Control of the Rheology of Concentrated Aqueous Colloidal Systems by Steric and Hydrophobic Forces

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The major role played by short-range steric forces and the hydrophobic force on the rheology of high-volume-fraction aqueous colloidal zirconia dispersions is demonstrated.

The attractive and repulsive pair-wise interactions between colloidal particles control, in a fundamental way, whether or not that system of particles is coagulated or dispersed.[1] Early theoretical and experimental work focused on whether the sum of attractive van der Waals and repulsive electrostatic forces induced rapid or slow coagulation in dilute dispersions. More recently, major advances in the field have come from studies of concentrated colloidal dispersions[2] using the powerful tools of neutron scattering[3] and rheology[4] and techniques developed for the direct measurement of the forces between macroscopic surfaces interacting across an aqueous or other medium. Direct force measurement has identified, as well as the van der Waals and electrostatic forces, a range of steric, hydration, structural and hydrophobic forces. The surface forces apparatus (SFA), in its various forms[5,6,7] involving the interaction of macroscopic surfaces across aqueous solutions, has provided quantitative verification of essential long-range electrostatic and van der Waals forces,[6] short-range steric,[8] hydration[9] and structural forces,[10] forces underlying the depletion flocculation effect[11] and the form, if not the essential physics, of the hydrophobic force.[12] Colloidal dispersions are clearly controlled by the long-range forces; depletion effects are well displayed in many colloidal systems, as are the steric stabilisation and aggregation forces, particularly with adsorbed and grafted polymer-coated colloidal particles.

As part of an ongoing rheological study of model silica[13] and zirconia[14] dispersions, we have identified the action of short-range steric, and hydrophobic colloidal forces. The essential advantages of particulate dispersion viscosity and yield-stress measurements have enabled us to use high-volume-fraction dispersions to view both long-range and short-range forces. Our approach follows that of Goodwin et al.[15] and more recently of Buscall.[16]

The colloid used was an ultra-pure zirconia of narrow particle size distribution. This has a specific surface area 15 m² g⁻¹, a mean particle size 0.30 µm (diam), with an

isoelectric point, determined by three different electrokinetic techniques at pH 7.2. The yield stress–pH behaviour of high-volume-fraction zirconia dispersions, determined using the Vane technique of Nguyen and Boger[17] is shown in Fig. 1. The maximum yield stress occurs, independent of volume fraction, at the isoelectric point of the ZrO_2–aqueous interface. This result identifies the general electrostatic repulsion forces, and the van der Waals attractive forces operating in this simple 1:1 electrolyte system. The yield stress varies as the square of the zeta potential as demonstrated earlier by
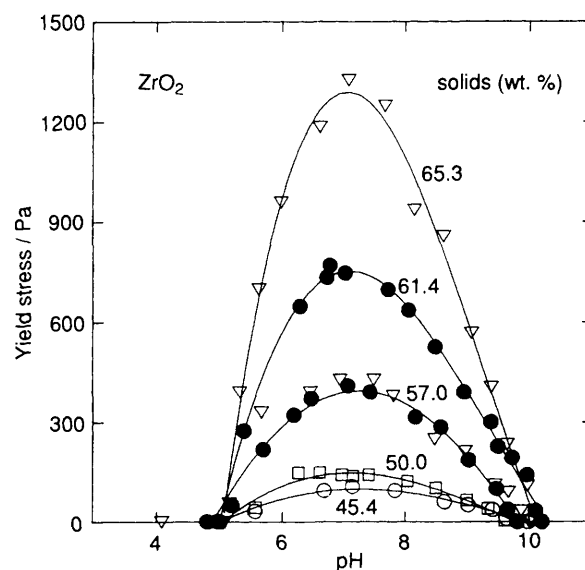

