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The Study of Liquid Suspensions of Iron Oxide Particles with a Magnetic Field-Flow Fractionation Device

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Abstract

A magnetic field-flow fractionation (magnetic FFF) device was used to determine the effects of a magnetic field upon a suspension of iron oxide particles in acetonitrile. The effects of surface modifiers on the stability of the suspension are discussed in terms of changes in retention, peak shape, and peak area. Particle elution was monitored by the use of a UV-visible spectrophotometer fitted with a flowcell.

INTRODUCTION

The understanding of small particle systems, which exist as suspensions in liquids, is important in many fields. Some examples are blood, viruses, paint, inks, and polymer latexes. It is important for a suspension to be stable to flocculation (aggregation) and/or sedimentation, particularly when characterizing small particles in terms of size and shape.

The principal cause of flocculation is the van der Waals attractive forces between particles, and stability against flocculation is a result of interaction between similarly charged electric double layers and particle–solvent affinity. Particle–solvent affinity promotes stability mainly by mechanical means, which can be considered in terms of the positive desolvation free energy change which accompanies particle flocculation. The adsorption of material on to the particle surfaces will usually promote stability through increased particle–solvent affinity and by an entropic mechanism. However, the surfactant may also cause flocculation by either a bridging

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mechanism or by the reduction of the repulsive forces associated with surface charge.

A comparison of the most frequently used techniques for characterization of particle suspensions in liquids will be useful in order to put the magnetic FFF technique into perspective. These techniques have been the subject of review articles (*1*, *2*) in which the authors agreed that the lack of correlation between the results obtained represents a serious limitation in our ability to characterize particle suspensions. Microscopy is commonly used to determine particle size, shape, and concentration. It is considered to be very reliable and is most often used as a reference to evaluate other methods of particle characterization. Microscopy is very tedious and time consuming, and is very dependent on operator skill. The major limitation of microscopy to the characterization of suspensions, however, is that the observations of an actual suspension is particularly difficult with a light microscope and impossible with an electron microscope, which requires a vacuum.

Turbidimetry, a photometric technique, involves the attenuation of a light beam by a suspension of particles. A detector is placed in the path of a light beam and the particle concentration is determined by the decrease in the intensity of the light beam. Nephelometry involves the measurement of light scattered by suspended particulates. The detector is placed at some angle other than 0° with respect to the incident beam (usually 90°) and the intensity of light that is scattered is related to the concentration of particles. These methods are particularly useful for the determination of particle concentration. In principle, particle size and shape can also be determined by light scattering, but this is only possible within a narrow range of particle sizes and only when well-characterized standards are available (*3*). Light scattering has been successfully used in flocculation kinetics studies, but these systems must be highly monodisperse because of the sensitivity of light scattering to the size and shape of the particles (*4*).

Zone detection techniques involve streaming a dilute suspension through a narrow orifice where the particles are detected. "Photozone" detection involves moving the particles through an orifice which is in the path of a light beam which is illuminating a photocell (*3*). The electronic pulses which are made as a result of particles that block the light beam are counted and sorted by a pulse height analyzer. It is assumed that stronger pulses correspond to larger particles. This technique is limited by the size range of the particles to be analyzed, since different orifices must be used for different size ranges. This "photozone counting" method is also much slower than light scattering in terms of response time, since each particle is counted individually. The "zone resistance" (i.e., Coulter Counter) method

has been in use for a long time for the determination of particle concentration and size (*5*). It is analogous to the "photozone" technique described above. Particles are moved through a narrow orifice by a rapidly flowing stream, but detection is by means of the change in electrical conductivity of the zone between two electrodes which are placed on either side of the orifice. This method has very similar characteristics to the "photozone" technique with one further disadvantage: the carrier solvent must contain an electrolyte.

These currently used techniques do not provide separation with respect to size and therefore a sample which contains a widely varying size distribution of particles must undergo several different determinations in order to be completely characterized. Given this limitation, none of the commonly available techniques plays a dominant role in the analysis of particle suspensions at this time.

