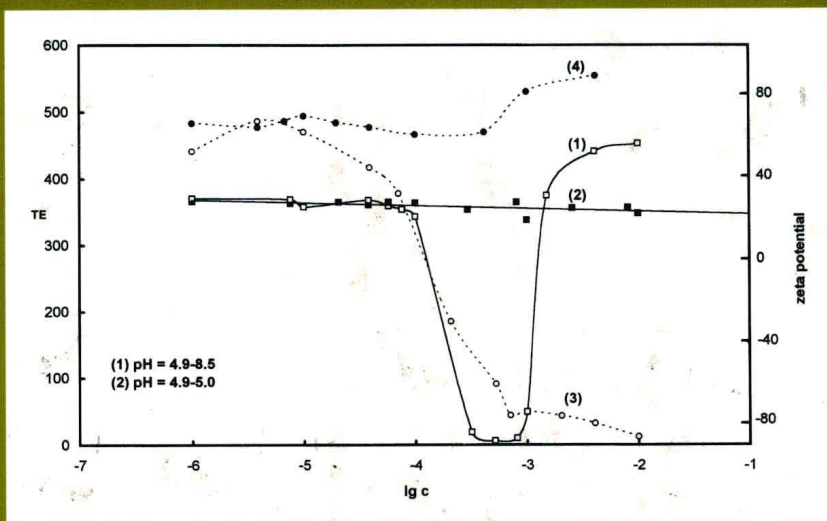


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SOLID-LIQUID DISPERSIONS



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SOLID-LIQUID DISPERSIONS

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Preface

Colloidal dispersions exist in our bodies, our food, our environment—in general, everywhere we look. Many industrial processes deal with colloidal dispersions, and they are also encountered in agricultural, pharmaceutical, and medical applications. Over the past fifty years, colloid dispersion science has undergone something of a revolution, transforming itself from little more than a collection of qualitative observations of the macroscopic behavior of some complex systems into a discipline with a solid theoretical basis.

It is no wonder that there is great interest in dispersion theory and its applications, as can be witnessed by the tremendous growth in the number of articles published in the scientific literature in this field. Surprisingly, however, very few textbooks are available to systematically guide the post-graduate or researcher or technician in both fundamental theory and new theoretical developments. Even though there are several books that deal with dispersion theory, they are too scattered, unsystematic or too specialized to include certain topics. It is hoped that this book will fill this gap.

The objective of this book is to review the fundamentals of dispersion theory together with the relevant aspects of colloidal and interfacial science and also recent developments in theory. It fills the need for a textbook that assumes a knowledge of elementary physical chemistry but no prior knowledge of colloid science and takes the subject through to a point where the reader can tackle the research literature with reasonable confidence. Hopefully, such a treatment will provide some grasp of the many areas that now form the basis of dispersion theory: dispersion forces, electrostatics, ther-

modynamics, statistical mechanics, hydrodynamics, and rheology, to name a few.

This book is directed as much toward senior undergraduate or postgraduate students, researchers and Ph.D. candidates and scientists in universities or institutes as it is toward the practitioners, technicians, and engineers in industry. The text has also been written with the needs of biologists, biochemists, and physiologists in mind.

Chapter 1 (B. Dobiáš and W. von Rybinski) gives a general description of the characteristics of colloidal dispersions and their classification and application, while Chapter 2 (X. Qiu and W. von Rybinski) deals with the preparation of colloidal dispersions. Chapter 3 (X. Qiu) describes the behaviors of colloidal dispersions with some emphasis on Brownian motion and diffusion. Colloidal hydrodynamics is discussed in Chapter 4 (X. Qiu). This is followed by three chapters—5 (X. Qiu), 6 (B. Dobiáš), and 7 (X. Qiu)—on the forces between colloidal particles, namely interparticle forces, electrostatic forces, and structural forces, and adhesive contact theory. Chapter 8 (B. Dobiáš and W. von Rybinski) deals with stability of dispersions concerning dispersion, coagulation, flocculation and its kinetics, sedimentation, centrifugation, and filtration. Chapter 9 (X. Qiu) focuses on the thermodynamics of dispersions with classical theories and new developments; particular attention is given to the modeling of polymer adsorption. Chapter 10 (B. Dobiáš and W. von Rybinski) is devoted to adsorption with electrolytes, surfactants, and polymers. This is followed by Chapter 11 (E. Suoninen), on the characterization of surface structure and adsorbate state and structure. The final chapter, Chapter 12 (B. Dobiáš and W. von Rybinski), deals with concentrated dispersions.

The authors would like to thank especially Professor Dr. Eero Suoninen for his valuable contribution of Chapter 11.

