

# Conceptual Clarification of the Terms Used to Describe Emulsion Behavior

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**Synopsis**—The “TERMS” used to depict EMULSION BEHAVIOR are critically examined and the analysis dictates that some of the terms are unwarranted and should be superseded by better justified vocabulary. An attempt has been made to present an account of the terms which should be employed to represent the STABILITY behavior of an emulsion. The underlying concepts and the implications of various manifestations of INSTABILITY phenomenon are illuminated.

The whole gamut of instability pattern is divided into physical and chemical forms. Physical instability is further represented by processes such as creaming, flocculation, inversion, coalescence, and demulsification. It is suggested that the use of the term “coagulation” should be avoided in describing the behavior of emulsion systems.

The concept of reversible and irreversible instability is emphasized. Both forms of instability are discussed in their various ramifications. The phenomenon of irreversible instability can be realized in practice in micro and macro forms.

## INTRODUCTION

The purpose of this communication is to check the pervasive confusion in the conceptual basis of the various manifestations of emulsion behavior, as regards its stability. It is of critical importance that all the terms should have clearcut meaning; the use of vague and ill-understood terminology serves only to compound confusion.

The terms creaming, flocculation, coagulation, coalescence, and demulsification are frequently employed to describe the stability behavior of emulsions; but, unfortunately, these have been used inadvertently and

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indiscriminately. In the present communication, only a few conspicuous examples—which are the source of confusion—have been cited; but the literature is replete with such instances. Ecanow *et al.* (1) applied incautiously the discussion, valid in the case of solid particle suspensions, to emulsions and foams. They mention, “The coagulated emulsion is represented by a creamed emulsion in which the films and protective colloids of adjacent particles are in contact. Flocculated emulsions are not recognized.” Fortunately, they have pointed out that their definitions are in contrast to those represented in the literature; but this does not warrant the perpetuation of unwarranted terminology. It will be shown later that the term “coagulation” should not be used to describe emulsion behavior and a creamed emulsion is not a coagulated emulsion. Furthermore, flocculation and coagulation have been used as synonyms and interchangeably (2, 3), whereas the terms coagulation and demulsification have been treated similarly (2, 4–6). One might construe from the above that the terms creaming, flocculation, coagulation, and demulsification all refer to the same process; but this is far from the truth. These terms represent widely different phenomena, as shown later. It is important to point out that some workers “coin” their own terms; such practice serves only to augment the problem of terminology. One such instance is the paper by Garrett (7), in which arbitrary terms and definitions are used to describe the behavior of emulsions. Such widespread confusion and discordance in the use of terminology in emulsion systems has prompted the writing of the present communication.

#### DEFINITION OF EMULSION STABILITY

An emulsion is a heterogeneous system consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets whose diameters, in general, exceed  $0.1\mu$  (2). The confusion stems after the emulsion has been formed. Ideally, an emulsion is stable when there is no change in certain parameters (i.e., number of particles of the disperse phase, particle size distribution, total interfacial area, mean droplet size, chemical composition of the components involved, and other related parameters) while standing undisturbed under normal conditions. This idealization cannot be realized in practice. Thermodynamics dictates that all emulsion systems will try to decrease their surface free energy, with the concomitant decrease in total interfacial area. Broadly speaking, an emulsion can show instability in one of two ways: chemical instability or physical instability.

*Chemical Instability*

This form of instability refers to the chemical changes, in either the liquid phases or the emulsifying agents, which produce an intrinsic emulsion instability or the tendency towards demulsification or breaking of the emulsion. The two kinds of instabilities (chemical and physical) are attributed to widely different causes and the chemical instability may precede the physical instability. Still, the nomenclature recommended for the description of the disperse droplets will be the same.

*Physical Instability*

Generally, this form of instability relates to the shelf life of the emulsion when only the gravitational forces are considered. Although the exact correlation between the accelerated ultracentrifugal and the shelf life instability is not established (7-9), it is not unreasonable to include both forms of instability under the generic title "physical instability."