Field-flow fractionation (FFF), as a family of techniques, has been developed by Giddings and co-workers at the University of Utah (*6–11*). In a field-flow fractionation experiment an external field is applied at right angles to a flowing stream in an open channel. The force field acts to drive the suspended particles downward toward the lower wall. The downward motion is countered by the tendency of the particles to diffuse due to the thermal motion of the carrier molecules. The balance of these forces results in a steady-state "atmosphere" of particles. Particles which interact more strongly with the field are found closer to the bottom of the channel, and will move more slowly because they are in slower flow streams due to the nature of the laminar flow profile (*6*). Typical means by which force fields have been induced are centrifugation (sedimentation FFF) (*7*), electrical potential gradients (electrical FFF) (*8*), cross-flow of solvent (flow FFF) (*9*), thermal gradients (thermal FFF) (*10*), gravity (steric FFF) (*11*), and magnetic field gradients (magnetic FFF) (*12*). Some of the properties which have been shown to affect the interaction of a particle with the field and carrier are mass, size, shape, density, porosity, and the surface nature of the particle. Giddings has suggested that FFF could be used to determine the "state of aggregation" (*13*).

Magnetic field-flow fractionation has been demonstrated to be another extension of this general approach (*12*). In addition to the previously mentioned parameters, magnetic susceptibility has been shown to be a consideration in determining the strength of interaction of a particle with the field. The use of a magnetic field to induce particle separations as well as the effect of a magnetic field on the stability of a suspension of particles of high magnetic susceptibility will be the subject of this article.

THEORY

Giddings has derived relationships which describe the retention behavior for FFF systems in general (*6*):

$$R = V^\circ/V_R = 6\lambda\{\coth(1/2\lambda) - 2\lambda\} \quad (1)$$

where R is the retention ratio, V° is the unretained volume, V_R is the retention volume, and λ is the dimensionless retention parameter.

The retention ratio is less than 1 for particles which are retained and decreases as retention increases. The unretained volume (V°) was taken to be the calculated channel volume. The dimensionless parameter, λ, is seen to be the ratio of l, the mean solute layer thickness, to w, the width of the channel. One can understand the meaning of l by considering it to be a ratio of the diffusion coefficient (D) to the field-induced velocity (U):

$$l = D/U \quad (2)$$

Thus, it is seen that retention increases with particle size (smaller D) and also increases with an increase in field strength (larger U).

EXPERIMENTAL

The iron oxide particles were obtained from Hercules (Wilmington, Delaware). They are reported to be approximately 0.80 μm in length with an aspect ratio of 6 to 1. BET surface areas are typically 13–15 m^2/g. Technical grade acetonitrile was used after distillation. Triton X-100 from Rohm & Haas (Cranston, Rhode Island) was used as received.

The channel is 18 × 1 × 0.025 cm and has a geometric volume of 450 μL. A model 341A syringe pump from Sage Instruments (Cambridge, Massachusetts) was used with a 10-mL syringe. The power supply was a Lambda model LE 101-M (Melville, New York) and could deliver 0.6 to 2.5 A dc current. The injector was constructed with nonmagnetic materials and had a capacity of 57 μL. Sample concentration ranged from 10–160 ppm (w/v). Detection was accomplished with a Schoeffel model 770 (Westwood, New Jersey) variable wavelength liquid chromatography detector (450 nm). A Spectra-Physics (Santa Clara, California) computing integrator model 4200 was used to determine peak heights and peak areas.

RESULTS AND DISCUSSION

Prior to studying retention characteristics, the detector response was determined by running a series of concentrations from 10 to 160 ppm iron oxide particles suspended in acetonitrile. These were done with the field off and the field on (magnet current, I = 1.2 A) to better understand the effect of the magnetic field on detector response. In general, the elution behavior was that of an exponential dilution flask or a flow injection analysis (FIA) device with one mixing chamber (*14*). The peaks rose sharply and then showed a distinct exponential tail. The response expressed as the integrated area of the peak was found to be linear for both the conditions of field on and off (Fig. 1). However, when the response is considered in terms of the peak height, it is linear, but with a great deal of scatter in the data with the magnetic field turned off (Fig. 2). When the field is on, the scatter is decreased measureably and the system is linear only to about 100 ppm. The nonlinearity of the response at the larger sample sizes is indicative of a

