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THE ROLE OF THE SURFACE IN THE DISPERSION OF POWDERS IN LIQUIDS

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Abstract - The overall process of dispersing a powder into a liquid involves a number of stages - incorporation, wetting, disagglomeration, flocculation - which in practice overlap. Implicit to an understanding of these stages is a study of the solid/liquid interface, and of the variety of interactions that take place at that interface. This paper reviews these interactions, their measurement, and their relevance to the dispersion process.

INTRODUCTION

Dispersion of powders in liquid is a very practical process, and has wide application. It involves a number of distinctly different stages, each of which can be reasonably well defined and related to established fundamental principles of colloid and interface science. But because these stages overlap in practice and because most practical systems are multicomponent, it is often difficult to identify what is controlling the observed effects, and to correct for failures with anything but empirical means. Nevertheless there is a lot of knowledge available, and some guiding principles which could be put to good use; much of this is related to studies of the solid/liquid interface. In the early stages of the process the solid/air interface is replaced by one between solid and liquid. A powder consists of aggregates/agglomerates of small particles and mechanical work is performed in dispersing particles into a liquid. The forces that exist at the interface determine the ease with which the process can be brought about. Once dispersed the particles are free to move in their new environment, and flocculation is prevented by various chemical and physical processes, all of which relate to the character of the solid/liquid interface. It is not surprising therefore that studies of this interface form an integral part of our understanding of the dispersion process.

In this paper we review, with particular reference to titanium dioxide pigments, the interactions that occur at the solid/liquid interface, their nature, how they are studied, and their relevance to the dispersion of powders in liquids.

NATURE OF SOLID/LIQUID INTERACTIONS

The work W_A required to separate unit area of solid/liquid interface into the two individual components was defined by Fowkes (1) in terms of the different kinds of interactions that take place across the interface. He expressed these in the following way

$$W_A = W_A^{d} + W_A^{h} + W_A^{\pi} + W_A^{p} + W_A^{e}$$

where the superscripts refer to the type of interaction; d=dispersion, h=hydrogen bond, π=pi-bond, p=other polar interactions, and e=contribution due to charge separation at the interface giving rise to an electric double layer. Dispersion forces are always present and the adhesion between dissimilar materials always depends on and is frequently dominated by these forces. Even in polar molecules the dipole-dipole interactions are usually insignificant compared with dispersion force interactions. However, with the exception of the aliphatic hydrocarbon solvents, all the components that are normally present in practical systems possess a certain degree of polarity. This polarity is associated with specific chemical groups that are present both in the liquid phase and on the surface of the solid. These groups may be acidic or basic in nature or even amphoteric (exhibiting both acid and base character), and give rise to those forces other than the dispersive type described above. We may identify specific effects, such as the chemical interaction or hydrogen bonding interaction between an adsorbed molecule and a specific group on the particle surface, as well as non-specific effects, e.g. the interaction between the hydrocarbon chain of a polymer with a carbon black surface.

So the nature and strengths of the interactions involved cover a wide range. For example, the highly polar titanium dioxide surface may be constrasted with the non-polar carbon black, the graphitised form of the latter representing the extreme end of the polarity scale. Similarly for the media - water is one of the most polar liquids and aliphatic hydrocarbons are the least polar, with many solvents of intermediate polarity in between. A wide variety of molecules are dissolved in the liquid phase, these range from small molecules through amphipathic molecules (surfactants) to polymers, all of which can contain molecular groups which may or may not ionise in a liquid phase.

The chemistry of the liquid phase is to a large extent well defined. It is possible through measurements of conductivity, dielectric constant etc. to characterise both pure liquids and solutions in terms of ionic dissociation, and to use spectroscopic techniques to investigate molecular interactions. For polymer solutions a number of techniques have been established for studying configuration and structure. It is possible therefore to say that most of the interactions that occur within the liquid phase can be defined, as well as the structure of the liquid components. Characterisation of the solid surface, in terms of the components of the surface that contribute to the interactions with adjacent molecules in the liquid phase, presents a little more difficulty. Taking, for example, titanium dioxide, we have a fairly clear picture of the surface in terms of the number and type of hydroxyl groups, and how water molecules interact with the surface from the vapour phase [2]. We know that under ambient conditions most of the surface is hydroxylated and several monolayers of water are adsorbed. To remove all the water from the surface requires fairly strong outgassing conditions, e.g. under vacuum at 150-200°C, and outgassing at about 450°C is necessary to remove all the hydroxyl groups. So under normal conditions the surface is polar and covered with molecular water, both of which play a prominent role in the interactions at the solid/liquid interface. An examination of the hydroxyl population and water content is readily carried out using infra-red spectroscopy, and this is well documented [2]. Measurement of surface polarity is more difficult. A useful technique for this purpose is measurement of the heat of immersion of the solid in pure liquids of various polarities. The heat of immersion is a linear function of the dipole moment of the liquid and the slope of this line is related to the electrostatic field strength of the surface [3]. Heat of immersion data can be used to establish the site energy distribution for a solid surface, and also gives a useful measure of the relative strengths of interaction with liquids and these are relevant to the wetting process.

