



Early (pre-DLVO) studies of particle aggregation

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ARTICLE INFO

Available online 27 December 2011

Keywords:

Particle aggregation
Critical electrolyte concentration
Aggregation rate
Colloid stability
DLVO theory

ABSTRACT

The history of colloid science, from its modern foundations in the mid-nineteenth century, has been strongly concerned with studies of the aggregation of colloidal particles. It was Thomas Graham (1861) who defined the word “colloid” (from the Greek word for glue) for those materials which could not pass through membranes, unlike smaller, truly-dissolved materials. Subsequently, Graham (1864), following earlier studies, principally by Selmi and Faraday, described “the power possessed by salts for destroying colloidal solutions”. Although numerous, quantitative studies of particle aggregation were made in the years that followed, in particular, the determination of minimum electrolyte concentrations for the onset of particle aggregation and aggregation rates, no general theoretical framework emerged to account for these quantitative findings until the middle of the twentieth century. It was during and immediately following the Second World War that two sets of authors, Derjaguin and Landau, in Russia, and Verwey and Overbeek, in the Netherlands, independently came up with the theory that is now universally referred to as the DLVO theory of particle interactions and aggregation. All modern developments of the theory of particle aggregation use the DLVO theory as the keystone. However, the DLVO theory itself was based on a large body of experimental data in regard to particle aggregation obtained over the previous hundred years or so. This article is an attempt to review that body of experimental data and to show how this guided the DLVO authors in their thinking.

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1. Introduction

A truly pivotal point in the history of colloid science was the emergence, around the time of the Second World War, of a quantitative theory of the stability to aggregation of dispersions of charged colloidal particles. This was based on the concept, originally suggested in 1936 [1], by Hugo Christiaan Hamaker (Fig. 1; from the Philips Laboratories in Eindhoven) that the stability of a colloidal dispersion depends on the interplay of two long-range interparticle forces: repulsive interactions resulting from double layer overlap and attractive van der Waals interactions. Hamaker sketched various possible total potential energy curves, as a function of particle separation, indicating maxima and minima in certain cases, to which conditions for stability and aggregation could be attributed. Quantitative theories of these interactions were developed and published independently by Derjaguin and Landau (Fig. 1) in Russia in 1941 [2], and by Verwey and Overbeek (Fig. 1) in the Netherlands in 1948 [3]. Boris Derjaguin was from the USSR Academy of Sciences and Lev Landau from Moscow State University; Evert Johannes Willem Verwey was Director of Research at the Philips Research Laboratories in Eindhoven and Theo Overbeek was professor of physical chemistry in the van't Hoff Laboratory in Utrecht. Together their work forms the basis of what has become

universally known as the “DLVO” theory of colloid stability. This term was first coined it seems by Samuel Levine.

Although, as we shall discuss later, there had been preliminary, separate publications by Derjaguin, Verwey and Overbeek, and their colleagues, in a UK journal (the Transactions of the Faraday Society) in 1940, the war prevented the two groups retaining awareness of each others subsequent work, both whilst the war was in progress and in the immediate aftermath. This led to some discussion [4] as to “priorities” when Derjaguin actually met Overbeek and Verwey for the first time (Landau was not present), at the Discussion meeting of the (UK) Faraday Society in Sheffield in 1954 on “Coagulation and Flocculation”. However, this issue was settled amicably at the meeting [4].

Much of the work in the area subsequently has been concerned with modifications to the basic ideas set out on the DLVO theory, including the introduction of additional types of interactions and its extension to concentrated dispersions, where the concept of pairwise-additivity breaks down. On the experimental side, over this period, there have been considerable developments in both systems and techniques. There are now much better defined colloidal particles for use in model studies, and a much greater variety of sophisticated techniques available for studying both aggregation processes and the forces between colloidal particles. The reader is simply referred to recent textbooks on colloid science for information on these topics. It is worth noting, however, that the first direct measurements of surface forces were reported at the 1954 Faraday Discussions meeting, again by Overbeek [5] and by Derjaguin [6] and their co-workers. In

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Hugo Hamaker

Overbeek, Derjaguin and Verwey
(at Portmeirion, Wales, 1968)

Lev Landau

Fig. 1. Hugo Hamaker Overbeek, Derjaguin and Verwey Lev Landau (at Portmeirion, Wales, 1968).

many ways that 1954 meeting marked another watershed in the development of colloid science.