After this introduction, the various terms used for representing emulsion behavior are described below. The author is strongly inclined to propose that an emulsion can show instability—especially physical instability—in one of the two ways: reversible instability or irreversible instability. The present classification is different and more comprehensive than those proposed earlier (2). Reversible instability can be further divided into: (a) creaming or sedimentation and (b) flocculation. Irreversible instability can be manifested by (a) coalescence, (b) demulsification or breaking, and (c) inversion. In the present text, demulsification and breaking are used as synonyms and interchangeably, as these represent the same process, as shown later. The concept of "reversibility" in emulsion instability, it is hoped, will prove useful in comprehending better the mode of aggregation of disperse emulsion droplets. Before proceeding further, it is important and necessary to point out that some of the confusion in emulsion systems arises from the nomenclature used in solid particle suspensions. A short synopsis of the accepted terminology in sols is in order.

TERMINOLOGY USED TO DESCRIBE THE BEHAVIOR OF SOLID  
PARTICLES IN SOLS

La Mer (10) pointed out that the terms "coagulation" and "flocculation" (both pertaining to the aggregation of sol particles) should be defined clearly and discriminately. According to La Mer, the term coagu-

lation comes from the Latin "coagulare" meaning to drive together. This is an appropriate term for the effect of neutral salt on a sol, where the mechanism generally accepted today results from the reduction of the repulsive potential of the electrical double layers surrounding the particles. Flocculation comes from the Latin "flocculare" meaning to form a floc; i.e., a tuft of wool or highly fibrous structure. While the new ideas advocated by La Mer and other groups (10–12) are still considered controversial (13), the new vocabulary and the underlying ideas are being published (14). I am inclined to agree with the ideas of La Mer and other groups. According to Ecanow *et al.* (1), in flocculation a network structure results. This, in turn, produces large bulky aggregates referred to as flocs or floccules. These floccules contain varying amounts of entrapped medium. The network structure referred to can occur by means of adsorption bridging (15) and chemical bridging (11, 12, 16).

The processes of flocculation and coagulation can be differentiated on the basis of multifold criteria (1, 10); but it is clear (1) that flocculation is reversible and the floccules contain entrapped medium, whereas coagulation is irreversible and the coagula are compact structures with no entrapped medium. It should be pointed out that I have regarded these criteria—reversibility, unchanged identity of the particles, and the presence of the entrapped medium—to justify the use of the terms flocculation and coagulation in describing the emulsion behavior. After this brief appraisal of the nomenclature in the case of sols, the various manifestations of emulsion instability, as mentioned earlier, are discussed below.

#### *Reversible Instability*

This simply signifies any manifestation of emulsion instability in which the disperse droplets have not lost their identity and there is a possibility of restoring the emulsion to its original condition. In most cases, particularly in dilute emulsions, the reversibly unstable emulsion can be restored to its original form by simple hand shaking. As mentioned earlier, creaming and flocculation represent this kind of instability, and these two forms are discussed below.

#### *Creaming*

Creaming is simply caused by the density differences between the disperse phase and the dispersion medium. In the case of true creaming, the emulsion is separated into two emulsions: one is richer in the disperse phase and the other poorer than the original emulsion. If the

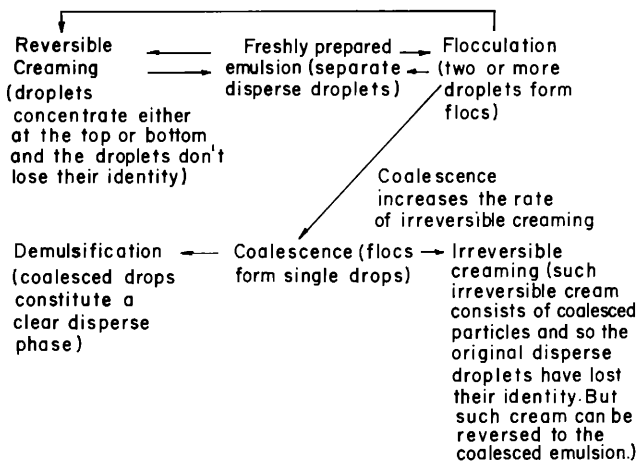


Figure 1. Overall possible behavior of an emulsion system

richer phase is lighter than the dispersion medium, the phenomenon is termed “creaming”; if it sinks to the bottom, it is called “sedimentation.”