Many studies have been carried out on the adsorption of molecules from the liquid phase at the solid/liquid interface. Kipling's book [4] covers solutions of non-electrolytes - adsorption from electrolyte solutions has not been adequately reviewed although a book covering all aspects of adsorption from solution at the solid/liquid interface is in course of preparation [5]. The technique is simple; solid and solution are equilibrated together and the change in solution concentration is noted. Adsorption isotherms are plots of amount adsorbed as a function of equilibrium concentration. These isotherms are of different shapes and reflect the molecular interactions that take place at the interface [6]. Interpretation of data for small molecules is relatively simple but for polymers it is a different story. The amount adsorbed depends on the configuration of the polymer and how much solvent it carries with it. For example, an alkyd resin of low acidity interacts strongly with the surface of an acidic titanium dioxide pigment and the alkyd molecules form a close-packed layer at the interface. However, for a basic titanium dioxide there are few interactions between alkyd and surface and the alkyd molecules are extended from the surface in a heavily solvated condition. Hence the difference between the adsorption (and stability) behavior of silica coated (acidic) and alumina coated (basic) titania surfaces [7].

Perhaps one of the most promising new techniques that have been established in studying the solid/liquid interface is the application of infra-red spectroscopy, as demonstrated by Rochester and his colleagues [8]. Up to now the interactions investigated have been between relatively simple molecules and relatively simple surfaces, but there is obvious potential for extending this work.

So we see that the interactions are many and varied and each system is controlled by its own chemistry; in any particular system it may be impossible to identify the one that dominates.

ADSORPTION AT THE SOLID/LIQUID INTERFACE

We may identify two extreme cases of adsorption involving van der Waals forces on the one hand (physical adsorption, or physisorption) and on the other chemical adsorption (chemisorption) when a chemical bond is formed between solid surface and adsorbed molecules. The majority of adsorption processes from the solution phase do not involve a chemical interaction but the strength of the physical force varies quite considerably from that of the dispersion type to the interaction involving hydrogen bonds. The energy of bond formation is readily established for adsorption of gases onto the solids, but little has been published on measurements for adsorption from solution. A good example of a chemical interaction is that reported by Smith [9] on the adsorption of stearic acid on to a commercial titanium dioxide pigment from hydrocarbon solution. Infra-red spectroscopic evidence is presented for the presence of a stearate ion at the surface. It is likely that the appearance of stearate ions is related to the chemical nature of the pigment surface, and is therefore a special case.

Normal long chain acids adsorb on to oxide surfaces by hydrogen bonding with the surface hydroxyl groups, and in addition for unsaturated acids there may be interactions between the surface and the alkene residue of the alkyl chain [10]. These two types of interaction may lead to changes in orientation of the adsorbed molecules as the surface coverage is increased [11]. Needless to say the presence of water on the surface of the solid can have a profound effect on the nature of the adsorption, e.g. in the case of the adsorption of n-octadecanol on to rutile from p-xylene solutions, the adsorption on a surface free of water is dominated by a strong alcohol-surface interaction. With increasing amounts of pre-adsorbed water on the surface the strength of this interaction decreases and the effects of competitive solvent adsorption and molecular interactions in the bulk phase become apparent. At any particular solution concentration the octadecanol adsorption is highest on the dry surface [12]. There is little evidence of chemisorption of alcohols at the oxide/liquid interface, but there are numerous examples for adsorption from the vapour phase [13].

