Characteristics of inorganic colloids

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<u>Abstract</u> - Interest in the technological applications of sol-gel processes in the synthesis of specialised materials such as ceramics, adsorbents, and catalysts has grown enormously recently. This development has arisen from a greater awareness of the inter relationships between the structure and properties of these materials and the characteristics of the precursor oxide colloids and gels. These advances have arisen partly from a better understanding of the structure and interactions in concentrated dispersions of oxide sols and the application of new experimental techniques, such as small angle neutron scattering (SANS). Here the application of SANS in the characterisation of concentrated aqueous dispersions of charge stabilised oxide sols and clay colloids is described. Several systems are considered and it is shown how the bulk properties, such as rheology (viscoelasticity, thixotropy) are related to colloid structure and interactions. Here the recent application of SANS measurements under shear conditions is highlighted. Finally, it is shown how the surface and porous properties of the resultant gel produced on dehydration is controlled by such colloid characteristics.

INTRODUCTION

The properties of oxide sols and clay colloids have long been of fundamental interest in colloid science and also have widespread importance in many areas which range from environmental chemistry (ref. 1) (soil science, mineral dissolution) to technological applications in ceramic fabrication which employ sol-gel processes for example (ref. 2). In the latter, a concentrated sol is converted into a solid hydrous oxide gel, as depicted schematically in Figure 1.
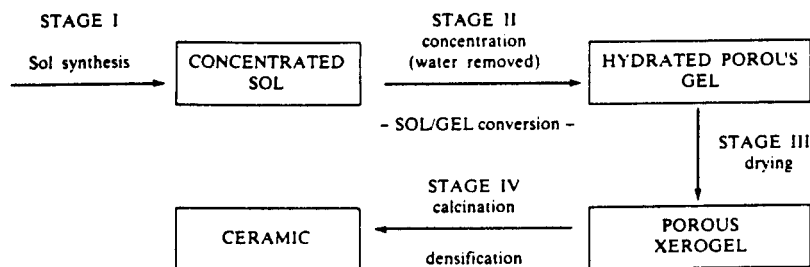

Fig. 1: Different stages in the formation of a ceramic from an oxide sol

The structure and interactions in the sol are of considerable importance, since these may predetermine the rheological behaviour during the conversion process and ultimately the final microstructure of the gel - in particular its surface are and porous properties (ref. 3). This feature is illustrated schematically in Figure 2 where gels of low and high porosity are derived from unaggregated and aggregated sols respectively. These contrasting types of sol will be referred to subsequently.

Apart from its relevance to this specific application a study of concentrated dispersions of oxide and clay in colloids can provide a direct insight into the nature of oxide/water interfaces, and interparticle forces which influence colloid stability. Some of the techniques which have been applied and the

information obtainable are summarised in Table 1. Many of these are familiar techniques and need not be dealt with here. The application of small angle neutron scattering (SANS) is, however, a quite recent development in colloid studies and has led to considerable advances in the understanding of concentrated dispersions (refs. 4,5). Recent progress in its application to studies of oxide and clay sols will be illustrated here with reference to three systems: (a) discrete isotropic particles, such as silica sols; (b) aggregated fractal systems; (c) anisotropic particles (rods, platelets).
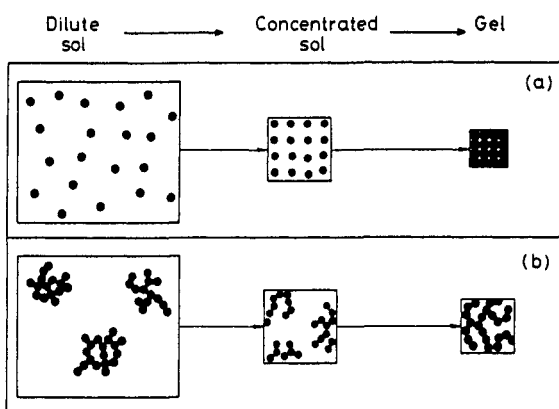

Fig. 2: Diagram depicting the formation of gels of low and high porosity from (a) unaggregated and (b) aggregated sols respectively

TABLE 1.   Techniques for characterisation of structure, interactions and equilibrium properties of inorganic colloids.

