

THE INFLUENCE OF SURFACE MODIFICATION ON THE SEDIMENTATION AND RHEOLOGICAL CHARACTERISTICS OF FERRIC OXIDE SUSPENSIONS IN NON-AQUEOUS MEDIA

By

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Ferric oxide of the highest analytical purity was used to prepare products organophilized to various extents with an aqueous solution of ammonium stearate or a benzene solution of stearic acid. The selection of the degree of sorptive surface modification (organophilization) was made on the basis of the results of preliminary sedimentation and sorption studies. The surface properties of the products were investigated by immersion microcalorimetry. From this, conclusions were drawn as to the nature of the sorption, the specific surface area of the pigment, and the extent of coverage of the surface. The sediment volumes of the organophilized products were determined in organic media of different polarities. Detailed studies were made of the rheological properties of concentrated (coherent) suspensions in a paraffin oil medium of the products organophilized to various degrees. The parameters calculated from the correlation between the Bingham flow limit and the concentration of the suspension proved characteristic of the structures of the suspensions. Correlations were established between the results of adsorption, sedimentation and rheological examinations.

Introduction

Suspensions in organic media are finding ever wider application in modern technology. A knowledge of their properties is not only of interest from a theoretical aspect; it is also of fundamental importance during the preparation and use of, among others, varnish paints, oil-based boring muds, lubricating greases and metal-casting nucleus coating materials (black washes). The need often arises for the preparation of organosuspensions possessing suitable sedimentation constants and rheological properties (viscosity, flow limit, plasticity, tixotropy). For this task to be fully achieved, it is absolutely necessary to know the basic laws that govern the sedimentation and structure-forming properties of suspensions.

In suspensions in non-aqueous media the aggregation is generally more extensive than in suspensions in aqueous media. The explanation of this is that in the large majority of cases particles with polar surfaces are suspended in a less polar, or even an apolar medium, and consequently it is not possible for a lyosphere of appropriate thickness and structure to develop, this lyosphere leading to a substantial decrease in the interactions (adhesion forces) between the particles [1, 2].

The condition for the formation of incoherent suspensions, that there is practically no interaction at all between the particles of the disperse part, is only rarely

valid in the case of organosuspensions. Even at a relatively low suspension density, the flow gives rise to a considerable hydrodynamic interaction (which is not constant in space and time) between the particles. Generally accepted laws are available in connection with the stability and rheological properties of such incoherent or semicoherent systems [3—5]. The same can by no means be said in connection with the structure-forming, sedimentation and rheological properties of coherent (structured) suspensions. At the same time, the majority of real suspensions belong in this group, for the forces between the particles (termed adhesion forces below, in accordance with BUZÁGH [1]) cause aggregation leading to the development of a looser or more compact structure at the suspension densities employed in practice.

Fundamental investigations on the structure-forming characteristics of organosuspensions have been reported by VOET [5], McDOWELL and USHER [6], ROSCOE [7], PARFITT [8] and REHBINDER [9, 10].

The stability of the structure developing in a structured system is governed by the number and strength of the binding points between the particles. The number of binding points is determined by the spatial filling of the disperse part, and by the dimensions and shape of the particles. The strengths of the linkages and the rate of their reformation after their shearing are determined primarily by the particle — particle and the particle — medium interactions, *i.e.* by the adhesion and the lyophilicity. If the lyophilicity of the particles of the disperse part towards the dispersion medium is increased, a decrease results in the magnitude of the adhesion forces between them, and hence in the structure-forming tendency of the system.

The lyophilicity and accordingly the properties of the structure developing in suspension can be regulated in the case of a given disperse part by the use of homogeneous organic media ensuring different degrees of wetting, and in the case of a given disperse part and a given dispersion medium by the modification of the interfacial layer between the medium and the particles with additives, generally tensides [2, 11, 12].

The influencing of the sedimentation and rheological properties of suspensions with tensides may be achieved in various ways:

(a) the lysphere developing on the surface of the particles may be altered with tensides dissolved in the dispersion medium; or

(b) the particles of a hydrophilic disperse part, for example, may be organophilized by the adsorption or chemisorption of tensides prior to the formation of the suspension.

The literature [2, 8, 11—18] contains a reasonable number of research results involving studies on the effects of the tensides dissolved in the dispersion medium or the tensides used for organophilization on the stability and rheological properties of suspensions. However, it is much rarer [18, 19] to find publications in which investigations are made of the correlations between the interaction between the disperse part and the tenside (sorption), and the sedimentation and rheological properties of the suspensions.

