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Formation of Agglomerates in a Complex Diluted Liquid in Absence of the Magnetic Field

I. Luminosu, N. Pop, V. Chiritoiu and B. Arvinti

University "Politehnica" of Timisoara, Department of Physical Foundation of Engineering,
Bv. Vasile Parvan No. 2, 300223, Timisoara, Romania

Abstract: The complex fluids, magnetic fluids used in technological applications in particular, should be stable so that the parameters of the installations don't change over time. Colloid, a ferrofluid in particular, is stable if aggregates formed under the effect of London and Van der Waals forces between solid particles (particularly magnetite), have small dimensions. This paper continues and develops the studies concerning the optical properties of ferrofluids [3] and shows that the dimensions of the aggregates can be estimated by measuring the spectral absorption coefficient. Since the size of aggregates from complex fluids influences the stability and opportunity of their utilization in practical applications, the purpose of our paper is to estimate, using optical methods, the dimensions and numbers of he solid particles from aggregates which are formed in a very diluted complex liquid. In this case, using optical measurements of the spectral absorption coefficient, the size of aggregates varies from 11 to 44 nm. Average number of nano-particles is 4. The ferrofluid studied is stable and, thus, can be trustfully used in technological and biological applications.

Keywords: absorption, extinction, ferrofluid, spectral, spectrophotometer.

1. Introduction

The complex liquid studied in the present paper constitutes a biphasic solid-liquid system, which behaves like an homogenous medium in the presence, as well as in the absence of an electromagnetic field [1]. For the complex liquid/ fluid under study, a ferrofluid in particular, the dispersant agent is earth-oil, the solid phase is constituted of nanometric magnetite particles and the stabilisant is oleic acid. The complex liquid studied is indexed by FP10.

The properties of the complex liquids are influenced by the preparation method, which also determines their microstructure [2,3].

The medium diameter of the magnetite particles imersed in FP10 liquid has been determined using the electronic microscope and has revealed the following results: d = 11.354 nm [4,5].

The studies concerning complex liquids are of importance because of their utility in practical applications, as we can mention two research directions:

- in biology, the magnetic liquids are used for transport of cells and viruses
- in heliotechnics, the magnetic liquids are used as absorbent agent, spread in a very thin layer, of the solar radiation [8,9].

Between the solid particles of the solution, London and Van der Waals forces appear. Under the action of these forces, the magnetite particles tend to group themselves in aggregates. The aggregates lie under the influence of gravitational and viscosity forces of the liquid and form sediments, modifying thus the composition of the system. This way, the opportunity of the technological utilization of the complex liquid is affected.

Inside the complex liquid, unique particles and smaller (including 4 – 20 particles) or bigger (over 1000 particles) aggregates coexist [10].

The magnetic liquids are studied, in the presence or in the absence of the magnetic field, using several methos: optical, electronic microscopy and magneto-optical techniques.

With regard to light, the magnetic colloid behaves like an homogenous medium and respects the law of Bouguer-Lambert-Beer if the medium diameter of the solid particles at most equals the tenth part of the wavelength of the radiation [11,12].

The present paper studies a very diluted complex system, in the absence of the electromagnetic field, using experimental data concerning the spectral absorption of unpolarized light. Experimental data have been obtained employing the spectrophotometer SPECORD UV-VIS.

The paper continues and develops the sudies regarding the optical properties of ferrofluids [13, 14, 15] and shows the fact that aggregates might be explored through measuring the spectral absorption coefficient.

Due to the fact that the dimensions of the aggregates of complex liquids influence the stability and also the opportunity of their use for practical applications, the paper proposes to estimate, applying to one optical method, the dimensions and the number of solid particles of aggregates which are formed in a very diluted complex liquid.

The paper highlights that in diluted solutions of the studied complex liquid, there coexist magnetite particles and aggregates with a diameter measuring between 11 nm and 44nm. As a consequence, the number of solid particles contained by aggregates varies between 1 and 4.

The small dimensions of the aggregates of the complex liquid studied add their contribution to the stability of the fluid and realize the necessary condition which enables the use of these liquids for practical applications.