	Technique for Study	Information
Colloid Interactions	Rheology; measurements under steady and oscillatory shear (viscoelastic behaviour)	Flow behaviour of dispersions - particle interactions at high volume fraction
	Electrophoresis - electrophorectic light scattering	Electrophoretic mobility - surface charge, colloid stability
	Inelastic and quasielastic neutron scattering I.r. spectroscopy neutron diffraction	Properties of interfacial water layers - particle interaction, polynuclear hydroxy ions
Colloid Structure	Static light scattering	Particle size of sol M.W. and size of sol aggregates
	Quasielastic light scattering (photon correlation spectroscopy)	Diffusional and rotational motion of colloid particles (surface/solvent interactions)
	Ultracentrifugation	Sedimentation coefficient
	Small angle X-ray scattering Small angle neutron scattering	Particle size/shape of sol; particle ordering (radial distribution function); interparticle forces

DISCRETE ISOTROPIC PARTICLES

Aqueous dispersions of spherical colloidal particles which are uniform in size (monodispersed) are ideal model systems which have been studied extensively by SANS. Considerable advances have been made here in understanding the structure and interactions in the concentrated dispersions by applying statistical mechanical theories of liquids to the colloid state (ref. 6).

Typical changes in the SANS which occur during the progressive concentration and conversion of sols to gels are illustrated in Figure 3 by the results for colloidal silica having a particle diameter of ~16 nm. Here the scattered intensity I(Q) is given by:

$$I(Q) = V_p^2 n_p (p_p - p_s)^2 P(Q) S(Q) \qquad (1)$$

where $Q = 4\pi \sin\theta/\lambda$ is the momentum transfer for scattering at an angle θ for a wavelength λ. V_p and n_p are respectively the particle volume and number concentrations. p_p and p_s are the scattering length densities of the particles and water. P(Q) and S(Q) are the particle form factor and structure factor respectively. For spherical particles P(Q) is given by:

$$P(Q) = \left[\frac{3 [\sin (QR) - QR \cos (QR)]}{Q^3 R^3} \right]^2 \qquad (2)$$

where R is the radius of the particles. S(Q), the static structure factor, is determined by the nature of the particle interaction potential. For non-interacting (viz. very dilute) systems, S(Q) = 1. This situation arises for the scattering at lowest concentration of silica shown in Figure 3. At higher concentrations the interference peaks, arise from the short-range ordering of particles which occurs due to the mutual electrostatic repulsion between the double layers surrounding the particles.
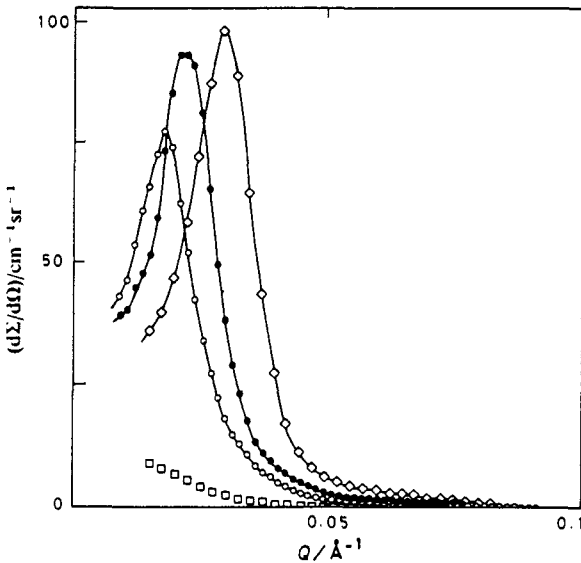

Fig. 3: Small angle neutron scattering from silica sols of different concentrations, c: □, 0.014; ○, 0.14; ●, 0.27; and ◊, 0.55 g cm^{-3}. Particle diameter is ~16 nm.

