


Tharwat F. Tadros

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Rheology of Dispersions

Principles and Applications



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Preface

The rheology (flow characteristics) of dispersions of both solid/liquid (suspensions) and liquid/liquid (emulsions) types is applicable to many industrial situations, including paints, printing inks, paper coatings, ceramics, cosmetics, food systems, pharmaceutical and agrochemical formulations, and liquid detergents. In all of these complex multiphase systems it is necessary to control the rheology of a formulation during its preparation, to maintain its long-term physical stability, and during its application. The requirements for a good paint formulation illustrate these points very well: a paint may consist of polymer particles (latexes) and pigments that must be maintained in a colloidally stable state not only in the formulation but also on coating, to produce a uniform film. In storage, the paint formulation should not show any sedimentation of the pigments, there should be no separation (syneresis), and it should produce a weak gel that is thixotropic in nature. This means that, on application, the gel structure must be broken under shear so as to produce a uniform film, but recovered within a controlled time scale so as to prevent the paint from dripping. But, if the gel structure is recovered too quickly after application, the paint film will show brush marks! In order to achieve such behavior on both storage and application, rheology modifiers—which sometimes are referred to as “thickeners” or “gels”—must be incorporated into the formulation. Today’s research chemist, when formulating a chemical product, must understand the basic principles of rheology and how to control the various parameters of the system so as to achieve a desired effect. In addition, the formulation chemist must design accelerated tests to predict any changes that might occur in the system during storage. Rheological measurements represent the most powerful tools for such predictions, as the formulation can be investigated without dilution or disturbing its structure.

This book is targeted at research scientists, both in industry and in academic institutes. Following a brief introduction (Chapter 1) which highlights the scope of the book, Chapter 2 is dedicated to understanding the colloidal properties of dispersions, where the theories of colloid stability—both for electrostatically and sterically stabilized dispersions—are briefly summarized. This is followed by a description of the conditions required for the stability/instability of a dispersion, with particular attention being paid to the states of suspensions and emulsions on standing. The various breakdown processes are described and analyzed in terms

of the interaction forces between the particles or droplets. Chapters 3 and 4 describe the basic principles of rheology, and the experimental techniques that can be applied to investigate the rheological properties of a system. In this case, it was convenient to separate the basic principles into two chapters. First, the steady-state principles (high deformation measurements) are outlined in Chapter 3, whereby a constant and increasing shear rate is applied to a system (which may be placed in the gap between concentric cylinders, parallel plates, or cone and plate geometry), after which the stress and viscosity are obtained as a function of shear rate so as to distinguish between Newtonian and non-Newtonian systems. The flow curves of shear stress versus shear rate can be fitted to various models, and particular attention is given to the reversible time-dependence of viscosity (thixotropy and negative thixotropy). Chapter 4 provides details of viscoelastic behavior (low-deformation measurements), with descriptions of three methods (that are equivalent, but not identical) which can be applied: (i) strain relaxation after the sudden application of stress (constant-stress or creep measurements); (ii) stress relaxation after the sudden application of strain; and (iii) dynamic (oscillatory) techniques. The models that can be applied to describe each of these measurements are briefly outlined. In this way, various rheological parameters can be obtained, such as creep compliance, residual (zero) shear viscosity, relaxation time, storage (elastic) and loss (viscous) modulus. Each of these parameters is important for controlling the physical stability of the dispersion, as well as predicting its long-term stability. Chapter 5 describes the rheology of suspensions, with four basic systems being outlined. The first of these is hard-sphere dispersions, where both repulsion and attraction are screened (neutral stability). In this case, the rheological behavior is simple as it depends only on the balance between Brownian diffusion and hydrodynamic interaction. These hard-sphere dispersions form the basis of the development of theoretical treatments of the rheology of suspensions. The second system is that of “soft” (electrostatic) interaction, where rheology is determined by double-layer repulsion. For this, models are available to relate some of the rheological parameters such as the high-frequency modulus to the double-layer repulsion energy of interaction. The third category is that of sterically stabilized systems which contain adsorbed or grafted nonionic polymers. In this case, the rheology is determined by the steric repulsion of the adsorbed or grafted chains. It is also possible to relate the high-frequency modulus to the steric interaction energy. Finally, flocculated and coagulated systems, where the rheology is determined by the van der Waals attractions, can be used to distinguish between weak (reversible) and strong (irreversible) systems. The rheology of these flocculated systems is complicated, as they are under nonequilibrium, and only semi-empirical models are available for this purpose. The use of a fractal dimension concepts allows information to be obtained on the structure of flocculated systems. Chapter 6 deals with the rheology of emulsions. It starts with a discussion of interfacial rheology and how this can be correlated with emulsion stability. The bulk rheology of emulsions is described at a fundamental level with special reference to the analysis of the rheology of concentrated emulsions and the effect of droplet deformability. A section is devoted to the rheology of high internal phase