An interesting attempt has been made to determine the uniformity of coverage of the surface by such organic molecules, using staining techniques with electron microscopy. The result of the experiment suggests that the organics adsorb on active sites on the surface and not in a uniformly distributed manner. Unfortunately the technique has not been developed further [14].

Adsorption from hydrocarbon solutions represents a relatively straight forward situation with respect to the mechanism and the nature of the forces involved. But from aqueous solutions there is the added complication of ionisation effects which give rise to an electric double layer at the solid/liquid interface. Two parameters are important, the pH and the ionic strength. The pH of the solution determines the sign and magnitude of the surface charge as well as the acid/base character of dissolved molecules containing acidic and basic groups. The ionic strength of the solution determines the characteristics of the electric double layer as well as the electric potential at the surface of the solid. All these factors determine the extent of adsorption of compounds containing ionisable groups, hence the situation is complex and each case must be considered on its own merit. A useful review of the adsorption behaviour of the surfactants at solid/water interfaces has been written by Fuerstenau [15]. In it he described the electric double layer and the parameters that are important in the physical adsorption of surfactants on to oxide surfaces, namely the role of the hydrocarbon chain, the effect of chain length and chain structure, and the influence of pH and ionic strength. Also presented are some examples of chemisorption, such as the adsorption of sodium oleate and oleic acid on ferric oxide (haematite). Further useful discussion on the thermodynamic and molecular considerations applied to adsorption of organic molecules is given by Healy [16].

The work of Tamamushi and Tamaki [17] on the adsorption of some long chain electrolytes (cationic and anionic) from aqueous solutions on polar and non-polar adsorbents (alumina, titania, barium sulphate, calcium fluoride and carbon black) admirably illustrates the effect of ionic strength and pH, and shows further that the adsorption reaches a saturation value at the critical micelle concentration of the electrolyte, a phenomenon which is commonly observed. Orientation effects - at low concentration the surfactant lying flat and changing to perpendicular orientation on increasing concentration - have been reported [18]. Such effects are relevant to the wetting stage.

Many reviews of polymer adsorption have been published in recent years, emphasising different aspects of the subject [19-21]. Numerous adsorption isotherms have appeared in the literature. Adsorption equilibrium is usually reached very slowly, and it may take several days or even weeks. Isotherms nearly always show a rapidly rising region followed by a plateau which suggests the formation of a monolayer, but the quantity of polymer adsorbed in the plateau region often exceeds the monolayer capacity of the adsorbent, from which one might conclude that the polymer is adsorbed in loops and chains. If that is the case, then one might expect that solvent is incorporated in the adsorbed layer. Not much attention has been paid to the fact that the isotherms are of a composite nature, involving both solvent and adsorbate. This phenomenon should give rise to maxima in polymer adsorption isotherms and these have been observed in systems containing alkyd resins [7] and polyesters [22].

Several important general findings have been established from polymer adsorption studies. The time taken to reach equilibrium depends on the molecular weight of the polymer and the amount adsorbed at equilibrium increases with increasing molecular weight. The amount adsorbed also increases with decrease in solvent power of the medium for the polymer. In a poor solvent, polymer/surface contacts are favoured, and as the polymer coils are more compact in a poor solvent, the surface can accommodate a greater number. The surface character of the adsorbent also affects the equilibrium adsorption, the extent depending on the nature of the surface groups and the presence of specific substituents in the polymer molecule; a good illustration of acid-base interactions in polymer adsorption was reported by Fowkes and Mostafa [23], comparing the adsorption of a basic calcium carbonate from acidic, basic and neutral solvents. Increase in temperature can either increase or decrease the amount of polymer adsorbed, for a variety of reasons which are mostly concerned with the interaction between polymer and solvent.

For an understanding of the behaviour of disperse systems in terms of polymer adsorption at the solid/liquid interface, we require to know the thickness of the adsorbed layer and its configuration. For layer thickness measurements both rheological and optical methods are available and both present difficulties in interpretation. Rheological measurements provide a hydrodynamic thickness which is likely to depend on the shear rate. At low shear rate the particles are likely to be flocculated, whereas at higher rates there is a danger that the adsorbed polymer layer will be hydrodynamically disturbed. An extrapolation method used by Doroszkowski and Lambourne [24] is probably the most satisfactory and gives results that can be related to the stability to flocculation. Of the optical methods, ellipsometry has been the most popular, which combined with infra-red spectroscopy and calorimetry can lead to a great deal of useful information on the thickness and nature of the adsorbed layer [25]. A useful review of the conformational states of polymers adsorbed at the solid/liquid interface by Eirich [26] illustrates the use of adsorption data for obtaining information on the density distribution of polymer within the adsorbed layer - no experimental method as yet provides direct information on this parameter.