Some of the vital characteristics of the creaming phenomenon are: (a) in creamed emulsion, the particles do not lose their identity; (b) creaming can be totally averted by adjusting the densities such that those of the dispersion medium and the disperse phase are equal; (c) while creaming is not a strict revelation of emulsion instability, as regards the separation of clear disperse phase, still it has a strong interplay with other forms of instability. Creaming brings the disperse droplets in close proximity, thereby rendering the situation conducive to demulsification, through various stages as shown in Fig. 1; (d) flocculation enhances the rate of creaming, if there are appreciable density differences between the dispersion medium and the floccules. In creaming accelerated by flocculation the particles do not lose their identity and the creamed emulsion can be restored to its original form. In fact, this form of creaming can be termed “reversible creaming”; (e) coalescence also increases the rate of creaming if there are appreciable density differences between the dispersion medium and the coalesced drops. Such creaming phenomenon differs from that accelerated by flocculation in the sense that the cream containing coalesced drops cannot be restored to the original form of emulsion. So it might well be designated “irreversible creaming.” It is obvious from the above that “creaming” does not, in any case, represent the phenomenon of coagulation, as it does not conform with the requirements set forth for “coagulation” in the case of sols. These

are two widely different concepts and should not be confused with each other. Furthermore, workers interested in the quantitative and mechanistic aspects of demulsification should resist the temptation to measure the rate of creaming.

### *Flocculation*

This is the second and, unfortunately, the most disconcerting representation of reversible instability. When two or more droplets approach each other and form an aggregate (in which the droplets have not lost their identity), this poses a problem. How should this aggregate and the aggregation process be denominated? In the case of sols, this difficulty is obviated by differentiating the aggregation process into two distinct processes—flocculation and coagulation—depending upon certain requirements.

In most of the aggregated emulsions, the droplets are separated by the intervening medium and the aggregated emulsions can be restored to their original state (17, 18). Thus, the process of aggregation of emulsion droplets should be termed “flocculation” not coagulation; this is in accordance with the requirements prescribed earlier. The above discussion suggests that the term “coagulation” should not be used to describe emulsion behavior; its use should be restricted to solid particle suspensions only. Furthermore, the statement made by Ecanow *et al.* (1) is not justified because flocculated emulsions *do exist*.

In the case of sols, two different mechanisms were proposed for the process of flocculation; however, in emulsions, flocculation can take place by one of the following three mechanisms: (a) by reduction of the zeta potential and can be termed “electrostatic” or “ionic” flocculation; (b) by adsorption bridging; and (c) by chemical bridging. The first category of flocculation is analogous to coagulation in sols only in the sense that both are brought about by the reduction of zeta potential. The mechanisms (b) and (c) correspond to those proposed for the flocculation in sols, as discussed earlier.

The process of flocculation in emulsions differs in some respects from that in sols, and the important characteristics of flocculation in emulsions are the following: (a) As regards creaming, the flocs behave as single drops and the rate of “reversible creaming” is accelerated if the density of the flocs is appreciably different from that of the dispersion medium. In such creaming the particles have not lost their identity. (b) As the droplets are in close contact, flocculation is precursor to the process

of coalescence, which might lead to demulsification, as shown in Fig. 1. (c) All the flocs may or may not coalesce. (d) The rate of flocculation will depend upon the mechanism of flocculation.

### *Irreversible Instability*

This represents the condition of the emulsion in which the identity of the original disperse droplets or particles is changed and the "irreversibly unstable" emulsion cannot be restored to its original form. Various manifestations of irreversible instability are discussed below.

### *Inversion*

This simply means the inversion of the disperse phase to dispersion medium and *vice versa*. Inversion is a special case of irreversible instability as there is a change in emulsion type (for example, O/W to W/O). In inversion the droplets lose their identity and the "inverted" emulsion cannot be brought back to its original form by simple treatment, e.g., hand shaking. It is needless to expatiate upon the subject of "inversion" as there is no confusion and discordance in the use of this term.

