Vertical Concentration Profiles in Colloidal Fluids Measured by FTIR-ATR Spectroscopy

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Introduction

Phase separation or sedimentation under gravity occurs in a wide variety of colloidal fluids.[1] An essential feature of these phenomena is the height dependence of the concentrations of the colloidal components. However, the measurement of such concentration profiles is not an easy task. In the study of sedimentation, one approach is to perform height-resolved light scattering measurements. From such measurements on nearly monodisperse latex spheres, Piazza et al.[2] could derive the hard-sphere equation of state. Mengual et al.[3] introduced a new technique (the "TURBISCAN") which can even be used with highly turbid systems, measuring both the transmitted and backscattered light intensities. However, two limitations of the light scattering approach are that the interpretation is model-dependent and that it seems to be limited to nonabsorbing systems. In the study of phase separation, the concentrations of different components in two coexisting phases have, to our knowledge, not been determined in situ. Colloidal phase diagrams have been determined by dispersing different amounts of colloids and visually inspecting the number of phases,[4] measuring their volumes,[5] or analyzing their concentrations ex situ.[6] Here, we introduce height-resolved FTIR-ATR, a technique with which the concentrations of different colloidal components can also be measured in highly absorbing systems such as ferrofluids. The Fourier transform infrared (FTIR) spectrum of a colloidal dispersion is recorded as a function of height, using the attenuated total-internal-reflection geometry (ATR).

Infrared spectroscopy is a long-standing technique for the analysis of liquids.[7] Different chemical species can be distinguished from the energies at which their vibrating

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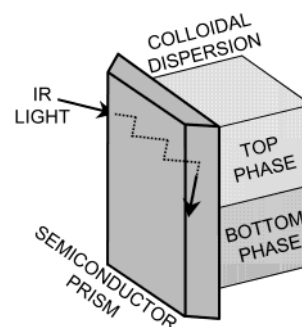

Figure 1. Schematic representation of the FTIR-ATR cell.

chemical bonds absorb. ATR spectroscopy is based on the interaction of light with matter at the boundary of two media with different refractive indices. In the ATR geometry, infrared light fully reflects internally inside an infrared-transparent crystal of high refractive index brought into physical contact with the liquid. Total internal reflection occurs because the angle of incidence exceeds a critical value (Mohammadi[8] proposed a highly sensitive method of measuring this critical angle to determine the index of refraction of colloidal dispersions). The light intensity is not abruptly zero on the liquid side of the crystal/liquid interface, but it drops exponentially across a distance which is a fraction of the optical wavelength. The radiation thus more or less penetrates into the liquid before it is reflected, and its intensity is attenuated due to absorption by the liquid.[9] Because of this sensitivity to the near-surface region, FTIR-ATR can for instance be used to study the surface (electro)chemistry of semiconductors[10] or the surface chemistry of colloids adsorbed to semiconductors,[11] provided that the semiconductors can be used as an internal-reflection element. In most commercial FTIR-ATR cells for the analysis of liquids, the crystal/liquid interface is horizontal, but we implemented a vertical configuration allowing measurements as a function of altitude in the gravitational field. The short, reproducible optical probe depth of the ATR method has the advantage that quantitative measurements are possible on highly absorbing samples.[9] The systems studied here are opaque to the naked eye even after 100-fold dilution, the ferrofluid being ink-black and the silica dispersion milky-white.

Experimental Section

Figure 1 illustrates the principle of the method. A semiconductor ATR prism is one of the sidewalls of a cell, which holds the colloidal dispersion. Infrared light is focused at a certain height on one of the two beveled vertical sides of the prism. Light propagates horizontally inside the infrared-transparent prism, making several total internal reflections. The light is detected as it comes out of the opposite beveled side of the prism. Upon each reflection at the semiconductor/liquid interface, absorbance

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occurs by chemical species near the interface. By using a FTIR spectrometer, spectra are obtained which allow the simultaneous detection of different species at different wavenumbers. Vertical profiles are obtained by varying the height at which the infrared light is focused.