Bohuslav Dobiáš
Xueping Qiu
Wolfgang von Rybinski

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1

Introduction to Solid-Liquid Dispersions

I. CLASSIFICATION AND CHARACTERIZATION OF COLLOIDAL DISPERSIONS

Colloidal dispersions and their chemistry play an important role in nature and in industrial applications. It is difficult to find products and processes in the chemical or related industries in which knowledge of colloid science is not applied to a greater or lesser extent. Solid-liquid dispersions are widely used for paints, pesticides, clay minerals, ceramics, detergents, cosmetics, pharmaceuticals, food, and many other products. A general classification of colloidal systems according to the properties of the dispersed systems is very difficult, because the properties can vary over a broad range. Voyutsky [1] describes the most important criteria, for the classification of colloidal dispersions. The degree of dispersion, the state of the dispersed phase and that of the dispersion medium, the interaction between the dispersed phase and the dispersion medium, and the interaction between the particles are the main criteria.

Seidentopf and Zsigmondy [1] introduced a system of classification based on the degree of dispersion. In this case the particles of the dispersed system are classified according to their microscopic size. One distinguishes between microns and ultramicros, which are subdivided into submicrons (particles 5–200 nm) and amicros (particles < 5 nm). This characterization of dispersed systems is incomplete and one-sided. In addition to this, the classification cannot be applied to polydisperse systems. Ostwald [2] introduced a classification according to the state of aggregation of the dispersed phase and the dispersion medium. An overview of the possible combinations of dispersed phases and dispersion media is given in Table 1.

TABLE 1 Types of Colloidal Dispersions and Examples

Disperse phase	Dispersion medium	Notation	Technical name	Examples
Solid	Gas	s/g	Aerosol	Smoke
Liquid	Gas	l/g	Aerosol	Hairspray, mist, fog
Solid	Liquid	s/l	Sol or dispersion	Printing ink, paint
Liquid	Liquid	l/l	Emulsion	Milk, mayonnaise
Gas	Liquid	g/l	Foam	Fire extinguisher foam
Solid	Solid	s/s	Solid dispersion	Ruby glass (Au in glass), some alloys
Liquid	Solid	l/s	Solid emulsion	Bituminous road paving, ice cream
Gas	Solid	g/s	Solid foam	Insulating foam

Source: Ref. 2.

Classification according to the state of aggregation is more suitable for a general characterization of the variety of colloidal systems than other approaches. A disadvantage, however, is the adaptation of the state of the dispersed phase of different colloidal systems with decreasing particle size. Based on thermodynamic criteria it is very difficult to use the term “state” for particles smaller than 0.1 nm that consist of no more than a few molecules.

Classification according to the interaction between the dispersed phase and the dispersion medium is valid only for systems with a liquid dispersion medium. In connection with this, Zsigmondy refers to the “reversibility” or “irreversibility” of the dispersed phase in the dispersion medium after evaporation of the liquid phase. Freundlich [1] proposed that the reversibility or irreversibility of colloidal systems can be defined by the interaction of the dispersed phase with the dispersion medium. Both types of classifications refer to dispersed systems that contain particles of colloidal size, so the characterization is valid for both typical colloidal systems and polymer solutions.

For a classification according to particle interactions, the dispersions are divided into freely dispersed and coherently dispersed systems. Systems without a structure belong to the first group, dispersion systems in which the particles are not bound in a network structure but move in the dispersion medium due to Brownian motion or gravitational forces. Examples are lyosols, stable dispersions, emulsions, and aerosols. In coherently dispersed systems, single particles attract each other (intermolecular forces) and form network structures in the dispersion medium. Gels, concentrated disper-

sions, concentrated emulsions, foams, and so on may be mentioned as examples of this type of system. This classification, too, can be applied not only to colloidal systems but also to solutions of polymers.

A colloidal system has a highly dispersed state in which single particles consist of aggregates of molecules. In contrast to pure homogeneous solutions, every colloidal system is a heterogeneous system consisting of at least two different phases. A characteristic property of colloidal systems is the instability of their aggregates. According to thermodynamic principles, the instability of the aggregates is caused by a sufficiently high and always positive Gibbs energy acting at the interface. As all dispersions with a high Gibbs energy are unstable, the Gibbs energy is responsible for the coagulation of colloidal systems as long as surface energy and Gibbs energy are of the same magnitude. During coagulation, the particles adhere to each other and their surface area is decreased. The Gibbs energy of the system decreases. A reduction of the contact area is not always necessary for a decrease of the Gibbs energy, however. This energy can also be reduced when the particles approach to within a defined distance of each other and the interaction occurs across the separating interface layer. The thermodynamic interpretation of the stability or instability of colloidal systems is very simple, but it is only a formal description. As with all thermodynamic approaches, this interpretation can only partly explain the phenomena that occur in dispersions.

