The Stability of Dispersions in Non-Aqueous Media

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Results obtained in studies of coagulation behaviour of some hydrophilic (rutile) and hydrophobic (graphitised carbon black Sterling MTG) materials in solutions of the anionic surface active agent Aerosol OT (Na-di-2-ethylhexyl sulphosuccinate) in hydrocarbons (xylene) are discussed. Using particle sizes, determined by electron microscopy, and zeta-potentials, obtained from micro-electrophoretic measurements, as parameters to calculate energy barriers, it was found that the Deryaguin-Landau-Verwey-Overbeek theory allows satisfactory quantitative interpretation.

INTRODUCTION

This paper is a review of work carried out in our laboratory on a study of the stability of colloidal dispersions of solid particles in hydrocarbon media. In this account we are concerned with dispersions for which the only significant factor which controls the stability to coagulation is the electric charge on the colloidal particles. There is strong evidence that adsorbed polymer molecules may play a significant role in stabilisation of dispersed particles, and there may be a contribution from structured media in the region of the interface; neither will be discussed here since they need not to be invoked to provide an explanation for the observed effects.

We have studied the coagulation behaviour of some hydrophilic and hydrophobic powders in solutions of the anionic surface active agent Aerosol OT (sodium di-2-ethylhexyl sulphosuccinate) in hydrocarbons. For the hydrophobic material we used Sterling MTG, a graphitised carbon black which has a homogeneous, hydrophobic surface; for the hydrophilic material a pure rutile which had been subjected to rigorous surface chemical analysis in our laboratory using infra-red and gas adsorption techniques. As will be demonstrated trace amounts of water in the medium and/or at the surface can have profound effects on the coagulation of the dispersions, particularly, as might be expected, with those containing rutile. The significance of trace water has been emphasised from time to time but few quantitative experiments demonstrating the effects have been reported in the literature. Furthermore, impurities are also very important since in hydrocarbon media the concentration of charged species is extremely small. Therefore, for experiments on such systems to be of value there must be rigorous control of the purity of all components, and we have in our work made every effort to comply with these requirements.

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It was van der Minne[1] who first recognised the correlation between zeta potential and stability of dispersions in non-polar media, and established the criteria for accurate measurement of electrophoretic mobility. For such systems the zeta potential is a very important parameter; the usual difficulties encountered with aqueous dispersions in relating zeta and surface potentials do not arise because the potential decay in hydrocarbon media is so slow (due to the very low ionic concentration) that they may to a good approximation be equated. So the zeta potential can, in principle, be used in a comparison of experimental coagulation data with those predicted by the classical D. L. V. O. (Deryaguin-Landau-Verwey-Overbeek) theory of stability of hydrophobic colloids[2]. We have measured electrophoretic mobilities with a simple microscopic electrophoresis technique[3] and used the derived zeta potential to relate the experimental and theoretical coagulation behaviour.

The stability of a colloidal dispersion is not precisely defined. Each experimentalist has his own idea of what he thinks is a stable system. Clearly this depends on the time scale of the observation. The D. L. V. O. theory treats the coagulation process in terms of the interaction between two spherical particles of equal radius approaching each other from »infinite« distance apart. An attractive force of the van der Waals type is assumed, and arising from surface charge there is a repulsive force which the theory treats in terms of the overlap of the electric double layers surrounding the two particles. The magnitudes of the net force and potential energy of interaction depend on the distance apart, and is a function of the ionic strength, the surface potential and the particle radius, and also the nature of the particles and medium in that these determine the attractive energy. Calculations of net potential energies of interaction for colloidal particles in aqueous media lead to two distinct features in the plot of energy *versus* distance. The first at larger distances is the »secondary minimum« which if deep enough will ensure coagulation; the second is the energy barrier occurring at shorter interparticle distances and must be surmounted if coagulation into the primary minimum (at very short distances) is to occur. It is common to accept that a secondary minimum of depth of the order of ten times the thermal energy (kT) or more will ensure coagulation, whilst an energy barrier of some fifteen times kt is required for long-term stability. It is readily shown that for dispersions in hydrocarbon media no secondary minimum can exist (because of the slow decay in the repulsive energy with distance), and therefore we may relate the height of the energy barrier to the experimental stability using the zeta potential for the calculations.