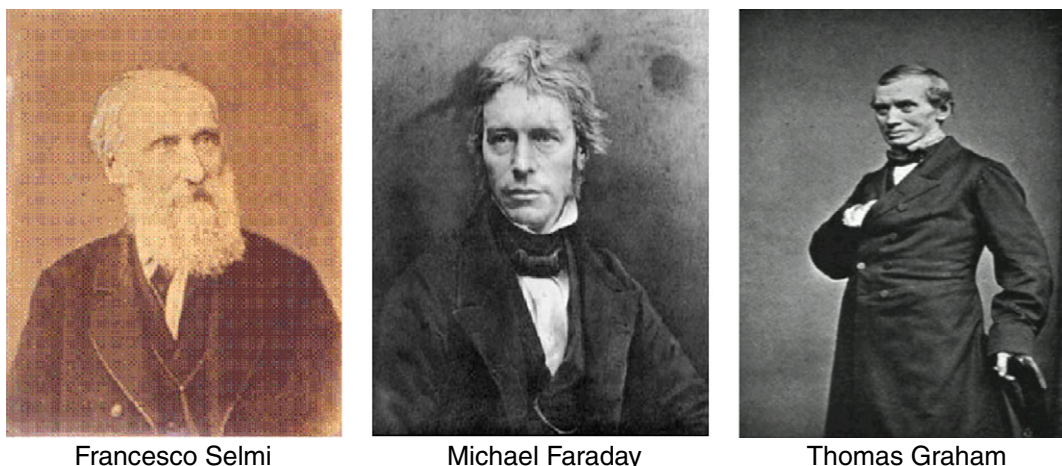
In this article I take a different perspective. My aim is to review the body of experimental and theoretical work *prior* to the DLVO theory, upon which the authors of that theory would have based their ideas regarding colloid stability and particle aggregation. In certain cases I shall briefly refer to more recent studies, but only where this helps to clarify an issue. I shall limit discussion, for the most part, to dispersions of *solid* particles (in the size range from a few nm to a few μm) in liquid media, as it is for these systems that the DLVO theory was primarily intended. The smallest particles in this size range would these days be called “nanoparticles” by many people. Most of the solid particles studied, pre-DLVO were inorganic (e.g. a metal, a metal salt or metal oxide). Some were organic, but I shall, for the most part, only consider here those comprising organic molecules of low molecular weight. I mostly exclude systems where the dispersed species would these days be considered to be macromolecules (e.g. proteins) or assemblies of amphipathic molecules (e.g. surfactant micelles). However, in the early days of colloid science, such distinctions could not usually be made, so some reference to them is inevitable. In addition, one major class of organic colloidal particles, widely used in more modern aggregation studies, namely synthetic polymer (latex) particles, were only really developed after the Second World War, i.e. post-DLVO. (On the other hand, *natural* rubber latex, originally

discovered in South America, had been known and exploited since the eighteenth century).

Finally, in this section, I would add a word on nomenclature, in particular, concerning the use of the words coagulation, flocculation and aggregation. To avoid confusion, except in specific circumstances, I have deliberately used the word aggregation as the generic word, to cover both coagulation and flocculation processes. Some colloid scientists, the first probably being Victor La Mer in 1964 [7], have wished to make a distinction between these two processes; in general, the earlier colloid scientists, whose work is reviewed in this article, such as Herbert Freundlich [8], used the two terms interchangeably. The I.U.P.A.C. publication “Definitions, Terminology and Symbols in Colloid and Surface Chemistry”, compiled by Douglas Everett in 1972 [9], is somewhat indecisive on this particular point. Similar definitions to those given by La Mer are recommended. However, the following statement is also included: “while this distinction has certain advantages, in view of the more general (but not universal) equivalence of the two words, any author who wishes to make a distinction between them should state so clearly in his publication”.

2. Aggregation Phenomena

Francesco Selmi (Fig. 2), whilst he was head of chemistry at the University of Modena in Italy, published, during the period 1845–1850 [10],



Francesco Selmi

Michael Faraday

Thomas Graham

Fig. 2. Francesco Selmi Michael Faraday Thomas Graham.

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