In the near future, complex liquids, ferrofluids in particular, will be used to develop some new techniques for preparing sintered materials. So, in a rotational external magnetic field, the ferrofluid rotates also. The centrifugal forces might separate the components of the complex liquid. Due to this fact, the reduction to Fe of ferroferric oxide, the mixture is obtained of non-magnetic materials (ceramics, polymers, glass and so on) and magnetic nanoparticles (Fe).

2. Theoretical aspects concerning the absorption of unpolarized natural light

The spectral absorption coefficient of monochromatic unpolarized light is:

$$K = \frac{\in}{l} \tag{1}$$

The significance of the notations used in Eq. 1 is as follows:

- K – the natural absorption coefficient, $\langle K \rangle_{SI} = m^{-1}$;
- $\in$ - the extinction of light;
- l - the thickness of the absorbent layer, $\langle l \rangle_{SI} = m$;

The natural extinction coefficient ε is described through the following formula:

$$\varepsilon = \frac{K}{c} \tag{2}$$

In Eq. 2, c represents the concentration of the solution. The coefficient ε shows the property of being independent of the concentration but dependent of the wavelength.

In order to establish if the magnetic liquid behaves like an homogenous solution, the following procedure has been applied:

- one of the samples has been considered as a reference sample;
- the extinction coefficient , $\varepsilon_{i,j}$, described in relation (2), has been exemplified for i concentrations and j wavelengths
- for each concentration and wavelength the rates have been calculated

$$Z_{i,j} = \frac{\varepsilon_{i,j}}{\varepsilon_{r,j}} = \frac{c_r}{c_i} \cdot \frac{K_{i,j}}{K_{r,j}} \tag{3}$$

The significance of the notations used in Eq. 3 is: i – the number of the sample, j – the order number of monochromatic radiation, r – the reference sample. $Z_{i,j}$ represents the natural spectral extinction coefficient of the sample i reported to the natural extinction coefficient of the reference sample.

If the solution is homogenous and the aggregates' diameters for the radiation λ_j have smaller values than $\lambda_j/10$, then for the radiation λ_j, the spectral extinction coefficient, $\varepsilon_{i,j}$, does not suffer any modifications with the variation of the concentration c_i. For another wavelength, the spectral extinction coefficient may have the another value but still the same value for all concentrations, in other words for a given wavelength $\varepsilon_{i,j} \neq f(c)$.

Taking these conditions into account, the ratio $Z_{i,j}$, calculated with equation (3) must equal the unity with respect to all values of i and j.

If the diameters of the aggregates are greater than $\lambda_j/10$, the law of Bouguer-Lambert-Beer is not respected anymore and the ratio $Z_{i,j}$ does not equal the unity any longer. Knowing the minimal starting wavelength, λ_{min}, when, with the increase of the radiation wavelength, the law of Bouguer-Lambert-Beer is respected ($Z_{i,j}$ tends to 1), the aggregates' diameter can be estimated with the following equation: $D=\lambda_{min}/10$. The approximate number of solid particles n which are forming an aggregate is: $n=D/d$ (d represents the medium diameter of the magnetite particles).

The medium spectral value of $Z_{i,j}$ is:

$$\overline{Z}_j = \frac{1}{n}\sum_{(i)} Z_{i,j}, n = 5 \tag{4}$$

At the processing of experimental data, the geometrical errors of sizes are considered as nulls, $\Delta l = 0$. The coefficient $\in$ has been determined employing the spectrophotometer SPECORD UV-VIS, with the following error: $\Delta\in = \pm 0.01$.

The errors taken in consideration for the sizes c and K are: $\Delta c = \pm 1.59 \cdot 10^{-6}$ m^{-3}, $\Delta K = \pm 1$ m^{-1}.