One aspect of polymer adsorption that is particularly relevant and as yet has received scant attention, is the distribution of molecular weight fractions during the adsorption process. For alkyd resins it is usually assumed that the polar, low molecular weight fractions are preferentially adsorbed, a result which is based on the fact that the acid number and the hydroxyl number of the adsorbed resin are larger than those of the initial resin [27]. The true situation is not that simple, as results obtained using gel permeation chromatography have demonstrated [28]. It appears that adsorption of fractions of all molecular sizes can take place on titanium dioxide, the final result depending on the affinity of the different fractions for the surface as well as their concentration in the original resin. It is also affected by molecular interactions in solution.

The ultimate fate of the resin fractions is therefore a complex function of the various interactions that take place both in solution and at the solid/liquid interface, and a thorough understanding requires application of a variety of techniques. Furthermore, the adsorption takes place in the presence of other non-polymeric surface active species, which are commonly used in practical systems. A study of the simultaneous adsorption of an alkyd resin in the presence of fatty acids on titanium dioxide pigments demonstrates the complexity of the adsorption behaviour [28]. The adsorption of fatty acids is strongly reduced by the presence of the alkyd resin - the relative strengths of the interactions are important and interpretation is difficult. Jettmar [29] has suggested a method, involving electron microscopy, for distinguishing the vehicle fractions adsorbed on pigment surfaces by their swelling behaviour.

So for a complete understanding of the total adsorption process experimental work using different techniques is necessary, and the literature contains very little information on this comprehensive approach.

DISPERSION OF POWDER INTO LIQUID

The term "dispersion" describes the complete act of incorporating a powder into a liquid medium such that in the final state the particles are uniformly distributed throughout the medium. Solid/air interfaces are replaced by solid/liquid interfaces. We identify various stages in this overall process - incorporation, wetting, disagglomeration, and flocculation. During milling each of these processes occurs simultaneously in some part of the liquid phase, and the final result depends on a variety of factors such as shear rate, surface tension and viscosity, cohesiveness of the powder, and contact angle between liquid and solid, as well as the various interactions that occur between the solid surface and the molecules in the liquid phase.

Incorporation, Wetting and Disagglomeration

The cohesiveness of the powder is an important parameter in the initial submergence process. Titanium dioxide powder is very cohesive - it has a high tensile strength. Surface treatment with other oxides greatly reduces this effect, and aids the breakdown of pigment/air agglomerates when the pigment and medium are brought into contact [30]. Surface moisture also has a profound effect - water bridges between particles increase agglomerate strength.

The phenomenon of wetting of powder surfaces has been the subject of much theoretical and experimental investigation, and the basic principles for simple geometry are well established. The initial stage involves both the external surface of the particles and the internal surfaces which exist within the agglomerates. The wetting process is therefore dependent on the properties of the liquid phase, the character of the surface, the dimensions of the interstices in the agglomerates, and the nature of the mechanical process used to bring together the components of the system. The energetics of wetting of a cube have been worked out [31]. It is only spontaneous, i.e. no work required to obtain complete wetting, when the contact angle θ is zero. For all other cases a substantial amount of work is necessary to obtain complete wetting. By the addition of surfactants the contact angle is reduced together with the work required for wetting. Numerous values of θ are published in the literature. Most have been measured on flat surfaces and even with these problems arise due to surface roughness [32]. For powders the measurement is more difficult although a number of methods have been reported [33, 34].

Zero θ is also required for spontaneous penetration of liquid into the complex structure of the agglomerate [35] and the rate of this process is improved the lower the contact angle [36]. However, wetting is better when the surface tension of the liquid is low; penentration and disagglomeration are favoured by low viscosity and by high surface tension. In practice, we are interested in "good" wetting, so it is necessary to compromise and at the same time ensure satisfactory cohesion (the degree of which varies with milling machine) within the mill paste.