It can be shown that the spatial distribution of the particles as a function of the mean interparticle separation, r, is given by the particle pair-distribution function g(r) and is related to S(Q) by the Fourier transform

$$g(r) - 1 = \frac{1}{2\pi^2 n^P} \int_0^\infty [S(Q) - 1] Q^2 \frac{\sin(QR)}{QR} \, dQ \qquad (3)$$

The maximum in g(r) relates to a corresponding maximum in S(Q) as reflected in the scattering behaviour. The position of this maximum in g(r), r^*, can be expressed approximately by

$$r^* = 2\pi/Q_{max} \qquad (4)$$

As the concentration, c, of such sols is increased the reputation between the spherical particles results in a mutual ordering in which the scaling of mean particle separation is given by

$$r^* \sim c^{-1/3} \qquad (5)$$

It can be shown that the ordering approximates to that of random close packing (ref. 4). On progressive concentration such systems show an increase in viscosity and eventually give rise to an efficiently packed rigid porous "gel" when the solid volume fraction, ϕ exceeds ~0.6.

AGGREGATED FRACTAL SYSTEMS

Another more complex system occurs where the sol is composed of aggregates of primary particles having a diameter somewhat similar to those already described. Dispersions of this type are typical of a wide range of colloidal systems occurring as flocs and particle clusters and arise in a variety of natural and commercial processes (ref. 7).

The SANS of aggregated alumina sols at increasing concentration is shown in Figure 4. At low concentration the scattering shows a power law behaviour of

$$I(Q) \sim Q^{-2.1} \tag{6}$$

at low Q typical of a fractal system. Here the power law exponent corresponds to aggregates formed by a process of reaction limited cluster aggregation (RLCA). With increasing concentration interference in the SANS occurs - the maxima moving to higher Q as the concentration is increased. This effect arises from interactions between particles in the aggregates as interpercolation occurs. This feature occurs at relatively low concentration ($<0.1 g\ ml^{-1}$) and corresponds with the development of viscoelastic properties as illustrated in Figure 5 by the increase in storage modules G' with concentration. Such systems give rise to weak gels showing thixotropic properties at low concentration $\phi < 0.1$, and have distinctly different rheological behaviour to the previous type of sol composed of discrete isotropic particles which remain relatively fluid. These differences in structure result in the formation of a rigid gel with considerably higher porosity than that which is formed by the efficient packing of discrete spherical particles. This porosity is typically $\gtrsim 0.7$ and corresponds to an average number of ~3-4 contacts per particle (ref. 8).
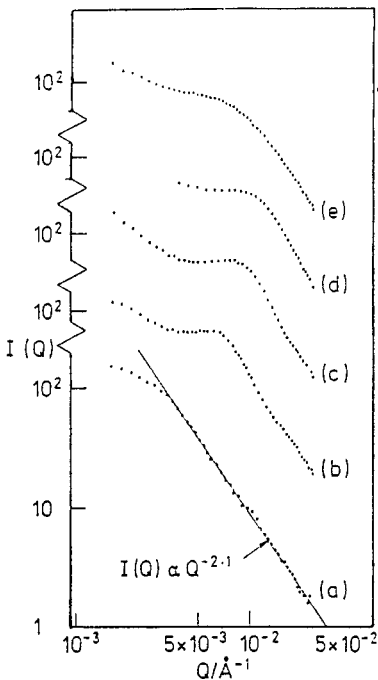

Fig. 4: SANS of aggregated alumina sols of different concentration, g ml^{-1} (a) 0.05, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.4 ionic strength ~ 0.1 mol dm^{-3}