It has been determined that the medium absolute error for the ratio $Z_{i,j}$ may be calculated using the equation:

$$\Delta\overline{Z}_j = \frac{1}{n}\sum_{(i)}\left[\frac{\in_{i,j}/l}{c_i K_{r,j}}\left(1+\frac{c_r}{c_i}\right)|\Delta c| + \frac{c_r}{c_i K_{r,j}}\left(1+\frac{\in_{i,j}/l}{K_{r,j}}\right)|\Delta\in|/l\right] \tag{5}$$

3. Experimental

The spectral absorption of light in the very diluted complex liquid has been studied using the spectrophotometer SPECORD UV-VIS. The working diagram of the spectrophotometer SPECORD UV-VIS is presented in Figure 1. The components of the apparatus are: 1 – light source (xenon flash lamp), 2 – entrance slit, 3 – dispersion device (prism and holographic grating), 4 – exit slit, 5 – sample (cuvette), 6 – detector (photomultiplier tubes).

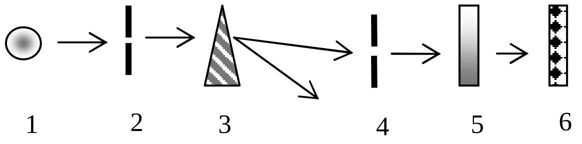

Figure 1. The working diagram of the spectrophotometer: 1 – source; 2 – entrance slit; 3 – dispersion device; 4 – exit slit; 5 – sample; 6 – detector.

The recording domain of the photometer is 200- 800 nm and raises the dependence $\in = f(\lambda)$.

Figure 2 presents the transmission of oil, the 1. curve, and the empty recipient, the 2 curve. The recipient is build of quartz with a wall thickness of 0.4 cm. Figure 2 shows that oil is transparent only in the visible domain. The natural coefficient of absorption is constant with the wavelength and takes the value $K'= 0.02$ cm^{-1}.

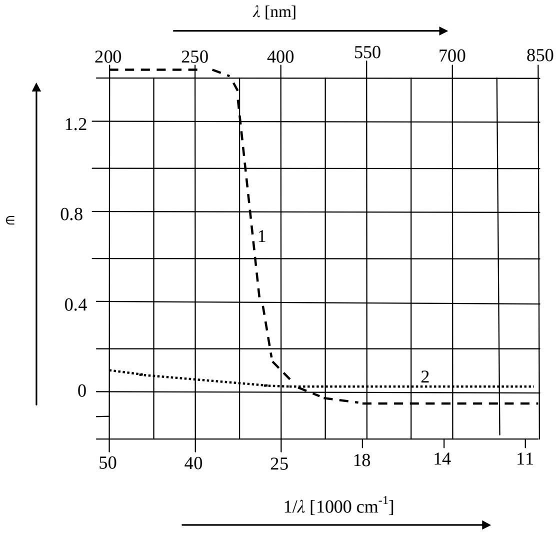

Figure 2. Light extinction:1- oil; 2 – recipient.

The studied ferrofluid has been prepared using the method of chemical precipitation detailed in [13]. Nanoparticles of magnetite are the result of the chemical reaction between ferric hydroxide and ferrous hydroxide. In order to avoid the formation of large aggregates and sedimentation, the solid particles have been coated with a layer of oleic acid. The polar groups of oleic acid are adsorbed by magnetite while the hydrocarbour group gets dissolved in earth-oil.

In Figure 3 is shown the micrography of the magnetite particles obtained using the electronic microscope (magnification $6{\cdot}10^4$X).

The ferrofluids has the following physical and chemical properties:
- a saturation magnetization of about 500 Gs;
- a global density of 1300 kg/m^3;
- the concentration of magnetite particles, $c=$ 550 kg/m^3;
- the medium diameter of solid particles, $d=$ 11.354 nm.

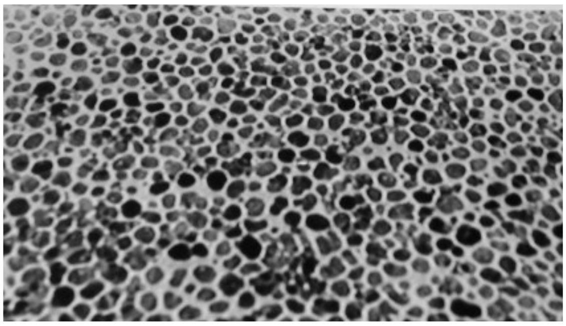

Figure 3. Micrography of the brown spar nano-particles.