emulsions (HIPE). Chapter 7 provides information on the rheology of modifiers, thickeners and gels, with various systems being described ranging from physical gels (obtained simply by an overlap of the polymer coils) to associative thickeners (hydrophobically modified polymers), crosslinked polymers, and particulate gels (including swellable clays and silica gels). One important rheology modifier that is used in many cosmetic creams and liquid detergents is based on surfactant liquid crystalline phases. In Chapter 8, the various rheological methods that can be applied to assess and predict the long-term physical stability of dispersions are described, with practical examples being given to illustrate the validity of these methods.

Although this book is by no means comprehensive, its aim is to provide both the fundamentals and applications of the rheology of dispersions. It should serve as a valuable text for those scientists in industry who deal regularly with the formulation of chemicals, and also as an introduction to those research workers investigating the rheology of dispersions.

February 2010

Tharwat Tadros

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1

General Introduction

Several types of disperse system may be defined, depending on the nature of the disperse phase and medium; these are summarized in Table 1.1.

The present book deals with the rheology of three main disperse systems, namely solid in liquid (suspensions), liquid in liquid (emulsions), and liquid in solid (gels). It is essential to define the dimensions of the particles or droplets of the internal phase. Systems where such dimensions fall within 1 nm to 1000 nm (1 μm) are classified as “colloidal systems,” whereas those which contain particles or droplets larger than 1 μm are outside the colloid range. However, in both cases, the property of the system is determined by the nature of the interface which separates the internal phase from the medium in which it is dispersed. Clearly, with colloidal systems the interfacial region presents a significant proportion of the whole system. The structure of the interfacial region determines the properties of the system, and in particular the tendency of the particles to form aggregate units or to remain as individual particles.

Two main types of interfacial structure may be distinguished. The first type occurs with charged interfaces, whereby a double layer develops as a result of the presence of a surface charge which is compensated near the interface by unequal distribution of counter-ions and co-ions. At the interface, there will be an excess of counter-ions and a deficiency of co-ions. This picture of the double layer has been introduced by Gouy and Chapman [1, 2], and is referred to as “the diffuse double layer.” Later, Stern [3] introduced a modified picture whereby the first layer of the counter-ions is regarded to be fixed (due to specific adsorption) and the rest of the double is diffuse in nature. In this way, Stern defined a potential ψ_d at the center of the first fixed layer; this potential may be close to the measurable electrokinetic or zeta potential. A modification of the Stern picture was later introduced by Grahame [4, 5], who considered two planes: an inner Helmholtz plane (IHP) at the center of the counter-ions that lose their hydration shell (chemisorbed counter ions); and an outer Helmholtz plane (OHP) at the center of the physically adsorbed counter-ions with their hydration shell. As will be seen in Chapter 2, the extension of the double layer depends on the concentration of counter-ions and co-ions, as well as their valency. At low electrolyte concentrations ($<10^{-2} \text{ mol dm}^{-3}$ for 1:1 electrolyte and $<10^{-3} \text{ mol dm}^{-3}$ for 2:2 electrolyte), the double layer is sufficiently extended.

Table 1.1 Types of disperse systems.

Disperse phase	Disperse medium	Type
Solid	Liquid	Suspension
Liquid	Liquid	Emulsion
Liquid	Solid	Gel
Liquid	Gas	Aerosol
Gas	Liquid	Foam
Solid	Solid	Composite

As will be discussed in detail in Chapter 2, when two particles or droplets with their extended double layers (at low electrolyte concentration) approach each other to a distance of separation at which the diffuse parts of the double layers begin to overlap, a strong repulsion occurs as the double layers can no longer develop unrestrictedly. This repulsion decreases exponentially with the decrease in the distance of separation h between the particles or droplets. The magnitude of the repulsive energy, G_{el} , at any separation distance h increases with a decrease in electrolyte concentration and a decrease in the valency of the electrolyte.

