by which the amount of an adsorbed substance is reduced.

## **Electrical Properties**

### ***Isoelectric Point (iep)***

For many ceramic systems, the pH at which dispersed *particles* show no *electrophoretic mobility* and the *zeta potential* has a value of zero. More generally, the pI value at which zeta is zero, where I is the *potential determining ion*.

### ***Point of Zero Charge (pzc)***

A *particle* carrying no fixed charge. The precise identification of pzc depends on the definition adopted for surface charge. Typically for ceramic systems, the pH at which hydroxyl and proton *adsorption* is just balanced to cancel net charge; here, the hydroxyl and proton are defined as the charge determining species.

### ***Surface Charge Density***

The quantity of electrical charge accumulated at a particle-solution interface, expressed per unit area; usually represented by the symbol  $\sigma_0$ .

### ***Shear Plane Potential***

The potential difference across the mobile part of the *electrical double layer* at a charged solid-liquid *interface*; potential at the *shear plane* during an *electrokinetic* measurement. Synonymous with *zeta potential* for the case of particles suspended in a liquid.

### ***Streaming Potential***

When a liquid under a pressure gradient is forced through a capillary or porous plug, excess charges (ions) near the wall are swept along by the liquid creating an accumulation of charge downstream. An electric field is also created, which opposes this accumulation. After a steady state has been established, the measured potential difference across the capillary or plug is called the streaming potential and is related to the pressure gradient and to the *shear plane potential*.

### ***Zeta Potential (Electrokinetic Potential, Shear Plane Potential)***

The potential drop,  $\zeta$ , across the mobile part of the *electrical double layer*, that is responsible for the *electrokinetic* phenomena.  $\zeta$  is positive if the potential increases from the bulk of the liquid phase towards the *shear plane*. Certain assumptions or estimations regarding the double layer properties must be made in order to calculate  $\zeta$  from experimental data. It is therefore essential to indicate in all cases which equations have been used in the calculation of  $\zeta$ . It can be shown, however, that for the same assumptions about the double layer properties, all electrokinetic phenomena must give the same value for the electrokinetic potential.

### ***Potential Determining Ions***

Those species of ions that by virtue of their equilibrium distribution between

two phases determine the difference in Galvani potential between these phases. They are often, but not always, identical with the ions that stabilize a *colloidal suspension* formed from these phases.

### ***Co-ions***

In systems containing large ionic species (e.g., *colloids*), co-ions are those that, compared to the large ions, have low molecular mass and the same polarity. For instance, in a *suspension* of negatively charged *particles* containing sodium chloride, the chloride ions are co-ions and the sodium ions are *counterions*.

### ***Counterions***

In systems containing large ionic species (e.g., *colloids*), counterions are those that, compared to the large ions, have low molecular mass and the opposite polarity. For instance, in a *suspension* of negatively charged *particles* containing sodium chloride, the sodium ions are counterions and the chloride ions are *co-ions*.

### ***Charge Reversal***

The process wherein a charged *particle* is caused to assume a new charge of the opposite polarity. Such a change can be brought about by oxidation, reduction, dissociation, *adsorption*, or ion exchange.

## **Electrokinetic Effects**

### ***Electrokinetics***

Referring to the relative motions of charged species in an electric field. The field may be applied, or it may be created by the motion of a liquid or adjacent solid phase.

### ***Electro-osmosis***

When a liquid moves in response to an applied electric field, while an adjacent



solid phase remains stationary (e.g., in a capillary or porous plug), this is called electro-osmotic flow. Fluid motion is due to the reaction of charged species within the fluid, usually dissolved ions, to the applied field.

### ***Electrophoresis***

The motion of charged *particles* in an applied electric field.

### ***Electrophoretic Mobility (Static, Dynamic)***

The *electrophoretic* velocity per unit field strength, symbol  $\mu_e = v/E$ ;  $\mu_e$  is positive if the *particle* moves toward lower potential and negative in the opposite direction. When measured in a d.c. electric field,  $\mu_e$  is referred to as the static mobility. When measured in a high-frequency field it is referred to as the dynamic mobility, and given the symbol  $\mu_d$  or  $\mu(\omega)$ . Dynamic mobility may be a complex quantity at high frequencies.

### ***Electroacoustics***

Referring to the electric-acoustic coupling in a fluid containing charged colloids or ions; an effect that is responsible for the *electrokinetic sonic amplitude*, *colloid vibration potential* and *ion vibration potential*.