It is difficult to find in the literature details of experiments that relate contact angle with phenomena that reflect conditions at the solid/liquid interface and the efficiency of the dispersion process. A correlation between contact angle and flotation rate for quartz in aqueous solutions of dodecylammonium acetate, with adsorption from solution and electrokinetic (zeta potential) data, was reported by Fuerstenau [37]. In a later review Fuerstenau discussed the relevance of the adsorption process to flotation technology illustrating the direct relationship between the amount of surfactant adsorbed and the contact angle [38]. Similarly for rutile in solutions of sodium dodecyl sulphate and dodecyltrimethyl ammonium bromide, this time relating the degree of dispersion of the powder to the contact angle [39]. Water spreads spontaneously on a clean rutile surface, but the addition of a small quantity of surfactant causes θ to increase to about 100°. Increasing the concentration reduces θ to 90° and below, but at about 90° there is a marked increase in dispersibility of the powder which supports the notion that the first two stages of wetting (adhesional and immersional) are spontaneous if $\theta < 90^\circ$. Nevertheless, work must be done upon the system to effect final submersion since the "total" process, including the final spreading stage, requires a zero contact angle to be spontaneous [31].

Some reports on the relationship between adsorption and wetting for a variety of systems were included in the S.C.I. Monograph on "Wetting" published in 1967 [40].

Flocculation

The stability of colloidal dispersions against flocculation is governed by the forces between the particles. Frequent encounters between particles dispersed in a liquid occur due to Brownian movement, to gravity and to convection, and whether these encounters result in permanent contact is determined by the forces between them. In dilute dispersions it is sufficient to consider only the interaction between pairs of particles, but in the very concentrated dispersions that one meets in practical systems it is necessary to take multiparticle interactions into account. Most of the published theoretical work has been concerned with pair interaction; little has been written on multiparticle interactions.

On the basis of pair interaction and considering only electrostatic repulsion (associated with the electric double layer) and van der Waals attraction a satisfactory explanation of the flocculation behaviour of so-called lyophobic dispersions/suspensions was published by Derjaguin and Landau [41], and Vervey and Overbeek [42]. The essentially identical approach of the two schools, working independently, is now known as the DLVO theory, and provides an adequate understanding of the stability of dilute dispersions of colloidal particles in liquid media ranging from water to hydrocarbons.

Essentially the electrostatic repulsion is a result of the charge on the particle surface. For titanium dioxide in aqueous media this is relatively simple to define - the charge arises from the acid-base character of the surface hydroxyl groups which are neutral (no surface charge) at pH ~ 5.5 [2]. At pH < 5.5 the surface is positively charged, and negative at pH values above the zero point of charge. If the surface is coated with alumina it will have a zero point at pH 8-9, and with silica at pH 2-3, with many other variations possible for mixed oxide coatings. The complex effects arising from coating titanium dioxide surfaces have been described [43, 44]. As already mentioned, these phenomena affect adsorption from solution, hence the ultimate particle charge. A similar situation arises in principle for non-aqueous liquids of moderate to high dielectric constant, in which there is a significant degree of ionization.

But in hydrocarbon media the extent and nature of the ionization is less readily defined. For ionic materials that are soluble in hydrocarbons there is a small but significant degree of ionization, but the ionic concentration are $\sim 10^{-10} - 10^{-12}$ g ions/litre, and this implies a very diffuse electric double layer. For this reason it is more obvious that multiparticle interactions have to be considered since even at fairly low particle concentrations there is overlap of electric double layers throughout the system. Another consequence of the low ionic concentration is the very small number of charges associated with each particle, and a marked dependence on adsorbed moisture, particularly for oxides, has been reported [45]. There is no simple relationship between particle charge/zeta potential and amount of surfactant adsorbed, for these hydrocarbon systems. The limited data have been reviewed [46]. Very often one observes a maximum in the zeta potential versus electrolyte/surfactant concentration plot, the potential decreasing over a range for which the amount of surfactant adsorbed remains constant. It is difficult to explain these effects, although for certain systems an attempt has been made. Fowkes proposed that the relative acidity of the particle and the liquid phase determines the sign of the particle charge; there is a transfer of protons across the interface, which is strongly influenced by the acid/base nature of the surface and of the additives in the liquid phase [47]. Titanium dioxide particles dispersed in solutions of alkyd resin in xylene exhibit a positive charge, whereas in melamine resin solution they are negative [48]. The change in sign on changing the chemical nature of the surface has also been demonstrated with titanium dioxide pigments in alkyd resin solutions [7].