We have therefore studied what changes occur in the sedimentation and rheological properties of ferric oxide suspensions in a paraffin oil medium (otherwise prepared in a fixed manner and with a fixed concentration) if:

(a) the stearic acid used to modify the interface is dissolved in the dispersion medium;

(b) the stearic acid is sorbed onto the surface of the ferric oxide from a benzene medium prior to preparation of the suspension;

(c) the ferric oxide in a water-*i*-propanol mixture is preliminarily reacted with the modifying stearate ion in the form of ammonium stearate.

A choice may be made from among these possibilities in, among others, the varnish paint industry, if the tensides are employed as dispersing, wetting or stabilizing agents.

Experimental

Materials. The ferric oxide used was Reanal Fe_2O_3 of the highest analytical purity, with a content of other oxides of less than 0.3%. The specific surface area of the ferric oxide was determined with the BET method in a nitrogen atmosphere and was found to be $7.0 \text{ m}^2/\text{g}$; this value did not change essentially as a result of the organophilization (surface modification). The dispersion medium was paraffin oil of pharmacopoeial quality. Fluka stearic acid of the highest analytical purity, and ammonium stearate prepared from stearic acid and ammonia gas, were used as wetting agents and for organophilization.

Methods. The surface of the ferric oxide was modified to various extents in a 10% suspension in benzene, by treatment with a 0.1% solution of stearic acid in benzene. In order to avoid the disturbing effect of water bound on the surface [20], before the suspension was prepared the ferric oxide was dried to constant weight at 105°C in a vacuum drying-oven. The benzene was made anhydrous with metallic sodium. In the organophilization with ammonium stearate, a 10% aqueous suspension was prepared from the ferric oxide; an equivalent amount of ammonium stearate, in the form of a 0.1% aqueous solution also containing 33% *i*-propanol, was added to the suspension at 60°C during vigorous stirring. After the adsorption equilibrium had been established (a period of 48 h proved sufficient for this in both cases), the ferric oxide was separated by centrifugation from the equilibrium solution, and then washed several times with the solvent. The washings were combined with the equilibrium solution. The organophilized samples were dried to constant weight at 60°C in a vacuum drying-oven, powdered, and passed through a DIN-30 sieve.

The rheological investigations were carried out with a Haake rotary viscosimeter, with the use of a two-slit, thermostatable measuring vessel. The shear gradient was varied in the interval $1.62\text{--}262 \text{ sec}^{-1}$, in 10 stages. For the rheological measurements the suspensions were prepared in an Erweka rotatable homogenizer fitted with a closed agate vessel, in which the mild shear and homogenization are ensured by a fairly large agate ball. The suspension concentration was in all cases $35.9 \text{ g}/100 \text{ g}$.

Results and discussion

The effects of the quantity of stearic acid or ammonium stearate on the sedimentation properties of ferric oxide suspensions in a benzene medium are shown in Fig. 1.

In pure benzene the ferric oxide gives a loose sediment with a large volume; the sedimentation occurs in an aggregated manner, with a sharp interface. As a

consequence of the adhesion decrease resulting both from the stearic acid and from the ammonium stearate, the sediment volume grows progressively smaller and the sedimentation becomes diffuse in character. It is also striking that the effect of the stearic acid is practically independent of the mode of its application. From the aspect

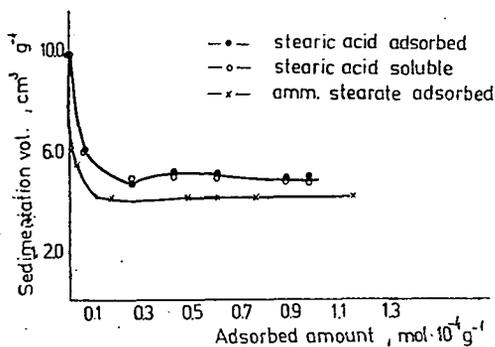


Fig. 1. The effects of the quantity of stearic acid or ammonium stearate on the sedimentation properties of ferric oxide suspensions in a benzene