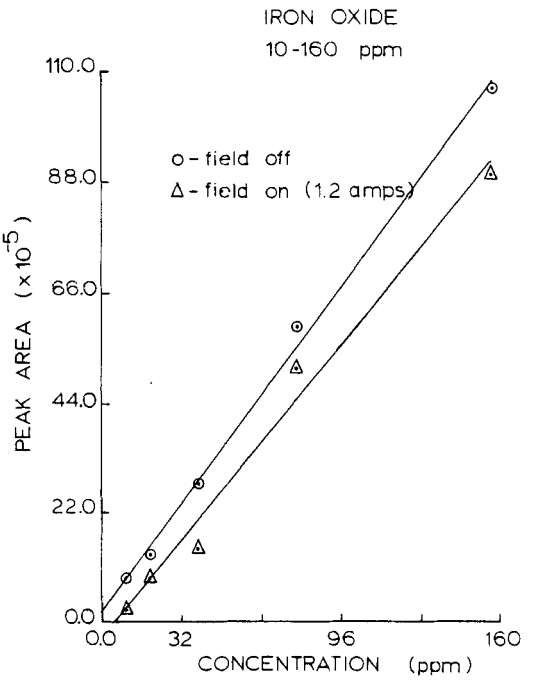

FIG. 1. Detector response as peak area vs particle concentration.

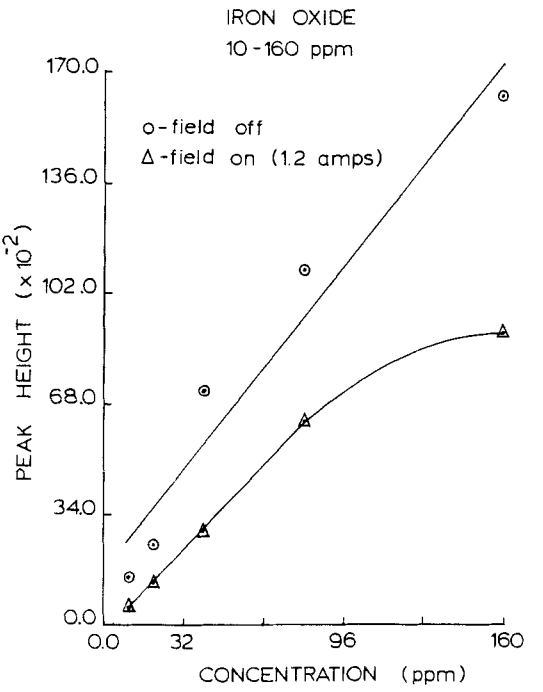

FIG. 2. Detector response as peak height vs particle concentration.

change in the effective field within the channel because of the presence of the particles. This causes a greater fraction of the sample to reside in the region very close to the wall where retardation by the FFF experiment is significant. This is consistent with the increased tailing for the larger sample sizes along with the linearity of the peak area measurements. The decrease in scatter for the field on case was attributed to an orientational effect of the field on the particles. This orientational effect has also been noted when performing a light-scattering experiment on these particles suspended in acetonitrile (*15*).

The impact of increasing the field strength on the elution of a 40-ppm suspension of the iron oxide particles is shown in Fig. 3. The peaks were reduced in size and broadened as a function of the increasing field; however, only a very small fraction of the injected sample was retained. Retention of the major portion of the sample was not observed because the sedimentation rate was quite slow for these particles in dry acetonitrile. Unacceptable band broadening resulted when stopped flow procedures, designed to increase the settling by increasing the relaxation period, were