The prism was made from a 2.0-mm-thick two-side-polished high-resistivity (10^3 Ω cm) silicon wafer grown by the float-zone technique (ITME, Poland). This material combines sufficient transmission in the infrared range with resistance against most nonoxidizing chemicals. A 15 × 40 mm rectangle was cut from the wafer, and the long sides were polished at angles of 45°. The prism was used to replace one of the windows of a rectangular glass cell, using a Teflon seal, with an area of 9 × 31 mm exposed to the colloidal dispersion (≈2.25 reflections at the semiconductor/liquid interface). The collimated light beam of the spectrometer was focused on a 1.0-mm-high rectangular hole in a metal plate in front of one beveled side of the prism; before being detected, the light coming out of the prism passed through a second 1.0-mm-high rectangular hole at the same height in a second metal plate. It was verified that the height resolution obtained in this way was 1.0 mm. The part of the liquid probed extended a distance of about $\lambda/25$ from the window surface (0.4 μm at a wavenumber of 1000 cm^{-1}).[12]

The FTIR spectrometer was a Perkin-Elmer 2000 with a Globar as the infrared source and a DTGS detector operating at room temperature. The absorbance at a given wavenumber and height is defined as $-\log_{10}[T/T_{ref}]$, where T is the transmission of the colloidal dispersion and T_{ref} is the transmission of pure solvent. According to Lambert−Beer's law,[7] the absorbance consists of different contributions $L\epsilon_i c_i$ of chemical components i, where L is the optical path length, c_i is the concentration of i, and ϵ_i is its extinction coefficient at the given wavenumber.

Results and Discussion

The infrared spectra A and B in Figure 2 were obtained at two different heights in a ferrofluid. The dispersion contained the solvent toluene, magnetite particles (Fe_3O_4, 9 ± 2 nm in diameter, sterically stabilized by an oleic acid surface layer), and free poly(dimethyl siloxane) polymer (41.5 kg mol^{-1}, radius of gyration ≈ 8.5 nm). Phase separation in this system was investigated before, using a magnetic sensing coil.[13] As was done in that study, samples were left to equilibrate for about 16 h to obtain a steady-state height profile. The contributions of different chemical components to the infrared spectrum are easily distinguished (compare with reference spectra C−E). Spectrum C of the polymer is dominated by peaks at 1261 cm^{-1} (Si−CH$_3$ bending mode[14]), 1096 and 1016 cm^{-1} (Si−O stretching modes[14]), and 804 cm^{-1} (CH$_3$ rocking mode[14]). The magnetite particles (spectrum D) have Fe−O vibrational modes[15] below 750 cm^{-1}, C−H modes of chemisorbed oleic acid at 2926 and 2854 cm^{-1}, and peaks at 1530 and 1440 cm^{-1}, ascribed to stretching modes of carboxylate groups[16] obtained when oleic acid becomes attached to the magnetite surface.[17] The absence of a strong carbonyl vibration at 1710 cm^{-1} (spectrum E) indicates that almost no free oleic acid is present in the ferrofluid.[16] The bottom of the ferrofluid is clearly magnetite-rich and polymer-poor, whereas the top is magnetite-poor and polymer-rich. The ratio of the absorbance by oleic acid surface
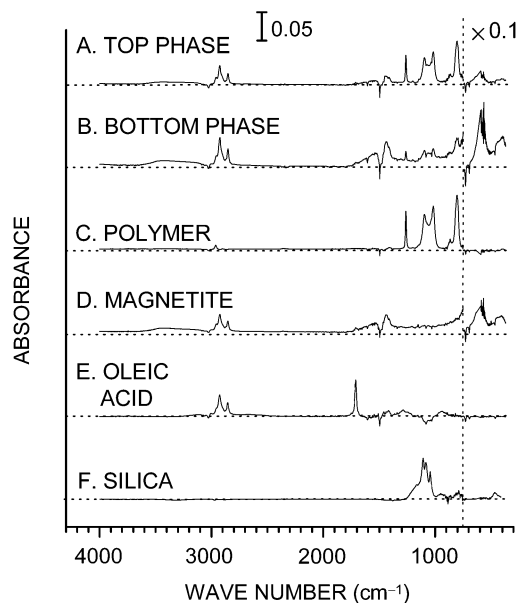
(12) The intensity E^2 of the electric field E drops by a factor of e^{-1} at a distance equal to $(\lambda/4\pi)(n_1^2 \sin^2 \theta - n_2^2)^{-1/2}$, where λ is the optical wavelength, θ is the angle of reflection (45°), n_1 is the refractive index of silicon (3.45), and n_2 is that of the liquid (1.50 for toluene, 1.36 for ethanol) (ref 9a).