Nevertheless it is still difficult to define explicitly what is meant by the stability of a colloidal dispersion in hydrocarbon media when experimental observations only involve qualitative assessment by visual or spectrophoto-metric methods. To make a quantitative analysis it is best to do the most fundamental experiment of all, namely follow the decrease in the number of particles with time during a coagulation process. This is the experiment we have carried out and compared the results with those predicted by the Fuchs' theory of slow coagulation[4] using energy relations calculated by the D. L. V. O. theory.

THEORETICAL

In calculations based on the D. L. V. O. theory the following relations have been used.

The attractive potential energy V_A between two spherical particles is given by the Hamaker expression[5].

$$V_A = -\frac{A}{6}\left(\frac{2}{s^2-4} + \frac{2}{s^2} + \ln\frac{s^2-4}{s^2}\right) \tag{1}$$

where A is the Hamaker constant and $s = r/a$. r is the distance between particle centres and a the particle radius. Defining A is difficult but fortunately for the systems under consideration the calculations of stability parameters are rather insensitive to variations in V_A and therefore any uncertainty in A is not serious.

The repulsive potential energy V_R for spherical particles in a system for which $\varkappa a \ll 1$ is given by[6]

$$V_R = \frac{\varepsilon\, a^2\, \psi_0^2\, \beta}{r}\,\exp\,(-\varkappa H) \tag{2}$$

where ε is the dielectric constant, $\varkappa^{-1}$ the »thickness of the electric double layer«, $H = r - 2a$, and β is a function which allows for distortion of the double layers as they overlap. This expression assumes that the surface potential remains constant during the interaction; that assuming constancy of charge leads to a very similar result. Since in hydrocarbon media the value of $\varkappa H$ falls almost to zero, the exponential term in the V_R equation approximates to unity and the expression becomes

$$V_R = \frac{\varepsilon\, a^2\, \psi_0^2\, \beta}{r} \tag{3}$$

If we assume that $\beta = 1$ i. e. no allowance is made for the double layer dirstortion, we arrive at an expression which is Coulomb's Law for the interaction of point charges separated by a medium having a dielectric constant ε. From these equations it is quite obvious that only a small surface charge is required to produce a significant repulsive energy. Of course the number of charged species available in hydrocarbon media is very small, so we are in effect considering particles containing very low surface charge densities (perhaps 5—10 per particle) leading to significant surface potentials.

The total potential energy V of interaction is given by $V_R + V_A$ and from its distance relationship one may obtain values of V_{max}, the height of the potential energy barrier, as a function of surface potential, radius and Hamaker constant.

The stability of a colloidal system is commonly expressed in terms of a quantity W, the stability ratio, defined as the ratio of the actual rate of coagulation, treating the process as a bimolecular collision reaction, to the most rapid rate in the absence of any potential energy barrier and assuming all collisions to be effective. We have derived a theoretical expression[7] for W which is as follows

$$W = \frac{\int_{2}^{\infty} \frac{\exp(V/kT)}{s^2} ds}{\int_{2}^{\infty} \frac{\exp(V_A/kT)}{s^2} ds} \tag{4}$$

Hence, using values of V_A and V we may calculate W for any system and compare with that derived experimentally. Assuming a bimolecular collision reaction the rate of disappearance of particles is given by

$$- dN/dt = k'N^2 \tag{5}$$

where N is the number of particles per cm^3 present in dispersion at time t, and k' is the rate constant. Integration using the boundary condition $N = N_0$ when $t = 0$ gives

$$1/N = 1/N_0 + k't \tag{6}$$

Hence plots of $1/N$ against t are linear with a gradient equal to the rate constant for the coagulation process. Assuming that the most rapid rate (k_0') occurs in the pure hydrocarbon we have derived values of $W = k_0'/k'$ for dispersions of rutile and Sterling MTG in hydrocabron solutions of Aerosol OT using microscopic particle counting methods, and the experimental and theoretical values of W compared to assess the applicability of the D. L. V. O. theory to these systems.

