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Chemical Industry & Chemical Engineering Quarterly 14 (3) 153-158 (2008)　CI&CEQ

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SCIENTIFIC WORK

UDC 66.011+54=148:66.022.362

MODELING OF THE EMULSION STABILITY USING FRACTAL DIMENSIONS

There are many developed strategies in the emulsion stability evaluation, for purpose of determining the life circle of emulsions. Most of them are based on the reological properties of the emulsions. There are very few which relay on the direct emulsion observations. In this paper we present the developed method for the emulsion stability evaluation by the direct observation of optical properties. As the stability quantification measure we propose the fractal dimension approach. The method is based on the measure of the emulsion transmittance properties, which are directly dependent on the emulsion stability at the moment of measurement. As the test emulsion the oil in the water emulsion was used. The system is classified as the stable emulsion and our intention was to find the moment when the emulsion starts to break. The emulsion transmittance properties were measured using an acquisition system, consisting of a CCD camera and a fast PC configuration equipped with the capturing software. The fractal dimensions were determined by the so called box counting method. The experimental emulsions were measured continuously within the period of 1200 h, from the moment of the emulsion creation. The changes of fractal dimensions were observed which indicates that the emulsion changed its state and therefore the stability during the time. Three regions of the emulsion life circle were divided according to the fractal dimensions measurement, which can be connected with the stable, unstable, and meta-stable states of the emulsion life circle. In the end, the model of the emulsion behavior was developed for the purpose of quantifying the changes in the experimental emulsion.

Key words: emulsions; stability; fractals; model.

Any colloidal suspension is susceptible to gravitationally induced sedimentation or creaming which can lead to phase separation of the particles, even if they are otherwise stable against aggregation or coalescence. This is particularly important for commercial products, where gravitational stability can ultimately limit the shelf life. Gravitational stability can be enhanced by density matching the particles to the suspending liquid, by restricting the particle size so that their Brownian motion helps keep them suspended, or by increasing the viscosity of the suspending liquid to slow the phase separation. A convenient means of inducing the requisite inter particle attraction is through the depletion interaction, caused by the addition of non-adsorbing particles or polymer to the suspension. Indeed, polymers added to the suspension to increase its viscosity to slow the phase separation may also induce a depletion attraction, leading to the gel formation, and providing an alternate means of stabilization. The ability of the network to support its buoyant weight is characterized by its compression modulus, from which we determine the stress, which can be supported as a function of the particle volume fraction. The dependence of the stress is analogous to the equation of the state for equilibrium particles, where osmotic pressure balances the buoyant stress, and this has been measured for hard spheres. The compression modulus has also been measured for networks of strongly attractive particles.

One of the methods for the evaluation of the emulsion stability is to monitor the changes in the mean drop size for a certain period of storage time [1]. It is often considered that an increase of a drop size with time is a clear indication for the emulsion destabilization [2]. Such a relation is quite understandable (at first glance) for at least two reasons: (1) the increase of a drop size reflects an ongoing coa-

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Paper received: October 19, 2007.
Paper revised: July 15, 2008.
Paper accepted: July 18, 2008.

lescence process inside the emulsion; (2) as shown in previous studies [3], the stability of emulsions containing larger drops is lower at equivalent other conditions. On the other hand, we have found that the coalescence stability of BLG emulsions significantly decreases after one day of storage, as compared to the stability of freshly prepared emulsions (aging effect) [3], while the drop size distribution remains practically unchanged.

This paper gives the analysis of the alternative method for the emulsion stability evaluation, using fractal dimensions, or the irregularity system quantification, to investigate the emulsion life circle. The purpose of this research was to develop the technique of the emulsion stability measurement in real time. This includes the development of the experimental cell, as well as the methodology of fractal dimension calculations from the measured emulsion transmittance properties. According to that data, the life circle of the emulsion could be evaluated.