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Figure 2. Infrared spectra obtained using the vertical ATR prism. (A) and (B) were measured at different heights in a phase-separated ferrofluid. For comparison, (C) is a 130 g/L poly(dimethyl siloxane) solution in toluene, (D) is a 890 g/L magnetite dispersion in toluene, and (E) is a 22 vol % solution of oleic acid in toluene. (F) is the silica dispersion used in the sedimentation experiments. The vertical scale bar indicates an absorbance of 0.05 per 2.25 reflections (10 times less sensitive scale below 750 cm^{-1}).
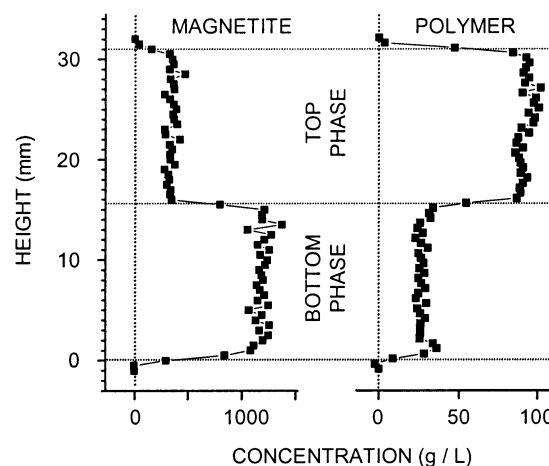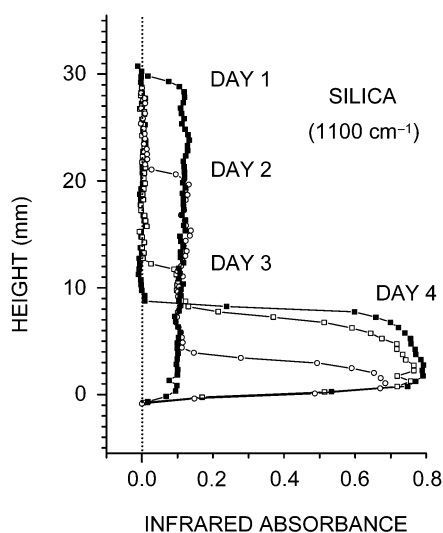

Figure 3. Vertical concentration profiles of magnetite and free polymer in a phase-separated ferrofluid.

groups to the absorbance by magnetite indicates that the particles at the top of the ferrofluid have a higher specific surface area than the (larger) particles at the bottom. Infrared spectroscopy appears to be a convenient technique to study size fractionation in this polydisperse system, an effect which severely complicates the study of phase separation using a magnetic sensing coil.[13]

Vertical concentration profiles of the ferrofluid are shown in Figure 3. The vertical axis gives the height in the dispersion (bottom and top at 0 and 31 mm; the distance scanned along the prism is slightly longer, see Figure 1). The spectra obtained at each height were fitted as linear combinations of reference spectra C and D (Figure 2), obtained for homogeneous samples of known concentration (fit range, 1350−370 cm^{-1}). The linearity of the absorbance of magnetite and polymer as a function of concentration was verified. This fit method is chosen here for its simplicity, to illustrate the technique; a more