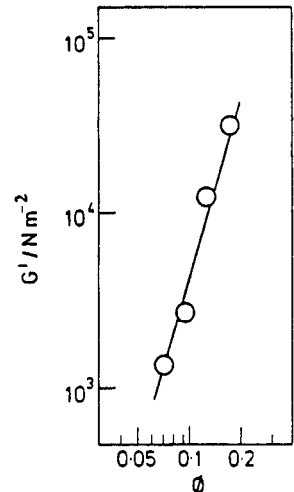*Fig. 5: Storage modulus, G', vs volume fraction, ϕ, for colloidal dispersions of pyrogenic alumina.*

ANISOTROPIC PARTICLES

Many inorganic colloidal systems are composed of anisotropic particles such as platelets and rods (ref. 9). Typical examples are oxide sols - alumina (boehmite), iron oxide (goethite), vanadium pentoxide and clays (smectites, kaolimite, sepiolite). This particle anisotropy may have a profound influence on the rheologyy of the dispersions leading to complex time dependent properties such as thixotropy. These characteristics may arise from the particle interactions which lead to local structuring in the dispersions. On dehydration this results in a preferred orientation of the particles. This occurs with the smectite clays and boehmite where layered structures are formed in the gel-containing slit-shaped pores (ref. 3).

Montmorillonite and hectorite are smectite swelling clays which form aqueous dispersions having viscoelastic and thixotropic properties at relatively low volume fraction ($\phi <0.02$) (ref. 10). In these systems the primary particles are ighly anisotropic, being composed of thin (~1 nm) platelets which are discrete at low electrolyte concentrations (ref. 11).
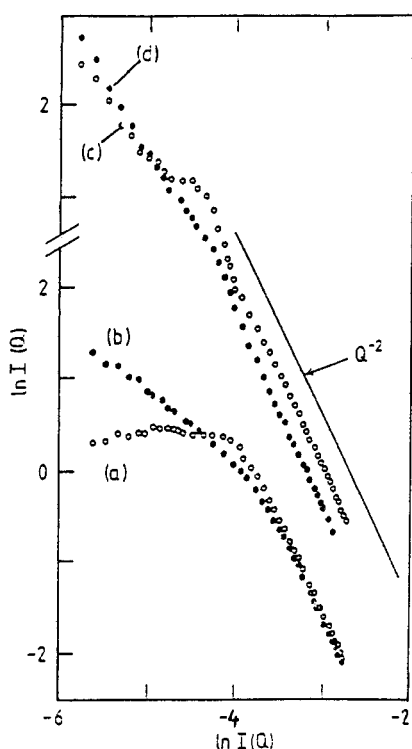
Fig. 6: SANS of aqueous dispersions of synthetic hectorite (a) static, (b) sheared; montmorillonite, (c) static, (d) sheared. Concentrations are 0.05 g ml^{-1} and is 1.2 x 10^4 s^{-1}.

The SANS from synthetic hectorite and montmorillonite clay dispersions under static conditions are shown in Figures 6(a) and 6(c) respectively. If this concentration (0.05g ml^{-1}) the dispersions are viscoelastic and have marked thixotropic properties. This feature corresponds with the interference maxima in the scattering curves at Q ~ 2 x 10^{-2} Å^{-1}. At higher Q both curves decay as Q^{-2} in accord with the P(Q) for thin discs. Thus the development of viscoelastic behaviour can be ascribed to the formation of a structure in which there is some preferred orientation of the platelets over short distances. Such an oriented structure would arise from the mutual interaction between the electrical double layers surrounding the particles. Evidence for this comes from measurements of SANS under in-situ shear as illustrated in Figures 6(b) and 6(d) for both hectorite and montmorillonite dispersions respectively. Here we note the disappearance of the interference and scattering which accords with that of a random orientation of the discs. Under static conditions the interference features develop again in parallel with thixotropic recovery.

Acknowledgements

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