The complex system obtained is opaque to light even if the layer is a very thin one. As a consequence, the colloid solution has been diluted using the method of dispersion, till the spectrophotometer has indicated the passing of radiation, with the wavelength measuring between 350 - 750 nm, through samples. This way diluted colloid systems have been obtained. Table no.1 presents the absolute and relative concentrations of magnetite in the prepared samples, samples which have been studied as referring to the concentration of sample no.1, $n_i=c_i/c_1$.

TABLE 1. Magnetite concentrations in the diluted colloid solutions

Sample no. (i)	1	2	3	4	5	6
c_i (kg/m^3)	0.0155	0.031	0.062	0.093	0.124	0.155
$n_i=c_i/c_1$	1	2	4	6	8	10

4. Results and Discussion

a) The variation of the extinction of colloid solution with the wavelength and the concentration is shown in Figure 4. For all concentrations, the absorption of radiation through the solution is first increasing with the wavelength, then decreasing and, finally, for wavelengths greater than 600 nm, the transmission of ligth is almost total.

There is a significant absorption of radiation through the solution for the wavelength interval 360 – 450 nm.

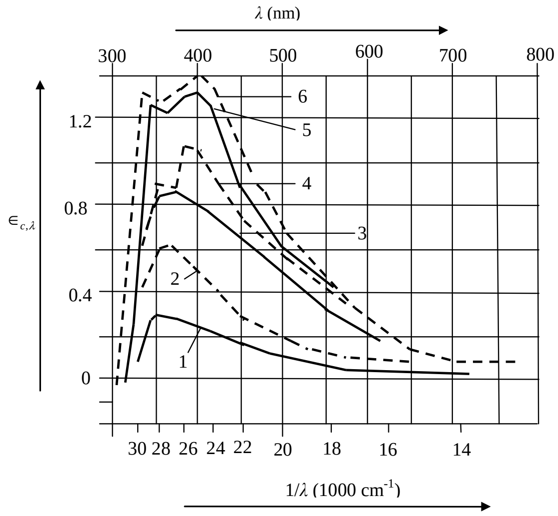

Figure 4. Extinction of colloid solution: 1-c=0.0155kg/m^3; 2-c=0.031kg/m^3; 3-c=0.062kg/m^3; 4-c=0.093kg/m^3; 5-c=0.124kg/m^3; 6-c=0.155kg/m^3.

b) The parametric variation of the spectral absorption coefficient $K_{c,\lambda}$ with the wavelength and respectively with the magnetite concentration is indicated in Figure 5 respectively in Figure 6. The absorption coefficient reaches maximal values for all concentrations found in the wavelength interval 380 – 400 nm, then rapidly decreases with the increase of the wavelength (Figure 5). The absorption coefficient increases with the concentration, for all wavelengths and tends to reach saturation values (Figure 6).

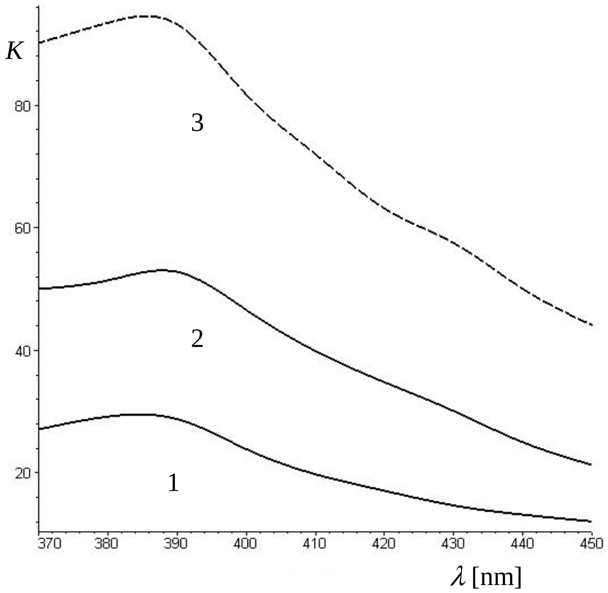

Figure 5. The variation of the absorption coefficient with the wavelength, c[kg/m^3]: 1- 0.0155; 2- 0.031; 3- 0.062.