Figure 4. Vertical profiles of the absorbance at 1100 cm^{-1} of silica particles dispersed in ethanol before (day 1) and after sedimentation (day 4).

complete analysis of the data would take into account size fractionation (by separately fitting the contributions of the magnetite core and the adsorbed surface layer of the colloid particles). The scatter of the points is due to the low signal-to-noise ratio at low wavenumbers, which still has to be improved. The curves in Figure 3 are equilibrium profiles and show phase separation with a sharp interface. The phase separation is due to the depletion interaction, a well-known entropy-driven effect when a concentrated dispersion of colloidal particles is mixed with nonadsorbing polymer molecules of similar radius of gyration.[18]

The height profiles in Figure 4 are of silica spheres dispersed in ethanol which take about 4 days to sediment to the bottom of the cell at 20 °C (spheres with a diameter of 880 nm, stabilized by a surface layer of 3-methacryl-oxypropyltrimethoxysilane,[19] initial silica volume fraction = 14%). The sedimentation rate was about 3 times as slow as the Stokes velocity for noninteracting particles at infinite dilution.[1] This hindered settling is due to repulsion between the negatively charged silica particles, as discussed in detail elsewhere.[19] The infrared spectrum (Figure 2F) is dominated by Si—O-related modes[20] below 1300 cm^{-1}; the wavenumber-independent baseline above 1300 cm^{-1} indicates that optical scattering is negligible in this range. As the particles sediment, the average absorbance of the entire sample at 1100 cm^{-1} almost doubles (Figure 4). The main reason is that the infrared probe depth is smaller than the particles[12] and that the detected silica particles are, on average, closer to the prism wall in the sediment than in the initial dispersion. Absorbance increases less at lower wavenumbers, where the infrared probe depth is larger.[12]

The limitations of the method are partly related to the fact that only a thin layer of colloidal dispersion near the cell wall is analyzed. For straightforward interpretation, the first micrometer of the dispersion must be representative of the bulk, and surface effects such as adsorption of the colloidal particles to the prism should be negligible. This is the case for concentrated dispersions of nanoparticles with an organic stabilization layer such as in Figure 3, but not for particles larger than the penetration depth of the IR radiation, such as the micrometer-sized particles of Figure 4. Other authors have used an evanescent wave of visible laser light to study the interaction of a flat surface with single colloidal particles of several micrometers.[21] Another difficulty is that, in principle, the penetration depth of the IR light depends on the concentrations of the chemical components, which affect the refractive index and can shorten the probe depth by absorption.[9] Quantitative measurements therefore require calibration measurements on homogeneous dispersions with known concentrations. Finally, the colloidal components whose concentrations are to be determined should have sufficiently distinct infrared spectra. It is difficult to separate the spectral contributions of various organic molecules with similar chemical groups. The technique appears well suited to study the phase behavior of colloidal systems with a small number of different components, for instance, two types of inorganic nanoparticles dispersed in an organic solvent.

Conclusion

Height-resolved FTIR-ATR enables the in situ measurement of vertical concentration profiles in inhomogeneous colloidal fluids. At first approximation, infrared absorbance is proportional to concentration, so that it can be seen as a linear way of counting particles. Different colloidal components can be analyzed simultaneously from their different contributions to the infrared spectrum. To our knowledge, Figure 3 presents the first in situ measurements of concentrations of colloidal particles and polymer molecules in two coexisting colloidal phases as a function of height. A wide range of systems can in principle be studied, because almost all chemical species absorb in the vibrational infrared range and the infrared spectrum is different for each species, especially when they contain different chemical groups. Not only organic molecules but also solid inorganic particles dispersed in a solvent can be investigated. An extremely high absorbance or turbidity is not a restriction, as demonstrated by the presented data. Soon, the method could for instance be used to gain new insight into the phase behavior and size fractionation of ferrofluids. Ferrofluids are of current interest as the starting point for preparing magnetic self-assembly structures, a wet process which puts stringent requirements on the monodispersity of the magnetic particles.[22]

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