

The impact of colloid science

(Adapted from RSC, Chemistry World 2003)

Colloids are everywhere that we look, so why is it that most people know so little about them, asks Mike Garvey. “Throughout my career what has been striking is the impact of colloid science in so many areas of industrial chemistry, evidenced by the strong colloid science base of companies such as BP, Shell, Unilever, ICI, Procter & Gamble, Kodak and many others. Yet despite its importance, it still surprises me that colloid science remains a subject that is glossed over in most chemistry degrees.”

Defining ideas

Colloid means glue-like, originating from the Greek, $\kappa\omicron\lambda\lambda\alpha$. It describes materials that are predominantly liquid but which have other properties: either optical, giving rise to turbidity such as milk, or viscous, with characteristics of mucus, gelatin or wet clay. These effects arise from the presence of macromolecules dissolved in liquid and/or by mixing two or more solid, liquid or gas phases.

Colloidal dispersions

The selected examples shown in Table 1 illustrate the scope and importance of colloidal dispersions. In general, emulsions and sols are termed lyophobic (liquid hating) colloidal dispersions, two-phase systems that cannot be prepared by dissolving the dispersed phase in the dispersion medium. Lyophilic (liquid loving) colloids describe true solutions of macromolecules. Owing to the high interfacial free energy, lyophobic colloids are thermodynamically unstable and tend to aggregate; in a stable dispersion instead, the particle collisions do not lead to coagulation because inter-particle repulsion forces dominate.

Colloid stability

The repulsive forces in a stable dispersion were long ago identified as being electrical in origin. A surface potential exists at the interface between the solid particle and the surrounding liquid due to the presence of a surface charge. To maintain electrical neutrality, ions of opposite charge present in the medium are attracted closer to the particle surface, resulting in a diffuse layer of highly concentrated counterions. The concentration of counterions in this layer decays

exponentially from the surface over a distance of tens of nanometres. The resulting ionic cloud is called the diffuse region of the electric double layer. Brownian motion ensures that the particles are in continual motion, giving rise to collisions at a rate determined by diffusion theory. On particle-particle collision, overlap of the ionic clouds gives rise to a repulsion that pushes the particles apart.

DLVO Theory

The DLVO theory of colloid stability, developed by Derjaguin and Landau, and Verwey and Overbeek during the 1940s proposes a balance of the repulsive electric double layer forces (positive by convention) and the attractive van der Waals' forces (negative by convention) that exist between all matter. These two forces were found to be of similar range and magnitude. The electrical forces increase exponentially as particles approach one another and the attractive forces increase as an inverse power of separation. As a consequence, these additive forces may be expressed as a potential energy versus separation curve. A positive resultant (Fig 1a) corresponds to an energy barrier and repulsion, while a negative resultant (Fig 1b) corresponds to attraction and hence aggregation. It is generally considered that the basic theory and its subsequent modifications provide a sound basis for understanding colloid stability.

Stabilisers

Owing to the high interfacial free energy, lyophobic colloids are thermodynamically unstable and tend to aggregate; the larger aggregates either sediment or cream depending on their relative density. This is generally undesirable and colloid scientists aim to prevent it from occurring. Common stabilisers are the polymeric dispersants used in formulating printing inks to ensure that the dispersed phase remains as discrete units. Whole industries are built around the design and selection of dispersants to optimise product performance. Invariably, together with other macromolecules or liquid crystalline surface-active agents, these agents modify the flow characteristics of the product. The formulator's skill lies in achieving the necessary product characteristics such as mouth-feel (organoleptic properties) with synthetic foodstuffs, non-drip properties of paints and prevention of fine mist with liquid aerosols. The list of uses is endless.

Preparation of hydrophobic collids

As we said, lyophobic dispersions cannot be prepared by dissolving the dispersed phase in the dispersion medium. They are made by one of two methods. 1) Condensation methods, in which molecules combine in solution to form a precipitate of colloidal dimensions. Examples include the precipitation of silver halides from soluble salts, the technology that underpins the photographic industry. Indeed, much of the fundamental understanding of colloid stability stems from the detailed investigation of silver halide sols, particularly by the Dutch colloid schools. Another example is the reduction of chlorauric acid to form gold sols. 2) Dispersion methods, where one phase is dispersed in the other by mechanical means. Examples include comminution, by which large particles in a liquid medium are broken down by mechanical force, using a colloid mill with an abrasive rotor and stator, a ball mill using the cascading action of hard ceramic balls, or a bead mill in which the beads and particles are sheared followed by separation of the dispersion. Emulsification is generally achieved using a homogeniser in which oil and water are forced, under pressure, through an adjustable orifice.