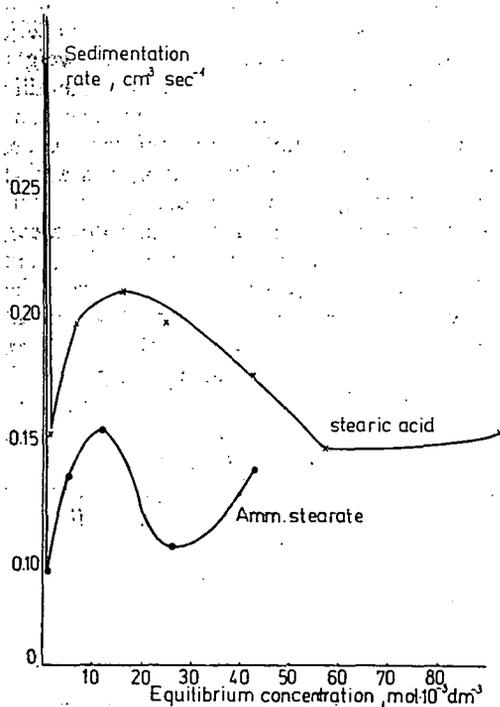


Fig. 2. The sedimentation rates of benzene suspensions of ferric oxide as functions of equilibrium concentration of stearic acid or ammonium stearate

of the sediment volume-diminishing effect, it is irrelevant whether the stearic acid is sorbed onto the surface of the ferric oxide particles and the suspension is then made in benzene, or whether the same quantity of stearic acid is dissolved in the dispersion medium (benzene) and hydrophilic ferric oxide is suspended in it. However, if the stearate ion reacts in the dissociated form in aqueous medium with the surface of the ferric oxide particles, and after drying the organophilized ferric oxide is suspended in an organic medium, then it is able to exert a larger adhesion-decreasing effect, and accordingly the sediment volume too naturally decreases to a greater extent.

These findings are supported by the results of sedimentation rate studies, which are illustrated in Fig. 2.

Fig. 2 shows the sedimentation rates of benzene suspensions of ferric oxide samples previously organophilized with stearic acid or ammonium stearate, as functions of the equilibrium concentration of stearic acid or ammonium stearate. In agreement with the data of earlier authors [2, 22—24], the sedimentation rate varies according to a complex (minimum-maximum) function with the quantity of the tenside. This complex correlation can be explained in that the sedimentation rate is influenced not only by the adhesion decrease resulting from the action of the adsorbed stearic acid or stearate ion, but at the same time by the disaggregation which takes place in parallel to this and by the increase in the

number of particles per unit volume too. Even so, however, it is quite clear that the ferric oxide samples organophilized with ammonium stearate in aqueous medium give suspensions that are more stable and sediment out at a substantially lower rate than the samples surface-treated with stearic acid.

The essential difference between the stearate adsorptions from the organic and the aqueous media is shown by the adsorption-desorption isotherms presented in Fig. 3.

On the basis of Fig. 3, it may be stated that in the first short section of the isotherms the equilibrium concentration is zero, and accordingly irreversible sorption may be assumed. During the further sorption of stearic acid the active sites on the surface of the ferric oxide particles rapidly become saturated and the adsorbed quantity increases. In this stage a considerable proportion of the amount of stearic acid adsorbed may be removed from the surface by extraction with the solvent. Subsequently, the concentration of the equilibrium solution gradually rises while the adsorbed quantity remains practically unchanged. The surface coverage calculated from the BET surface area of the adsorbent, the maximum amount chemisorbed and the surface area requirement of the stearic acid molecule (0.205 nm^2), does not attain 100%.

In the course of the sorption of ammonium stearate the situation is different. In this case, a measurable equilibrium concentration is already observed at comparatively low adsorbed amounts. On proceeding towards higher equilibrium concentrations, however, here too there are gradual increases in the quantities of both the reversibly and the irreversibly bound stearate ion. At the same time, our calculations indicate that the maximum quantity of chemisorbed stearate ensures total monomolecular coverage of the surface.

We also used immersion microcalorimetry to investigate the surface characteristics of the organophilized ferric oxide samples. These results will be reported in our following publication.

The effect of organophilization is manifested most markedly in the rheological properties of the concentrated suspensions. The degree of organophilization of the ferric oxide used for the rheological examinations was determined from the characteristic points of the adsorption-desorption isotherms.

Figure 4 depicts the branches of the equilibrium flow curves of paraffin oil

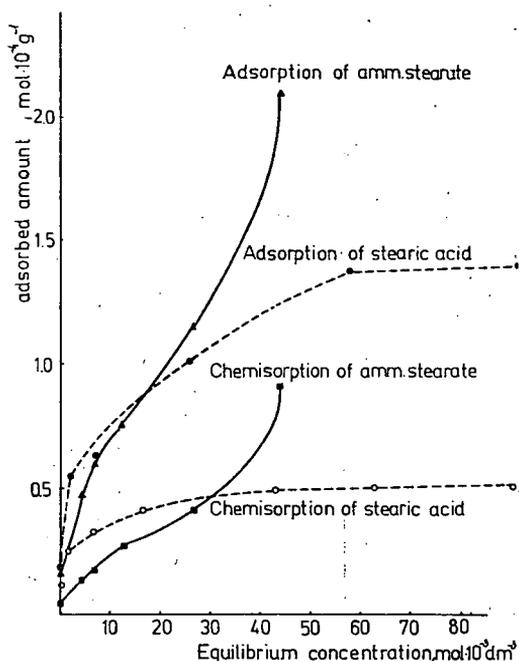


Fig. 3. The adsorption-desorption isotherm of stearic acid and ammonium stearate

suspensions of ferric oxide organophilized to various extents with stearic acid, these results being obtained at increasing shear gradient values:

Fig. 4 shows that the Bingham flow limit found by extrapolation of the final linear section of the flow curve increases slightly on the action of a small amount of stearic acid, which is in good agreement with the variation of the sedimentation rate values in Fig. 2. As the quantity of stearic acid chemisorbed increases, the flow limit progressively decreases to a limiting value. The plastic viscosity values arising from the slopes of the linear sections do not vary substantially with the amount of stearic acid chemisorbed. Paraffin oil suspensions of the hydrophilic ferric oxide and of the ferric oxide organophilized to various extents are otherwise plastic systems, and display practically no thixotropy.

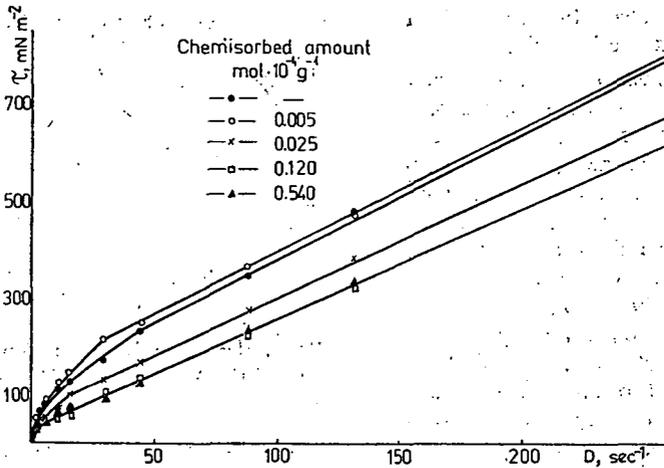


Fig. 4. Rheological curves of Fe_2O_3 organophilized with different quantities of stearic acid in paraffin oil

Essentially totally identical flow curves were obtained when the stearic acid was dissolved in paraffin oil and hydrophilic ferric oxide was always used in the suspension preparation.

If the preliminary organophilization of the ferric oxide was carried out with ammonium stearate in aqueous medium, under the same conditions the flow curves span a substantially larger shear stress interval (Fig. 5).

The suspension prepared with the hydrophilic ferric oxide is a form-retaining system possessing a relatively high Bingham flow limit (200 mNm^{-2}). In the case of a given suspension concentration, an increase in the amount of ammonium stearate causes the suspension to become progressively dilutely fluid, and its flow limit falls practically to zero. The adhesion decrease resulting from the organophilization, and the disaggregation occurring in parallel, are well observable in the colour of the suspensions too; this gradually changes from a dull light-red to a shiny dark-red.

If the ammonium stearate is dissolved in increasing amount in paraffin oil and the hydrophilic ferric oxide is suspended in it, the effect of the ammonium stearate is by no means so considerable. This is to be seen in Fig. 6, where it may readily be

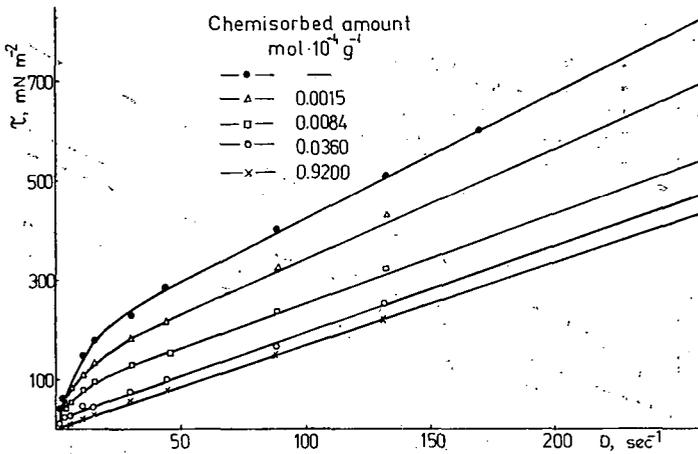


Fig. 5. Rheological curves of Fe_2O_3 organophilized with different quantities of ammonium stearate in paraffin oil