It is relatively easy to follow the flocculation of dilute colloidal dispersions, for example, measurement of particle number or optical density as a function of time, and such techniques have been used successfully to verify the general principles of the DLVO theory. But for concentrated systems it is much more difficult to relate stability data e.g. from sedimentation rates, rheological experiments etc. to theory, if in fact such theory exists. The most useful attempt to describe the stability of concentrated systems has been made by Levine [49, 50] who concluded that electric double layer effects are unable to provide the necessary energy barrier for dispersions in hydrocarbon media. A similar conclusion was reached from experimental observations of the stability/opacity of dispersions of titanium dioxide pigments in alkyd resin solutions [7].

The third force between particles is due to the interaction of long-chain molecules adsorbed on the particle surfaces. The stabilisation of colloidal dispersions by adsorbed macromolecules has been known for a very long time. The Egyptians and Chinese used such materials as glue, gums and resins to prepare dispersions of pigments for use in fresco paints and inks, and in present day technology a variety of high molecular weight compounds (alkyd resins, block and graft copolymers) are used in organic coatings. The term "steric stabilisation" is now used to embrace all aspects of the stabilisation of colloidal particles by adsorbed non-ionic macromolecules, and is equally effective in aqueous and non-aqueous media.

In the context of steric stabilisation we are particularly interested in the thickness of the adsorbed layer, the configuration of the polymer chain, the fraction of segments adsorbed and the segment density distribution, both normal and parallel to the surface. This is illustrated in the work of Joppien and Hamann [51] who studied polymer adsorption from aqueous and hydrocarbon media on to oxide surfaces, and related the structure of the adsorbed layer to dispersion stability.

Polymers adsorbed at particle/medium interfaces may take up any configuration from lying flat (strong interactions between the surface and many points along the polymer chain) to higher extended into the medium (interaction at few points). For the extreme case of parallel orientation the only effects on flocculation are (a) the modification of the attractive force between particles which is likely to be small in most cases, and (b) the effect on the zeta potential which could be significant depending on the chemical character of the surface and polymer. When the polymer chains are extended into the liquid phase there is a major effect which arises when particles approach sufficiently close for the adsorbed layers to interact. The extent of this interaction is the basic problem in the theory of steric stabilisation.

There are essentially two types of interaction. In the first place each chain loses some of its configurational freedom, thus its contribution to the free energy of the system is increased and this results in a repulsive force. There is no mixing of the two polymer layers, just a restriction in the volume that each can occupy. A number of authors have attempted a theoretical analysis of this situation [52-55]. When the chains start to overlap there is a local increase in concentration of polymer which again leads to an increase in free energy, and a repulsive force results [56, 57].

There has been considerable controversy over the relative merits of the two approaches to steric stabilisation [46]. Perhaps one model is more relevant to one type of system e.g. the mixing model for "good" solvents and the volume restriction theory for "poor" solvents. Napper has suggested [58] from studies of incipient flocculation, measurements of the repulsive interactions between stable particles, and of stability in polymer melts, that two separate regions of close approach must be distinguished. The first corresponds to a separation between the approaching surfaces of one to two adsorbed layer thicknesses, within which mixing of the polymer chains occurs. At close approach there will be a region where both mixing and compression occurs. Significant advances have been made over the last two decades in our understanding of steric stabilisation, and very recently measurements have been reported on the force between two surfaces containing adsorbed polymer [59, 60]. Such data will help to clarify the mechanism.

Finally, we should not lose sight of the fact that adsorbed polymers can cause flocculation. Use is made of this phenomenon in the clarification of water, separation of minerals, and in the improvement of the structure of soils, but it is not normally considered in coating systems. It occurs under conditions of partial coverage of the surface with the polymer, and flocculation is brought out by the polymer becoming simultaneously adsorbed on two or more particles - a "bridging" mechanism leading to a rather open structure in the flocculates. The mechanism has been summarised by Kitchener [61]. Since polymer adsorption is usually irreversible the method of mixing of the components can have a profound effect on the flocculation process. Tadros has reported [62] a good demonstration of the effect, using silica and aqueous solutions of polyvinyl alcohol. The effect depends on the pretreatment of the silica, hence the surface hydroxyl population, and on the pH of the solution which determines the particle charge, both factors influencing the adsorption sites for PVA adsorption.

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