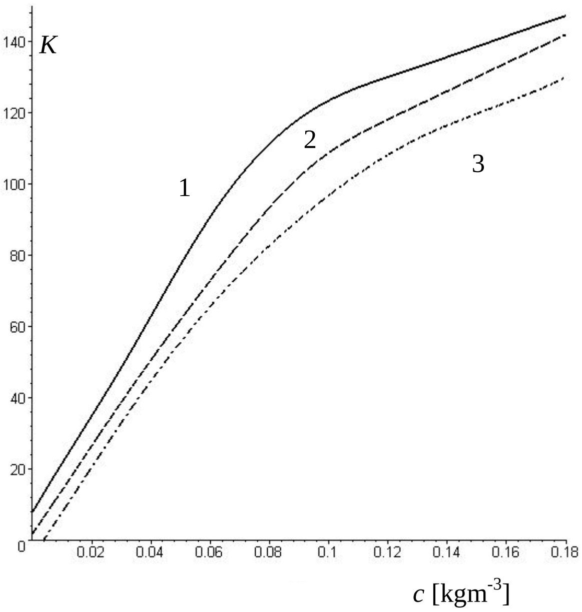

Figure 6. The variation of the absorption coefficient with the concentration, λ[nm]: 1- 390; 2- 410; 3- 430.

c) Table no.2 presents the the variation of the ratio $Z_{i,j}$ with the wavelength. As a reference sample has been considered the sample i=3 (c = 0.062 kg m^{-3}). The points' dispersion is greater for small wavelengths and great concentrations. The points are grouping around the unity-value as the wavelength increases and the magnetite concentration of the samples decreases.

d) The values of the ratio $\overline{Z}_j$ and the absolute errors $\Delta\overline{Z}_j$ are indicated in Table no.3. The ratio $\overline{Z}_j$ tends to the unity-value for wavelengths greater than 400 nm. As a consequence, the diameter of the aggregates measures D=40 nm and the approximate number of particles contained by an aggregate is n=4.

TABLE 2. The values of the ratio $Z_{i,j}$

λ[nm] c[kgm^{-3}]	370	380	390	400	410	420	430	440	450
0.015	1.20	1.28	1.18	1.10	1.14	1.20	1.17	1.10	1.20
0.031	1.12	1.12	1.03	1.16	1.14	1.18	1.22	1.08	1.13
0.062	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.093	0.80	0.84	0.84	0.96	1.00	1.00	1.05	1.18	1.18
0.124	0.94	0.74	0.96	0.88	1.13	1.17	0.91	0.93	0.96
0.155	0.73	0.64	0.66	0.70	0.77	0.79	0.88	0.95	0.96

TABLE 3. The medium values and the errors of the ratio $\overline{Z}_j$

λ_j [nm]	360	370	380	390	400	410	420	430	440	450
$\overline{Z}_j$	0.89	0.96	0.91	0.93	0.94	1.03	1.06	1.05	1.05	1.05
$\Delta\overline{Z}_j$	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.05	0.05	0.06
$\bar{\varepsilon}_j$[%]	3.37	2.08	3.29	3.22	3.19	2.91	2.83	4.76	4.76	4.76
$Z_{j,ad}$	0.89± 0.03	0.96 ± 0.02	0.91 ± 0.03	0.93 ± 0.03	0.94 ± 0.03	1.03 ± 0.03	1.06 ± 0.03	1.05 ± 0.05	1.05± 0.05	1.05± 0.05

5. Conclusions

In very diluted solutions of the ferrofluids FP10, aggregates with the diameter measuring between 11 nm and 44nm are formed. The medium number of the particles contained by an aggregate is 4.

The reduced number of particles contained by an aggregate indicates the good stability of the diluted solutions of the studied ferrofluids.

The stability of the diluted colloid indicates the opportunity of using it in technical application.

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