THEORETICAL BACKGROUND

The world of mathematics has been confined to the linear world for centuries. That is to say, mathematicians and physicists have overlooked dynamical systems as random and unpredictable. The only systems that could be understood in the past were those that were believed to be linear; the systems that follow predictable patterns and arrangements. Linear equations, linear functions, linear algebra, linear programming, and linear accelerators are all areas that have been understood and mastered by the human race. The name "chaos theory" leads the reader to believe that mathematicians have discovered some new and definitive knowledge about utterly random and incomprehensible phenomena; however, this is not entirely the case. The acceptable definition of chaos theory states, chaos theory is the qualitative study of unstable aperiodic behavior in deterministic nonlinear dynamical systems. A dynamical system may be defined as a simplified model for the time-varying behavior of an actual system, and a periodic behavior is simply the behavior that occurs when no variable describing the state of the system undergoes a regular repetition of values. A periodic behavior never repeats and it continues to manifest the effects of any small perturbation; hence, any prediction of a future state in a given system that is aperiodic is impossible. What is so incredible about the chaos theory is that unstable aperiodic behavior can be found in simple mathematical systems. These very simple mathematical systems display the behavior so complex and unpredictable that it is acceptable to merit their descriptions as random. An interesting question arises from many skeptics concerning why chaos has just recently been noticed. If chaotic systems are so mandatory to our everyday life, how come that mathematicians have not studied the chaos theory earlier? The answer is: computers. The calculations involved in studying chaos are extremely demanding. No human is stupid enough to endure the boredom; however, a computer is always up to the challenge. Computers have always been known for their excellence at mindless repetition; hence, the computer is our telescope and microscope or better to say, our visualization device when studying chaos. However, as with any media covered item, many misconceptions have arisen concerning the chaos theory. The "chaos" in the chaos theory is order - not simply order, but the very essence of order. It is true that the chaos theory dictates that minor changes can cause huge fluctuations [4].

Applied to the emulsion systems, small variations in the initial conditions result in huge, dynamic effects in the events that follow. The question is how to measure the effect of the system variations and to predict the system stability. Chaos and randomness are no longer ideas of a hypothetical world; they are quite realistic here in the status quo. A basis for chaos is established in the Butterfly Effect, the Lorenz Attractor, there must be an immense world of chaos beyond the rudimentary fundamentals. This new form mentioned is highly complex, repetitive, and replete with intrigue.

But one of the central concepts of the chaos theory is that while it is impossible to exactly predict the state of a system, it is generally quite possible, even easy, to model the overall behavior of a system. Thus, the chaos theory lays emphasis not on the disorder of the system - the inherent unpredictability of a system - but on the order inherent in the system - - the universal behavior of similar systems. Thus, it is incorrect to say that the chaos theory is about disorder. The chaos theory predicts that complex nonlinear systems are inherently unpredictable - but, at the same time, it also insures that the way to express such an unpredictable system often lies not in exact equations, but in representations of the behavior of a system - in plots of strange attractors or in fractals. Thus, the chaos theory, which many think is about unpredictability, is at the same time about predictability in even the most unstable systems.

The extending and folding of chaotic systems give strange attractors, the distinguishing characteristic of a non integral dimension. This non integral dimension is most commonly referred to as a fractal dimension. Fractals appear to be more popular in the status quo for their aesthetic nature than they are for their mathematics. Everyone who has seen a fractal has admired the beauty of a colorful, fascinating image, but what is the formula that makes up this handsome image? The classical Euclidean geometry is quite different than the fractal geometry mainly because fractal geometry concerns nonlinear, non integral systems while Euclidean geometry is mainly oriented around linear, integral systems. Hence, Euclidean geometry is a description of lines, ellipses, circles, so called regular geometrical figures. Fractal geometry is a description of algorithms. There are two basic properties that constitute a fractal. First is self-similarity, which is to say that most magnified images of fractals are essentially indistinguishable from the unmagnified version. A fractal shape will look almost, or even exactly the same, no matter what size it is viewed at. This repetitive pattern gives fractals their aesthetic nature. Secondly, as mentioned earlier, fractals have non-integer dimensions. This means that they are entirely different from the graphs of lines and conic sections that we have learned about in fundamental Euclidean geometry classes.