<div align="center">RESULTS</div>

The first paper[8] in our series on *Stability of Non-Aqueous Dispersions* demonstrates that the magnitude of the repulsive energy resulting from the overlap of electric double layers, as predicted by the D. L. V. O. theory, is sufficient to explain qualitatively the observed stability. Dilute dispersions of rutile in solutions of Aerosol OT in xylene were prepared by ultrasonic irradiation, and the stability followed visually and by optical density measurements. The latter technique serves only to put the changes on a relative basis since there is no simple way of relating the optical behaviour (as determined spectrophotometrically) to the state of dispersion at any point in the coagulation process. The measurements, therefore, only lead to a qualitative assessment of stability. If no significant change in optical density occurred over several weeks the dispersions were assumed to have long term stability for which the theory suggests that an energy barrier of at least 15 kT is necessary. Obvious changes in the disperse character of the system over a period of days might be termed intermediate stability and be associated with smaller energy barriers, whilst rapid coagulation is readily distinguished.

For the rutile dispersions the zeta potential passed through a maximum with increasing surfactant concentration thus making a range of potential and stability available for study. Using particle sizes determined by electron microscopy and the zeta potentials, it was found that the D. L. V. O. theory shows satisfactory qualitative agreement, in terms of the energy barrier, with experiment. Similar experiments with alumina, a carbon black (Vulcan R) and copper phthalocyanine pigment supported this conclusion.

From these experiments two important facts were noted:

(a) the magnitude of the zeta potential associated with rutile at any one surfactant concentration varies significantly with the amount of water in the system;

(b) the size of the particle charge depends on the nature of the surface, positive charges being found for hydrophilic surfaces containing adsorbed water while the hydrophobic materials (Vulcan and CuPC) exhibited negative charges. Rutile in a water-free system was negative, but became positive on adding water, the charge being time dependent suggesting diffusion to the interface.

The origin and magnitude of the charge on particles dispersed in hydrocarbon media are not readily defined. Clearly adsorbed water is an important factor; the positive sign might in this case be associated with an excess of sodium ions in the interfacial region, or as Fowkes proposed[9], a proton exchange could be involved.

A more quantitative assessment of coagulation is described in two later papers in the series, one devoted to studies on Sterling MTG[10] and the other to rutile[11]. In both cases the rate of coagulation was measured by particle counting, and the theoretical and experimental stability ratios compared.

The magnitude of the negative zeta potentials for the graphitised carbon black varied with Aerosol OT concentration and as with rutile passed through a maximum. Similar phenomena have been reported elsewhere for glass (by electro-osmosis)[12] and carbon blacks (by electrophoresis)[1,13] but no explanation has been proposed; perhaps Fowkes' acid-base mechanism is relevant[9]. Considering the nature of the experiment and the complexity of the calculations involved together with the implicit assumptions, we were satisfied with the correlation between theoretical and experimental stability ratios although the range of W (1—6) is not large. Fortunately, the rutile system presented a wider range of stability behaviour (W values from 1 to 80) together with the possibility of varying the sign of the particle charge as described above. Over this range of W values theory and experiment showed good agreement and this was independent of sign of charge.

Further evidence of the profound effect of water was demonstrated[14] by additions to rutile dispersions at constant surfactant concentration, such that at low water contents the correlation between zeta potential and stability ratio is as expected but at higher concentration some divergence was observed with W remaining high but zeta decreasing to low values. It was suggested that water adsorbed on the rutile surface leads to an increase in the affective particle (aggregate) size which compensates for the decrease in potential and maintains the stability.