In addition to the repulsive energy described above, the particles or droplets in a dispersion have an attractive energy, sometimes referred to as van der Waals attraction, G_A , which is universal to all disperse systems. The main contribution to the van der Waals attraction is the *London dispersion energy*, and expressions have been derived by Hamaker [6] for G_A (as will be discussed in detail in Chapter 2).

The combination of G_{el} and G_A results in the well-known theory due to Derjaguin–Landau–Verwey–Overbeek (DLVO [7, 8]; this is discussed in detail in Chapter 2). The DLVO theory predicts the presence of an energy barrier at intermediate distances of separation between the particles that prevents flocculation of the dispersion. The height of the barrier depends on the surface or zeta potential, the electrolyte concentration, and the particle radius.

The second type of interfacial structure arises when surfactants and/or macromolecules are adsorbed at the particle surface. With surfactant molecules consisting of few units, adsorption simply occurs with one part of the molecule being preferentially attached to the particle surface. For example, with ionic surfactants adsorbed onto charged surfaces, an electrostatic attraction occurs between the charged head groups of the surfactant molecule and the charged sites on the surface. The surfactant molecules may adopt either horizontal or vertical orientations. With nonionic surfactants, such as alcohol or alkyl phenol ethoxylates, the alkyl or alkyl phenyl chain may become adsorbed onto a hydrophobic surface, leaving the poly(ethylene oxide) (PEO) chain dangling in solution.

With polymer molecules consisting of a large number of units, the adsorbed molecule adopts different configurations depending on the concentration, the molecular weight of the polymer, and its structure (e.g., flexibility, branching, etc). The most general configuration is that whereby a number of units become attached

to the surface, in so-called “trains,” with loops in between and tails at the ends of the chain. However, with block copolymers of the A–B or A–B–A type (where B represents the “anchor” chain that is strongly attached to the surface by small loops and A is the stabilizing chain), the polymer can adopt a configuration whereby the B chain becomes strongly attached to the surface, leaving one or two A chains (which are strongly solvated by the molecules of the medium) that provide a strong steric repulsion; in this way, a very stable dispersion is produced.

When two particles or droplets which have a radius R and contain adsorbed layers with thickness δ approach each other to a surface-to-surface distance h that is less than 2δ , a strong repulsion will occur as a result of two main effects [9]. When the layers begin to overlap, the segment density in the overlap region becomes larger than the rest of the layer, and this results in an increase in the osmotic pressure in this region. Provided that the stabilizing chains are in good solvent conditions, this increase in osmotic pressure resists any overlap of the layers (unfavorable mixing of the stabilizing chains) and results in a strong repulsion that is given by G_{mix} (which has a positive sign). As a result, solvent diffuses to the overlap region, thus separating the particles or droplets. The second repulsive energy arises from the loss of configurational entropy of the chains on significant overlap; this is referred to as elastic interaction, G_{el} . A combination of G_{mix} and G_{el} gives the total steric interaction free energy which, when added to the van der Waals attraction, causes the energy–distance curve to show a shallow minimum at separation distances comparable to 2δ ; moreover, when $h < 2\delta$ a strong repulsion will occur with a further decrease of h .

As mentioned above, the structure of the interfacial region determines the interaction between particles in a disperse system. For example, with systems containing double layers or adsorbed layers of surfactants or polymers, an interaction will lead to a repulsion as soon as the double layers or the adsorbed layers begin to overlap. This repulsion leads to a colloiddally stable system. On the other hand, if the repulsive energy is not sufficiently large, then the van der Waals attraction will dominate the interaction and an aggregated system will result. These interactions determine the flow characteristics (rheology) of the disperse systems.

The main objective of this book is to describe the rheology of dispersions in terms of the various forces between the particles or droplets. The rheology of a dispersion is determined by the balance of three main forces [10–12]: Brownian diffusion; hydrodynamic interaction; and surface forces (repulsive or attractive). For this reason, Chapter 2 will be dedicated to describing these interaction forces, and how these can be controlled in practice. As will be seen, four different types of interaction must be considered:

- Hard-sphere interaction, whereby both the repulsive and attractive forces are screened (this is sometimes referred to as “neutral stability”). In this case, the rheology of the dispersion is determined by the balance between Brownian diffusion and hydrodynamic interaction. This simplifies the analysis and, as will be seen in Chapter 3, theories are available to describe the variation of relative viscosity η_r with the volume fraction ϕ of the dispersion.