With respect to kinetics, the stability of colloidal or micro-heterogeneous systems depends on the ratio of interparticle forces. One distinguishes between attractive forces (van der Waals forces), which lead to an approach of the particles, and repulsive forces (e.g., electrostatic forces), which hinder that approach. The particle size is not relevant to the interpretation of the properties of colloidal systems, but interfaces, adsorption processes, and chemical reactions at the interfaces must be taken into account.

Additionally, colloidal dispersions exist that originate from the aggregation of associated molecules. This behavior is characteristic of surfactants that form micelles by self-association at a certain concentration. These structures have colloidal dimensions and are called association colloids. These dispersions are not considered in this volume.

II. TECHNICAL AND BIOLOGICAL ASPECTS

A. Technical Aspects

Numerous and very different applications of solid-liquid dispersions are described in the literature, e.g., Ref. 3. This is because in technical applications systems are very often used that require a homogeneous partition of solids in liquids. The position of the dispersion step within the process as a

whole is one possible basis for a general classification of the application of dispersions. Using this type of classification it is possible to distinguish three groups:

1. Use of dispersion technologies for the formulation and processing of raw materials and products from mixtures of solids and liquids
2. Direct application of dispersions
3. Application of products that are not dispersions, but during the use of which dispersions are generated that affect product performance

This classification is particularly useful as it combines different applications and chemicals that have similar mechanisms in one group. However, many types of dispersions and applications simultaneously belong to two or even three groups. An example of this are liquid detergents or cleaners. These products may be stable solid-liquid dispersions, and in addition the dispersion of solid soil is part of the cleaning process. Therefore the additives have to fulfill two different types of specifications.

In the following paragraphs, some important and especially characteristic applications of solid-liquid dispersions are summarized that cover the three classes just listed. The applications are not discussed in order of importance but provide an overview of the vast possibilities of applications of solid-liquid dispersions. The different application areas are only briefly summarized, as a detailed description is not within the scope of this volume. Therefore for each application, specific monographs are cited in which the interested reader will find more details.

1. Ceramics

One of the oldest applications of colloid chemistry in technical processes is the manufacture of ceramics, the raw material of which, a highly concentrated suspension of aluminum oxide, has been produced since ancient times. Ceramics ranging from china clay to bricks are manufactured from clay-water gels. Advanced colloid chemical techniques are used to generate highly break-resistant ceramic materials that can be used for engines, for artificial joints, or in the space industry [4,5]. The quality of the clays (aluminum silicates) is defined by the physical properties such as the size, shape, or surface structure of the particles more than by the chemical properties.

2. Polymers

Dispersion technology is used in processing as well as in application of polymers. Liquid-liquid dispersions and liquid-solid dispersions are widely

used. A common technology for processing polymer dispersions is emulsion polymerization [6]. Partly soluble monomers are dispersed in a liquid phase. One distinguishes between oil-water (o/w) emulsions and water-oil (w/o) emulsions depending on the solubility. Examples of o/w emulsion polymerization are latices for paper coatings [7]. Polyacrylamide flocculation aids are manufactured according to the w/o type [8]. In o/w emulsion polymerization the monomer emulsion is placed in a reactor together with the starter solution to initiate the polymerization step. During the reaction a dispersion is formed that contains the product in finely dispersed form. The size of the particles can be influenced by the type and concentration of the dispersants [9]. As emulsion polymerization is not one of the main topics in a discussion of solid-liquid dispersions, we do not go into further details in this volume.

Additives are an important application of solid-liquid dispersions in the polymer industry. Many additives, especially pigments, are not soluble in the application system. Therefore they have to be finely dispersed in order to guarantee optimal efficiency. Their main purpose is coloration, but they are also used to enhance fire resistance and light resistance. On the other hand, the additives must not have a negative influence on the basic properties of the polymers such as film formation. An effective way of dosing the additives is to use a dispersion. One distinguishes between solid and liquid dispersions. An important application of liquid dispersions are pigment pastes in plasticizing agents such as phthalates or epoxidized oils for polyvinyl chloride. An overview of the composition and different applications for additive dispersions is given in Ref. 10. Surfactants may be added to increase the wetting of pigments in the dispersions. The rheological parameters are of crucial importance for the properties of dispersions. Viscosity is adjusted by the addition of surface-active substances so that sufficient storage stability as well as good flowability at high shear rates is guaranteed. The most important applications of polymer dispersions are paints and additives for paper and paper coatings, textile treatment, and the coloring of plastics.

3. Textile Industry

In the textile industry, dispersions are used for dyeing fibers, which is the most important application, and for generating and improving other properties like water resistance. Generally, one can distinguish between natural and synthetic fibers. For synthetic fibers the statements made above with respect to polymer dispersions are valid. If one looks at the dyeing process, the dispersions must have sufficient stability throughout the process. In addition, the dispersants should not interfere with the efficiency