Molecular Configuration of Adsorbed Cis- and Trans-1,2-Ethylene Dicarboxylic Acids and Interparticle Forces in Colloidal Dispersions

1 AUTHOR:

Yee-Kwong Leong
University of Western Australia

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Molecular Configuration of Adsorbed *cis*- and *trans*-1,2-Ethylene Dicarboxylic Acids and Interparticle Forces in Colloidal Dispersions

Y. K. Leong

School of Engineering, James Cook University, Townsville 4811, Australia

Introduction

There has not been a study linking the molecular configuration of adsorbed small charged molecules and the interparticle forces in flocculated dispersions. This study will illustrate the linkage with *cis*- and *trans*-1,2-ethylene dicarboxylic acids in a 24 vol % α-Al$_2$O$_3$ dispersion. The interparticle forces were evaluated from the yield stress[1-8] of the dispersion. The cis-form acid weakens the flocculated network structure by forming a steric layer. The trans-form acid greatly reinforces this structure by bridging at the joints and network junctions. As a result, the dispersion developed a high yield stress and viscosity. This study may give rise to a new family of thickening agents based on small organic molecules that may be of use in products such as toothpaste, printing inks, cosmetics, paints, concrete mix, and paper-coating slurries.

The particles in a flocculated dispersion of moderately low concentration are linked together by a net attractive force to form a very open three-dimensional structure that occupies the whole volume of the dispersion. This occurs when the van der Waals attractive force is stronger than the electrostatic repulsive force. The majority of the particles in the network structure are joined by only two particles or have two nearest neighbors.[9] At the network junctions, the particles may have three or four nearest neighbors.[10] Within the network structure, the strongest attraction is at the joints (the bond between two particles is a joint) and junctions where the surface-to-surface distance is smallest, about 5 Å.[1] It is the magnitude of this attraction that determines the strength of the structure. With adsorbed molecules, it is possible to strengthen or weaken the joints and junctions.[1,2,11]

The yield stress is a direct measure of the strength of the flocculated network structure.[1,2,10,12] It is maximum at the charge neutral condition where the van der Waals is the only force contributing to the stress. With adsorbed additives, there are other forces contributing to the stress such as steric, bridging, hydrophobic, and charged patch. Adsorbed additives affect the maximum yield stress. The difference in the maximum yield stress between dispersions with and without adsorbed additives can therefore be attributed to the various surface forces.

Although the yield stress technique[13] used in this study cannot measure the forces and their range directly, it has several advantages over the other more elegant and established surface force characterization techniques such as surface force apparatus (SFA),[14] total internal reflection microscopy (TIRM),[15] and atomic force microscopy (AFM).[16,17] This technique is capable of detecting very small forces. The millions of particle-pair interactions in the dispersions will amplify any small forces. It characterizes the interactions at the (Derjaguin−Landau−Verwey−Overbeek) minimum separation distance in the flocculated state.

In this study, the *cis*- and *trans*-1,2-ethylene dicarboxylic acids (HOOCCH=CHCOOH) are two of the simplest and possibly smallest molecules where their spatial configuration in the adsorbed state is limited and well defined. The adsorption behavior of these compounds at various pH conditions is dependent upon their acid strength. The acid strength is characterized by the pK_a values. The cis-form acid has a pK_{a1} of 1.83 and a pK_{a2} of 6.07, while the trans-form acid has a pK_{a1} of 3.03 and a pK_{a2} of 4.54.

Experimental Section

A dispersion of α-Al$_2$O$_3$ in water was prepared by dispersing an ultrapure α-Al$_2$O$_3$ (AKP-30) powder produced by Sumitomo Chemical Co. The powder has a purity greater than 99.99%, a Brunauer−Emmett−Teller area of 6.4 m^2/g, a narrow size distribution with a mean diameter of 0.34 μm, and a density of 3920 kg/m^3. The dispersion was prepared in a dispersed state at an alkaline pH of about 12. Concentrated HCl was added stepwise to progressively lower the pH. The yield stress was measured at a number of pHs using a vane rheometer.[13]

Results and Discussion

The effects of 0.1 dwb % *cis*- and *trans*-1,2-ethylene dicarboxylic acid additives on the yield stress versus pH behavior of the α-Al$_2$O$_3$ dispersion are shown in Figure 1. Also included in Figure 1 is the yield stress versus pH curve for the dispersion without the additives. The curve for the dispersion without the additives showed that the isoelectric point (pI) is at pH 9.0 and the yield stress is at its maximum value of 450 Pa. At a pH below pI, the adsorption of the negatively charged additives is expected to be favorable as the particle surface is positive. The data in Figure 1 showed that the maximum yield stress of the dispersion with the trans-form acid is increased by more than 3-fold. For the cis-form acid, the maximum yield stress not only has not increased but it has in fact decreased marginally. The yield stress versus pH measurements for the cis-form acid were repeated, and the data showed excellent reproducibility.