Fig. 1 The static yield stress–pH behaviour of concentrated colloidal dispersions of zirconia, in the absence of additives, as a function of weight percent solids. A solids content of 65.3 wt/wt.% corresponds to a volume fraction of 24 vol.% and 45.4 wt./wt.% solids is 12 vol.%.
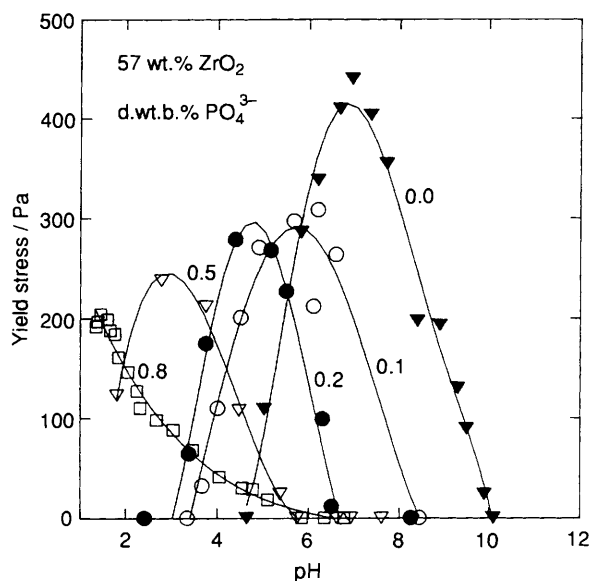
Fig. 2 Yield stress–pH behaviour of 57 wt./wt.% solids colloidal zirconia as a function of increasing concentrations of sodium phosphate expressed as d.w.t.b.% (% dry weight basis)

Fig. 3 Yield stress–pH behaviour of 57 wt./wt.% solids colloidal zirconia as a function of increasing concentrations of sodium dodecyl sulfate (SDS) expressed as d.w.t.b.%

Table 1 Variation of the maximum yield stress with the predicted steric barrier thickness (δ) in comparison with molecular sizes based on minimum and maximum interfacial conformations

Anion present	Limiting maximum yield stress/Pa	Predicted δ/Å	Sizes from molecular modelling	
			Minimum conformation/Å	Maximum conformation/Å
None	440	—	—	—
Sulfate	269	1.26	1.69	1.95
Phosphate	205	1.94	1.68	1.94
Pyrophosphate	200	2.02	2.23	4.38
1,2,3-BTC	145	3.28	2.06	4.35
Lactate	135	3.61	2.27	3.59
Malate	134	3.64	3.29	4.32
Citrate	99	5.26	4.59	5.26

Firth and Hunter[18] using the less than satisfactory extrapolated Bingham yield parameter.

The yield stress–pH behaviour was then determined in the presence of a wide range of anionic small-molecule additives known to affect the viscosity of oxide dispersions. Included were the sodium or potassium salts of sulfate, phosphate, pyrophosphate, lactate, citrate, malate, 1,2,3-benzenetricarboxylate (BTC) and dodecylsulfate. Also examined were the effects of linear polyphophosphates of mean degrees of polymerisation of 5 and 12, as models of the general 'Calgon' dispersants. The effect of added phosphate is shown in Fig. 2 where the pH of maximum yield stress moves systematically to lower pH. All anionic additives produced this effect, and in all cases the pH of maximum yield stress corresponded to the pH of zero zeta potential. The anions all exhibit typical specific adsorption behaviour that is ameanable to analysis in terms of site binding electrical double-layer models.[19]