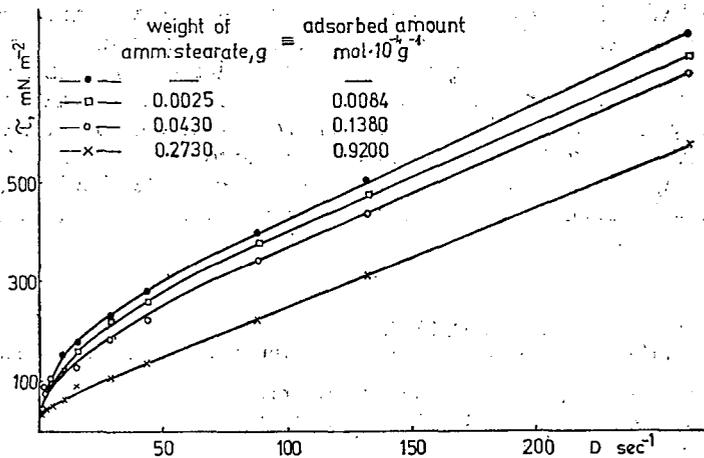


Fig. 6. Rheological curves of Fe_2O_3 in paraffin oil in presence of different amounts of ammonium stearate

observed that the flow limit has a value of only about 55 mNm^{-2} , even for the highest quantity of ammonium stearate.

Fig. 7 shows together the equilibrium flow curves of paraffin oil suspensions of the starting hydrophilic ferric oxide, and ferric oxides modified with the same quantity of dissolved or preliminarily adsorbed stearic acid or ammonium stearate.

From Fig. 7 too it may be stated quite clearly that the most extensive flow limit and plastic viscosity-decreasing effects can be obtained with the chemisorbed ammonium stearate.

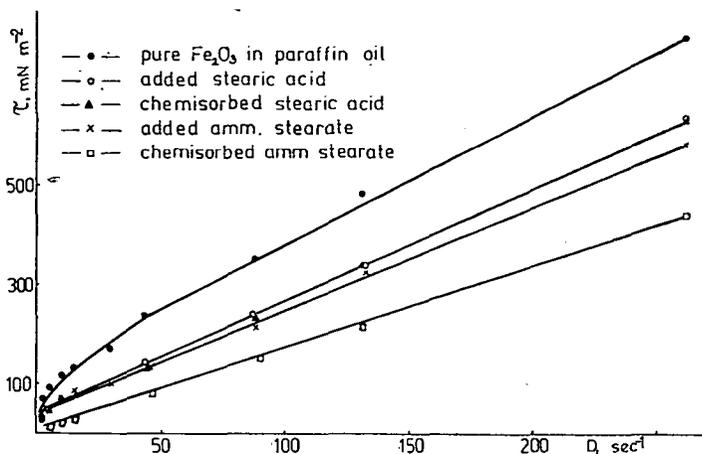


Fig. 7. Rheological curves showing the adsorbed and the added amounts of stearic acid and ammonium stearate

On the basis of the experimental results reported here, it may be said that concrete conclusions concerning the optimum conditions of organophilization of a pigment to be ground into a given dispersion medium may be drawn from the results of adsorption, sedimentation and rheological examinations that are relatively simple to carry out. Our experimental results may serve as additional data in support of the fact that not only the correct choice of the nature and quantity of the pigment and the tenside, but also the conditions of the pigment — tenside interaction exert a substantial influence on the practically important characteristics of varnish paints.

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ВЛИЯНИЕ ПОВЕРХНОСТНОЙ МОДИФИКАЦИИ ОКСИДА ЖЕЛЕЗА
 НА СЕДИМЕНТАЦИОННЫЕ И РЕОЛОГИЧЕСКИЕ ХАРАКТЕРИСТИКИ ЕГО
 СУСПЕНЗИЙ В НЕВОДНЫХ СРЕДАХ

А. А. Абу-Эл-Хаким, Я. Балаж и Ф. Санто

Оксид железа высокой степени чистоты использовался для получения органофилизированных до разной степени продуктов. Органофилизацию проводили стеаратом аммония из водной и стеариновой кислотой из бензольной среды. Поверхностные свойства продуктов были изучены с помощью иммерсионной микрокалориметрии. Проведено подробное исследование реологических свойств концентрированных суспензий, органофилизированных до разных степеней образцов, в среде парафинового масла. Найдено хорошее соответствие между результатами адсорбционных, седиментационных и реологических испытаний.