The shift in the maximum yield stress to a lower pH is a typical behavior of anion adsorption.[1] The extent of the shift can be used as a measure of the degree of adsorption. In the case of the cis-form acid, the shift was quite small, less than a pH unit, indicating a low degree of adsorption. The low degree of adsorption is not unusual as the molecule is capable of internal hydrogen bonding between the two

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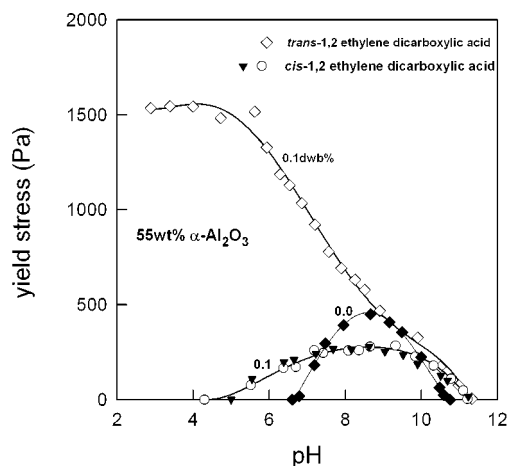
Figure 1. The plot of yield stress as a function of pH for the α-Al₂O₃ dispersion with 0.1 dwb % (0.1 g additives/100 g α-Al₂O₃) *cis*- and *trans*-1,2-ethylene dicarboxylic acids and without additive. For dispersions with the dicarboxylic acids, the onset of yield stress behavior occurred at a higher pH. This was an ionic strength effect. The initial ionic strength was 3 times higher for these dispersions. The average ionic strength measured in terms of conductivity ranged from 1.1 mS/cm for no dicarboxylic acid additive to 3.5 mS/cm for the trans-form acid.

carboxylic groups. For the trans-form acid, a shift of 5 pH units was observed reflecting a high degree of adsorption.

The spatial configuration of the adsorbed *cis*- and *trans*-1,2-ethylene dicarboxylic acid molecules may significantly affect the strength of the flocculated network structure and hence the maximum yield stress. Two factors that may determine the spatial configuration are the requirement of a stable molecular conformation and the delocalized nature of the negative charge of the carboxylate group. With the trans-form acid, the carboxylate groups are located diagonally across the planar ethylene unit. With the cis-form acid, they are on the same side of the unit. The carboxylate group is also planar and is free to rotate at the carbon−carbon single bond linking the carboxylate group to the ethylene unit. The most stable conformation is when the carboxylate group, in particular its two oxygens, and its adjacent hydrogen group of the ethylene unit are the farthest apart. This occurs when the plane of the carboxylate group is perpendicular to the plane of the ethylene unit. The negative charge of the carboxylate group is delocalized between its two oxygens. When this carboxylate group is adsorbed on a positive site, it will most likely be sitting upright on the particle surface. This means that the plane of the ethylene unit of the adsorbed molecule will also be normal to the particle surface. For the cis-form acid, both carboxylate groups will be facing the same particle upon adsorption. For the trans-form acid, the second carboxylate group is free to adsorb on a second particle provided it is close enough. That is, the separation between particles must be equal to or smaller than the width of the trans-form acid molecule. That width is about 5 Å.

The large increase in the maximum yield stress by the trans-form acid is attributed to bridging at the joints and the network junctions. Assuming that the adsorption of the trans-form acid was 100%, at the additive concentration of 0.1 dwb % this gave a surface coverage of 123.3 Å²/molecule or 61.7 Å²/carboxylate group.

On the basis of monolayer coverage data of 21 Å²/carboxylate group,[18] this represents a surface coverage of
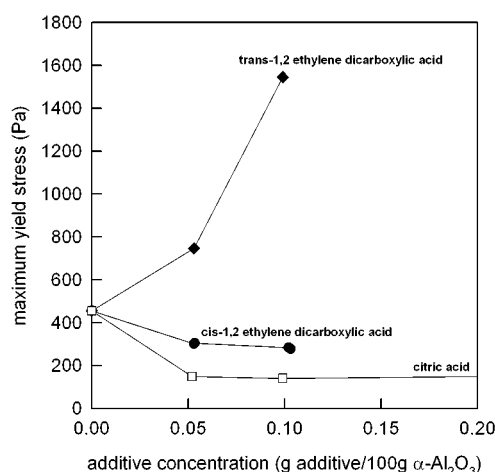
Figure 2. The plot of maximum yield stress of a 24 vol % α-Al₂O₃ dispersion as a function of additive concentration for *cis*- and *trans*-1,2-ethylene dicarboxylic acids and citric acid.

30%. At such low coverage, bridging of particles by the trans-form acid is favorable.[2] For a greatly increased network strength, there must be sufficient bridging molecules available for each particle bond. From the particle number calculations based upon the whole size distribution, the number of molecules per particle was in excess of a quarter million for 0.1 dwb % trans-form acid. Note that the interparticle distance of less than 5 Å at the joints and junctions is at least an order of magnitude smaller than that obtained by TIRM for interactions between a micron-sized particle and a plate.[15]

The marginal decrease in the maximum yield stress by the cis-form acid is attributed to steric effects. The adsorbate formed a steric layer that kept the interacting particles farther apart where the van der Waals attraction is weaker. For the steric effects to be observable, only a small adsorbate concentration is required. It is not necessary to have an adsorbed molecule available at each particle bond. This is due to the flocculated structure's tendency to yield or fail at the weakest joints and junctions during the yield stress measurement.

The effects of additive concentration on the maximum yield stress are shown in Figure 2. Data for citric acid were included for comparison. The maximum yield stress increased quite sharply with concentration for the trans-form acid. It however decreased with concentration for both the cis-form and citric acids. The decrease in the maximum yield stress reached a limit at a relatively low concentration of 0.1 dwb %. At this limit, the decrease was about 37% for the cis-form acid and as much as 69% for the citric acid. This result was not unexpected as the citric acid molecule is much larger than the cis-form acid. The projected size of the adsorbed citric acid molecule is about 5 Å,[1] whereas that of the cis-form acid is 3 Å. Also, citric acid adsorbed more readily and strongly than the cis-form acid. For example, the pH of maximum yield stress was shifted by 7 units at the concentration of 0.38 dwb % citric acid.

Conclusion

trans-1,2-Ethylene dicarboxylic acid enhances the strength of the flocculated structure of the α-Al₂O₃ dispersion via bridging at the joints and network junctions.

cis-1,2-Ethylene dicarboxylic acid weakens the flocculated structure of the α-Al₂O₃ dispersion by forming a steric layer on the particles.

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