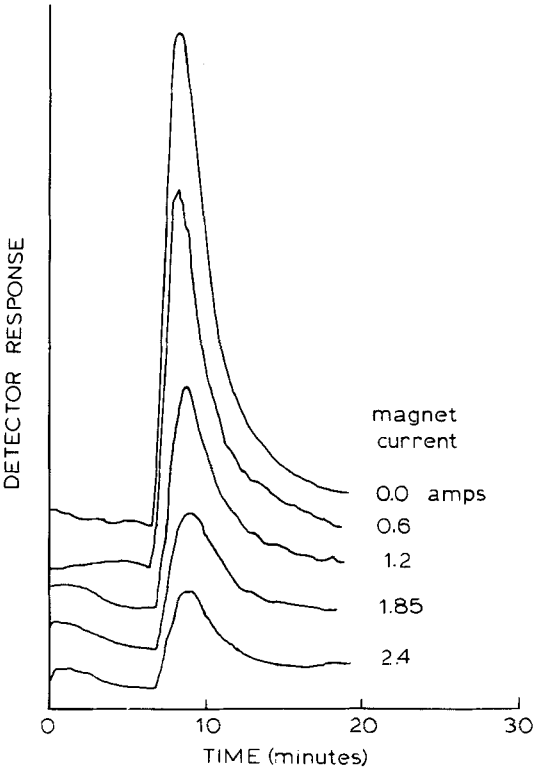

FIG. 3. Fractograms at 0, 0.6, 1.2, 1.85, and 2.4 A (magnet current).

used. This is most probably due to the long flow time constant inherent in a system with a large extra channel volume. It was decided that the addition of a surface-active agent would enhance settling and provide retention without increasing band broadening. An increased sedimentation rate and some degree of flocculation was accomplished by the addition of trace amounts of water. The increase in the fraction of the sample experiencing field-flow behavior is evidenced by the three peaks shown in Fig. 4. The first peak is unretained material that did not settle into the slower flow streams. The second and third peaks represent retained material, and their elution volume increases with an increase in field strength as seen in Fig. 5. The retention of the third peak increases at a faster rate than that of the second one. The critical parameter for retention in magnetic FFF is the volume of the particle and, based on this understanding, peaks two and three have been shown to be "monomers" (single particles) and "dimers," respectively

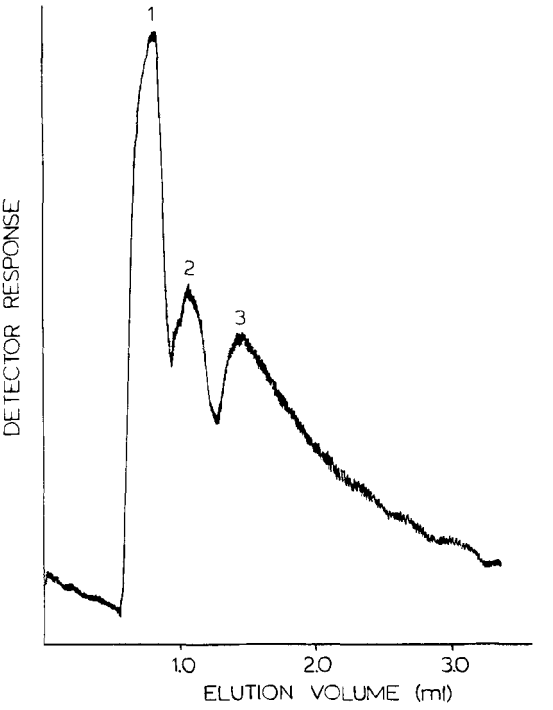

FIG. 4. Fractogram of 0.8 μm iron oxide particles at a magnet current setting of 1.2 A. A 57-μL sample of a 40-ppm suspension of iron oxide particles in CH_3CN with 5 ppt H_2O was added to a carrier solvent of CH_3CN (flow rate = 100 μL/min.).

(*12*). It is important to note that "trimers" and further oligomers would be expected to elute later than the dimers if they were present, since the results of such aggregation would be even larger particle volumes. The finding of only "monomers" and "dimers" in the experiment is consistent with the concept of a diffusion-controlled flocculation rate, which predicts a very low probability for the formation of larger oligomers in the time frame of this experiment.