The one to one correspondence between the pH of zero zeta potential and the pH of maximum yield stress is expected from the sum of electrostatic and van der Waals forces. What was not anticipated was the systematic reduction in the magnitude of the maximum yield stress as the additive shifts the pH of zero zeta potential. The decrease in maximum yield stress accompanying the specific adsorption of these relatively small
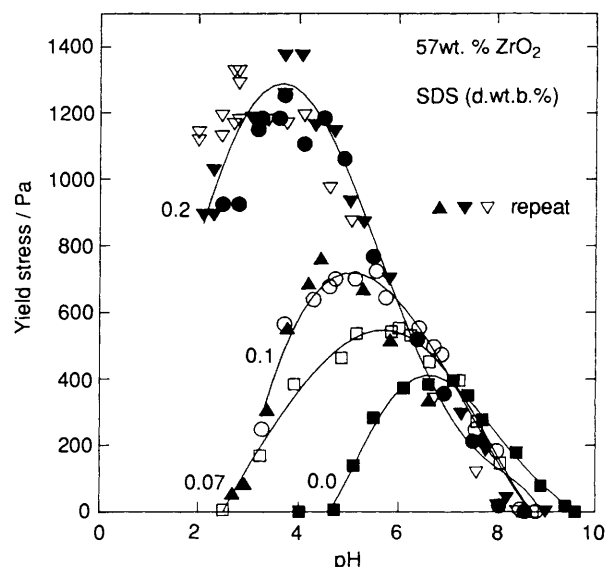
anions could in principle be due to an overall reduction in the van der Waals attraction as the ZrO_2 particles are 'coated' with a layer of lower refractive index. Adsorption isotherm studies and computations fail to substantiate this hypothesis,[20] observed adsorption densities producing a trivial reduction in the attraction.

An alternative is that the specifically adsorbed ions introduce a steric barrier that allows approach of the ZrO_2 particles at zero zeta potential into a less deep energy well than in the case of zero specific adsorption. We have tested this hypothesis by equating the maximum yield stress to the force of attraction per unit area for particles sitting in an attractive well. The attractive force in the absence of additives operates over a particle–particle separation of H. In the additive case, the attractive force operates over separations of (H + 2δ), where δ is the additive adsorbate layer effective thickness on each particle. This layer thickness, computed from the yield-stress data for several additives, is compared in Table 1 with the diameters derived from molecular modelling. Conformations leading to both maximum and minimum adsorbed thicknesses are listed. The predicted values compare well with molecular sizes that one would expect for specifically adsorbed species. Two important exceptions should be noted. First, sulfate appears to be acting as a smaller steric barrier than expected, probably owing to its low extent of specific adsorption. More importantly, pyrophosphate appears to lie flat, generating essentially the same size steric barrier as monophosphate.

We have explored the action of phosphates further, by examining two linear polyphosphates of degrees of polymerisation (DP) of 5 and 12. These produce limiting values of the maximum yield stress at zero zeta potential of 171 and 154 Pa respectively, corresponding to predicted thicknesses of 2.6 and 3.02 Å respectively. Thus all four phosphates of DP = 1, 2, 5 and 12 give steric barriers with all four agents lying flat. The familiar 'dispersant' action of polyphosphates ('Calgon'-type agents) must therefore be due to the increase in molar specific adsorption coefficients as the molecular mass increases and not to the increased size of their steric barriers.

We turn finally to the action of dodecyl sulfate (SDS). The observed change in yield stress as a function of pH and SDS concentration is shown in Fig. 3. Zero zeta potential occurs at the same pH as that of the maximum yield stress. Note the major increase in the value of the maximum yield strength at zero zeta potential in the presence of SDS. Based on the data

from Fig. 2, where the effect of a steric contribution to the total force is observed to be significant, the steric effect due to an SDS layer on the zirconia surface might be expected to decrease the maximum yield stress as a function of concentration. This contribution to the total force is not observed. We suggest that this is because of the operation of the hydrophobic force.[21] Further, since the maximum yield stress at zero zeta potential increases uniformly from the zero additive value of 440 to 1300 Pa, the hydrophobic force is clearly of longer range at all separations than the van der Waals force. Our computations indicate that the attractive hydrophobic force operating in the presence of adsorbed SDS must involve a decay length of ca. 14 Å in order to produce the major increase in attractive well depth corresponding to the 1300 Pa maximum yield stress at zero zeta potential shown in Fig. 3.

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