### ***Acoustophoresis***

The induced motion of *particles* subjected to an acoustic field. Charged particles will generate an electric field as a result of this motion (see *ultrasonic vibration potential*).

### ***Ultrasonic Vibration Potential (UVP)***

When a sound wave propagates through a fluid containing charged *particles* (ions or *colloids*), coherent *acoustophoretic* motion of the particles creates alternating dipoles that generate a macroscopic

potential difference termed the ultrasonic vibration potential.

### ***Ion Vibration Potential (IVP)***

The *ultrasonic vibration potential* of an ionic solution; also known as the Debye effect.

### ***Colloid Vibration Potential (CVP)***

The *ultrasonic vibration potential* of a *colloidal suspension*. The resulting potential difference is related to the *dynamic mobility* of the particles; reciprocal effect to *electrokinetic sonic amplitude*.

### ***Electrokinetic Sonic Amplitude (ESA)***

When a high-frequency alternating electric field is applied to a *dispersion* of charged *colloids*, the oscillatory *electrophoretic* motion of the *particles* relative to the surrounding medium results in a measurable acoustic field whose amplitude is related to the *dynamic mobility*; reciprocal effect of *colloid vibration potential*. The phase difference between the applied field and the resulting acoustic response can also be used to estimate the particle size distribution.

## **Related Terms**

### ***Amphoteric***

Refers to a type of surface in which the same surface group (reactive site) is able to function as both an acid and a base. That is, the site may dissociate to release a proton or accept a proton.

### ***Zwitterionic***

Refers to a type of surface in which two distinct surface groups (reactive sites) are present. One is capable of dissociating to release a proton (acid group), and the



other is capable of accepting a proton (base group).

**Hydrophilic**

May be used to describe the character of interaction of a particular atomic group (or substance) with an aqueous medium. In this usage the term has the relative qualitative meaning of "water loving." The more general term, lyophilic ("solvent loving"), is used to distinguish a class of colloidal systems.

**Hydrophobic**

The tendency of hydrocarbons (or of lipophilic hydrocarbon-like groups in solutes) to form intermolecular aggregates in an aqueous medium, and analogous intramolecular interactions. In this usage the term has the relative qualitative meaning of "water fearing." The more general term, lyophobic ("solvent fearing"), is used to distinguish a class of colloidal systems.

**Indifferent (Supporting) Electrolyte**

An ionic solution, whose constituents are not electroactive (i.e., they have no significant effect on the surface potential of the material under study; no oxidative or reductive capacity) in the range of applied potentials being studied, and whose ionic strength (and, therefore, contribution to the conductivity) is usually much larger than the concentration of an electroactive substance to be dissolved in it. The ions constituting an indifferent electrolyte are said to exhibit no specificity for the particle surface.

**Ionic Strength**

A measure of electrolyte concentration given by  $I = \frac{1}{2} \sum c_i z_i^2$ , where  $c_i$  are the concentrations, in moles per liter, of the individual ions,  $i$ , and  $z_i$  are their ion

charge numbers.

**Debye-Hückel Parameter**

A parameter in the Debye-Hückel theory of electrolyte solutions, denoted as  $\kappa$ . For aqueous solutions at 25 °C,  $\kappa = 3.288\sqrt{I}$  in reciprocal nanometers, where  $I$  is the ionic strength. See *Thickness of the Electrical Double Layer*.

**Double Layer Compression (Screening)**

Increasing ionic strength causes the electrical potential near a charged surface to fall off more rapidly with distance. This is referred to as double layer compression or screening, because the double layer thickness shrinks as the Debye-Hückel parameter increases with increasing ionic strength.

**Electroviscous Effects**

For dispersions of charged particles, these are those components of the viscosity connected with the charge on the particles.

**Suspension Effect**

The Donnan e.m.f. between a suspension and its equilibrium liquid. The effect is most commonly encountered with pH measurements in colloidal suspensions.

**Potentiometric Analysis**

Analysis based on the measurement of electrical potential using, for example, a pH or ion-selective electrode. Potentiometry is often combined with titrimetric analysis in the determination of particle surface charge.

**Titrant**

The solution containing the active agent with which a titration is made.

### **Titration**

The process of determining the amount of a substance A by adding increments of substance B with provision for some means of recognizing the point at which all of A has reacted. This allows the amount of A to be found from the known amount of B added up to this point.

### **Titrimetric Analysis**

Analysis of test sample properties based on titration.

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