In a more careful attempt to optimize the behavior of the iron oxide/acetonitrile suspension, it was decided to use a nonionic surfactant (Triton X-100) in order to increase the sedimentation rate without increasing flocculation. At a level of 500 ppm of Triton X-100, one could see that large aggregates were forming in the suspension and it settled very rapidly compared to the dry or water-modified acetonitrile suspensions. These Triton-modified systems could be easily redispersed by shaking or ultrasonic mixing.

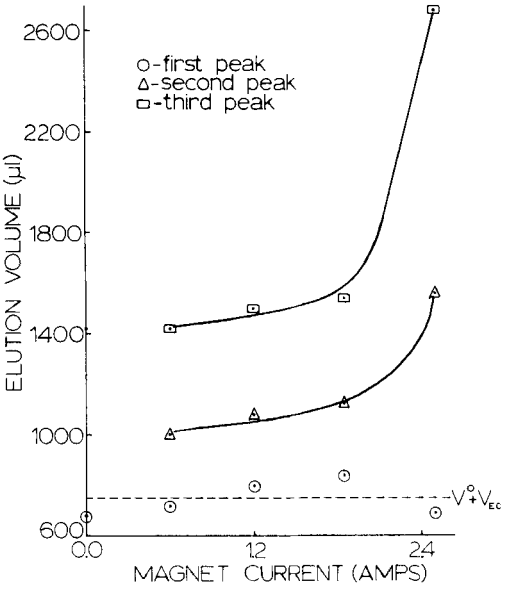

FIG. 5. Elution volume of iron oxide particle fractogram peaks as a function of magnet current. Sample and carrier solvent conditions are the same as shown in Fig. 4.

When fractograms were run with the surfactant-modified acetonitrile without the magnetic field, large spikes and jagged peaks were observed which were indicative of large aggregates that occasionally got stuck in the detector cell (Fig. 6). One could see the large aggregates moving through the clear plastic tubing which exited the detector. The detector cell had to be cleaned after each run when the field was off. When this experiment was repeated with the field on, there was no evidence of flocculation. The fractogram had two peaks which were smooth and returned to baseline with no help needed from the operator (i.e., the detector cell did not need to be cleaned). These peaks were at 750 and 1100 μL, respectively. Based on the previous discussion of the water-modified system, this would suggest that the material in the second peak is "monomeric" (i.e., not flocculated) and the first peak is unretained material. Thus, it is seen that for this surfactant-modified system, the magnetic field causes enhanced stability to flocculation.

The reason for the increased stability is that the particles are oriented in a specific direction and also are restricted somewhat in their ability to move in three dimensions. This enhanced stability was not perceptible with the water-modified system, although it is certain that the particles were oriented by the field. This is due to the nature of the surface modifiers and the way

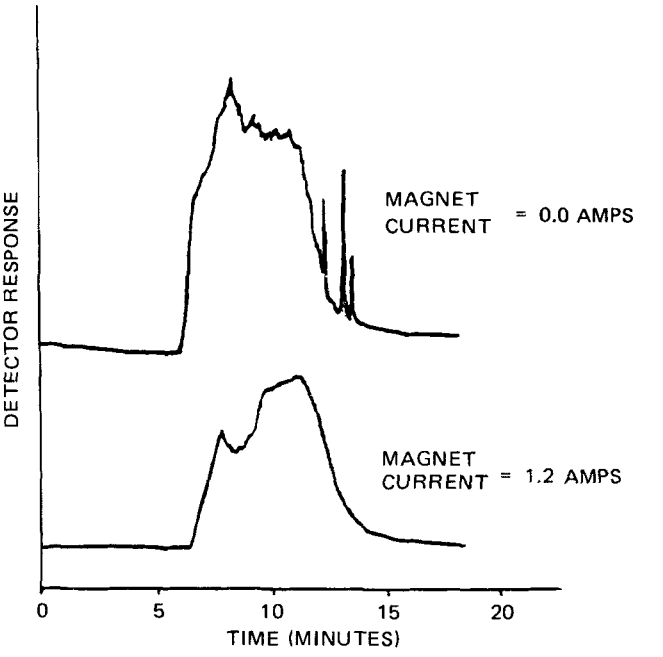

FIG. 6. Fractograms of a 40-ppm suspension of iron oxide particles with 500 ppm Triton X-100 added. Both field on (1.2 A) and off. (Flow rate = 100 μL/min).