### *Coalescence and Demulsification*

Once the droplets are in close contact (by flocculation), the intermingling of the droplets is possible and the flocs transform into single drops. A similar process is not possible in the case of sols, and the terms flocculation and coagulation cannot be used to represent this behavior. The appropriate term for the process of transformation of flocs into single large drops is "coalescence." Coalescence comes from the Latin "coalesce" meaning to unite by growing together or mix.

Broadly speaking, the coalesced emulsion can be classified as a demulsified or broken emulsion; but this is not entirely satisfactory. Coalescence brings about internal changes in the emulsion and there is no conspicuous outward manifestation. As the coalesced drops grow larger, these constitute a separate phase and the process is termed "demulsification" or "breaking."

The above distinction poses a problem: When does a coalesced drop constitute a separate phase? This difficulty can be obviated by prescribing that the coalesced drop is regarded as a separate phase when it is visually observable. This definition may not be in strict conformity with the thermodynamic definition of a phase, but it is not unreasonable from the pragmatic point of view. Keeping the above definition of a

phase in mind, irreversible instability can be observed on micro and macro scales.

#### *Coalescence or Micro Instability*

As discussed earlier, in flocculation the droplets approach each other and form a floc, but the droplets do not lose their identity; whereas in coalescence each floc combines to form a single large drop. The coalesced drop cannot be disintegrated into its constituent droplets. Some of the vital characteristics of the coalescence process are: (a) The process of coalescence cannot be followed visually as the coalesced drops are too small to be seen; this is in conformity with the definition of a separate phase set forth earlier. (b) The rate of coalescence is controlled by the parameters which affect the properties of the intervening medium between the droplets, and the absorbed films of the emulsifying agents (9, 18). (c) Progress of coalescence can be followed by microscopic observation. (d) Coalescence is precursor to the separation of the clear disperse phase, i.e., demulsification. (e) Depending upon the conditions, coalescence may or may not be followed by demulsification. (f) The rate of coalescence may or may not represent the rate of demulsification, depending upon the site of coalescence. If the site of coalescence is such that the transport of the coalesced drops is not required, then the two rates may be identical. (g) Rate of creaming is accelerated if the densities of the coalesced drops and the dispersion medium are appreciably different. In such "cream" the original particles of the disperse phase have lost their identity and the phenomenon is termed "irreversible creaming."

#### *Demulsification or Breaking or Macro Instability*

This represents the second and the final form of irreversible instability. The rate of breaking can be followed visually. As pointed out earlier, the appearance of the separate clear disperse phase constitutes demulsification. The broken emulsion cannot be restored to its original state unless subjected to reemulsification by severe shear forces. The overall possible behavior of an emulsion system is depicted in Fig. 1.

It is clear from Fig. 1 that the rate of demulsification may be contingent upon the rate of flocculation, the rate of coalescence, or the rate of transport of the coalesced drops to constitute a visually observable phase. To illustrate this point, a specific example is in order. The rate of separation of clear disperse phase is measured on an emulsion (which is already flocculated) in the ultracentrifuge (9, 18) and this rate may or



may not represent the rate of coalescence. This is plausible, if the rate of transport of the coalesced drops—from the site of coalescence—is the slowest step in the overall kinetics of the separation of the disperse phase.

#### CONCLUSION

It is hoped that the present communication will be helpful in understanding the underlying ideas and the implications of various forms of emulsion instability. A few important points are recapitulated:

1. The term "coagulation" should not be used to describe emulsion behavior because it causes unnecessary misunderstanding. Its use should be restricted to sols only.

2. The terms creaming, flocculation, coalescence, and demulsification or breaking should be used judiciously and with discernment.

3. The use of unwarranted terminology should be avoided.

4. The property of the system measured as an index of emulsion instability should be mentioned explicitly. This is very important because different information and conclusions regarding emulsion instability are possible, depending upon the criterion chosen (9).

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