From the agreement between these experimental observations of stability and theoretical predictions, we were encouraged to make a more detailed quantitative analysis of the D. L. V. O. theory as applied to dispersions in hydrocarbon media. The computer data are published[15] in terms of the relation between W and potential, particle radius, height of potential energy maximum, and dispersion half-life. The half-life ($t_{1/2}$) of a dispersion is given by

$$t_{1/2} = \frac{6\eta \int_{2}^{\infty} \frac{\exp(V\,kt)}{s^2}\,ds}{4\,kTN_0} \tag{7}$$

where η is the viscosity of the medium. Surface potentials were taken over the range 5 (5) 80 mV and radii over the range 200 (200) 5000 (500) 10,000 Å for Hamaker constants of 0.5, 1.0, 2.5, 5.0 and 10.0×10^{-12} erg. The insensitivity of the results to significant variations in Hamaker constant is demonstrated, as well as the marked dependence of stability on particle radius. A significant result is the relation between the surface potential and the separation between particle surfaces at which the total potential energy is at a maximum; the distances are too large for steric effects due to adsorbed macromolecules to be felt, so a combined repulsion mechanism involving both electrical and steric effects is most unlikely. The published graphs allow the stability of a colloidal dispersion in hydrocarbon media, if due solely to an electrical mechanism, to be predicted from a knowledge of the size of its particles and of their surface (zeta) potential.

It should be emphasized that the discussion above refers to dilute systems *i. e.* the particles in the completely dispersed state are sufficiently far apart for there to be no overlap of electric double layers, and therefore the interaction may be considered in terms of a two particle collision from infinite separation. If we assume that double layer overlap is relevant then for dispersion of higher particle concentration it is necessary to consider the fact that for potential energy calculations the interparticle interaction does not start at infinite separation but at distances where there is already overlap of the double layers. Furthermore, the case of a two-particle interaction is probably not sufficient; some preliminary calculations on the effect of other particles in the vicinity of two interacting particles have been reported by Albers and Overbeek[16] in connection with their experiments on the stability of water in oil emulsions. As far as we know neither a detailed theoretical or experimental examination of the coagulation of concentrated dispersions have yet been carried out.

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IZVOD

Stabilnost disperzija u nevodenim medijima

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Iznesen je pregled istraživanja o stabilnosti koloidalnih disperzija u hidrogen-karbonskom mediju, koja su vršena u autorovom laboratoriju. Kao modelni sistem proučavane su disperzije i hidrofobnih i hidrofilnih materijala. Model hidrofobnog materijala bio je Sterling MTG, grafitizirani karbon, koji ima vrlo homogenu površinu. Kao hidrofilni materijal upotrebljen je rutil, ispitan na odsustvo onečišćenja pomoću infra-crvene spektroskopije i plinske adsorpcije. Uspoređuju se i rezultati dobiveni istraživanjima na hidrofobnom karbonu Vulcan R i na hidrofilnim materijalima aluminium oksida i kuprum ftalocijanina. Hidrogen-karbonskom mediju (ksilen) bio je dodavan anionski površinsko-aktivni materijal Aerosol OT (natrium di-2-etilheksil sulfosukcinat).

Eksperimentalni rezultati mjerenja stabilnosti disperzija vrlo dobro se slažu s predskazivanjima na osnovi teorije Derjagin-Landau-Verwey-Overbeek. Izvedena je i relacija koja polu-život disperzije povezuje s viskozitetom medija, potencijalnom energijom privlačenja, udaljenošću i promjerom čestica. Teorija dozvoljava predskazivanje stabilnosti disperzija na bazi poznavanja veličine čestica i njihovog zeta-potencijala. Utvrđen je i ogromni efekt tragova vode. Kod niskog sadržaja vode postoji korelacija između zeta-potencijala i kvocijenta stabilnosti, dok kod visokog ima slučajeva, da je stabilnost visoka, a zeta-potencijal nizak. Svi rezultati odnose se samo na razrijeđene sisteme, tj. čestice, kojih je međusobna udaljenost tolika, da ne dolazi do preklapanja dvoslojeva. Te su udaljenosti prevelike, da bi se osjetio utjecaj steričkih efekata zbog adsorbiranih makromolekula, te je i mehanizam repulzije, koji bi uključivao međudjelovanje električkih i steričkih faktora, najmanje vjerojatan. Do sada u literaturi nije opisano eksperimentalno istraživanje koagulacije koncentriranih disperzija ovog tipa.

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