they change particle–particle and particle–solvent interactions. In the case of both the water and the surfactant, one would expect a partial destabilization of the suspension due to a reduction in the surface charge which causes interparticle repulsion. The surface of the water-modified iron oxide is more compact and presents less viscous drag when a particle moves through the solvent than does a surfactant-modified particle. Also, when flocculates are formed with the water-modified system, they tend to be more tightly bound together and are more difficult to redisperse. The surfactant-modified particles, on the other hand, have a gel-like surface which extends farther out from the particle. These systems flocculate more quickly because of the large, soft shell of material on each particle, but are also redispersed easily (this situation is also desirable for paint pigments; for instance, see Ref. *16*). The sluggish motion of the surfactant-modified particles is further slowed by the presence of the magnetic field, and therefore no appreciable amount of flocculation is seen.

A study of the time dependence of this system was done in terms of peak areas as a function of flow rate (Fig. 7). As the flow rate increases, the area

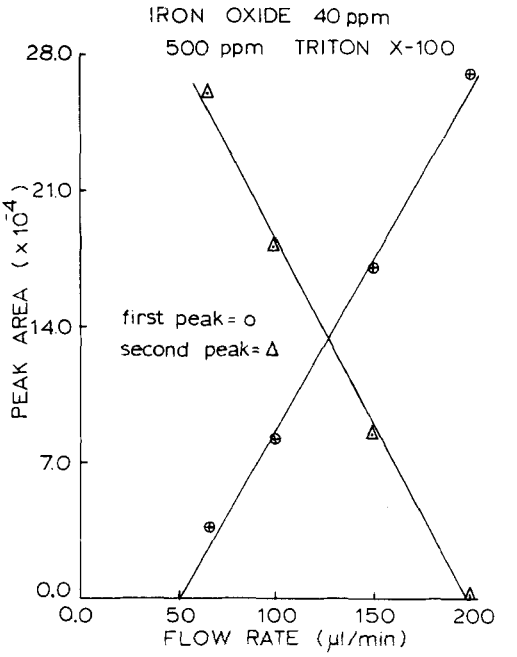

FIG. 7. Variation of peak areas with flow rate for Peaks 1 and 2 in Fig. 6.

of the first peak (unretained) increases because there is less time for the particles to settle into the lower flow streams near the wall. The second peak diminishes in area until it is virtually gone at the highest flow rates. The reverse situation is the result of using slower flow rates. At the slowest flow rates used, the first peak nearly disappears and only the second one is present. In Table 1 it can be seen that the sums of the areas of these two peaks is nearly constant. This "mass balance" effect would not occur if a significant amount of material were flocculated because the detector

TABLE 1

Flow rate (μL/min)	A	A'	Sum
65	3.5	25.9	29.4
100	8.1	18.3	26.4
150	17.0	8.4	25.4
200	27.0	0.2	27.2

response factor would be expected to be quite different for dimers or larger flocs as compared to single particles.

CONCLUSIONS

The magnetic FFF technique has been shown to be quite sensitive to the surface nature of particles which have been suspended in a liquid. The retention of iron oxide particles has been shown to be a function of surface modification and also shown to be influenced by the strength of the magnetic field. Magnetic FFF is also able to provide information that will increase the understanding of the surface interactions of small particles in terms of other parameters such as size, shape, and magnetic susceptibility.

The response of a photometric detector has been shown to reflect the orientation of the particles by the field as well as providing a useful linear range in terms of concentration vs peak area.

Future studies will include the use of alternate surface-active agents as well as the characterization of other magnetic materials such as chromium oxide. Sedimentation and flocculation rate studies can be done by using the change in flow rate vs the change in peak areas as described above. The use of this system as an FIA device will be investigated by treating the effective magnetic field as a reagent or experimental parameter in particle characterization.

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