Perhaps the most basic aspect of a set is its dimension. Also, the frequency with which orbits visit different regions of a chaotic attractor can have its own arbitrarily fine scaled structure. In such cases the assignment of a dimension value gives a much needed quantitative characterization of the geometrical structure of a complicated object. Furthermore, the experimental determination of a dimension value from data for an experimental dynamical process can provide information on the dimensionality of the phase space required of a mathematical dynamical system used to model the observations.

The box-counting dimension, also called the "capacity" of the set, provides a relatively simple and appealing way of assigning a dimension to a set in such a way that certain kinds of sets are assigned a dimension which is not an integer. Such sets are called fractals by Mandelbrot, while, in the context of dynamics, attracting sets with fractal properties have been called strange attractors. The latter term was introduced by Ruelle and Takens [2]. Assume that we have a set which lies in an N-dimensional Cartesian space. We then imagine covering the space by a grid of N-dimensional cubes of edge length e. (If $N = 2$ then the "cubes" are squares, while if $N = 1$ the "cubes" are intervals of length ε). We then count the number of cubes $N(\varepsilon)$ needed to cover the set. We do this for successively smaller ε values. The box-counting dimension gives the scaling of the number of cubes needed to cover the attractor. For strange attractors, however, it is commonly the case that the frequency with which different cubes are visited can be vastly different from cube to cube. In fact, for very small ε, it is common that only a very small percentage of the cubes needed to cover the chaotic attractor contain the vast majority of the natural measure on the attractor. That is, typical orbits will spend most of their time in a small minority of those cubes that are needed to cover the attractor.

The box-counting dimension definition counts all cubes needed to cover the attractor equally, without regard to the fact that, in some sense, some cubes are much more important (*i.e.*, much more frequently visited) than others. To take into account the different natural measures of the cubes it is possible to introduce another definition of dimension which generalizes the box-counting dimension. This definition of dimension was formulated in the context of chaotic dynamics by Grassberger, Hentschel and Procaccia [5]. These authors define a dimension F_d which depends on a continuous index q,

$$F_d = \frac{1}{1-q}\lim_{\varepsilon\to 0}\frac{\ln I(q,\varepsilon)}{\ln\frac{1}{\varepsilon}} \tag{1}$$

where

$$I(q,\varepsilon) = \sum_{i=1}^{\tilde{N}(\varepsilon)} \mu_i^q \tag{2}$$

This approach was used in our research because it makes the correlation between the optical properties of the emulsion and the the corresponding fractal dimension as the measure of irregularity.

EXPERIMENTS

For the purpose of measuring the transmitance emulsion properties, the experimental cell was designed and made. The main cell structure is a T-shaped plastic container which was painted inside with non-reflective black cardboard paint. On one side, the ten white led diodes were fixed as the light source. On the other side, the CCD connector was made. The CCD camera had no lens and was used to mesure the intesity changes of the light through the emulsion during the experiment. The emulsion was placed in a special optical glass container. The place of the container was between the light source and the measuring CCD device (Figure 1).

The changes of fractal dimensions of the emulsion in time was determined by taking the intensity of the light measured in a given camera pixel, as proportional to the number of pixels. Normalizing the values then gives an approximation to the natural measure on the attractor. By using boxes of varying size ε (Figure 2a) as the numerator and plott *versus* the denominator, Eq. (1), we obtain the linear correlation presented in Figure 2b. The correspondent fractal dimension is the gradient of the line or tg α.

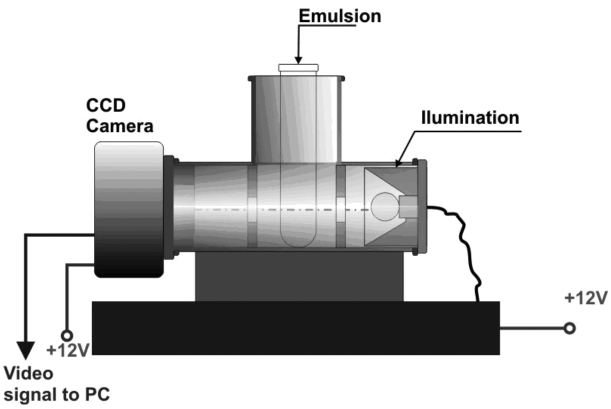

Figure 1. Experimental chamber.

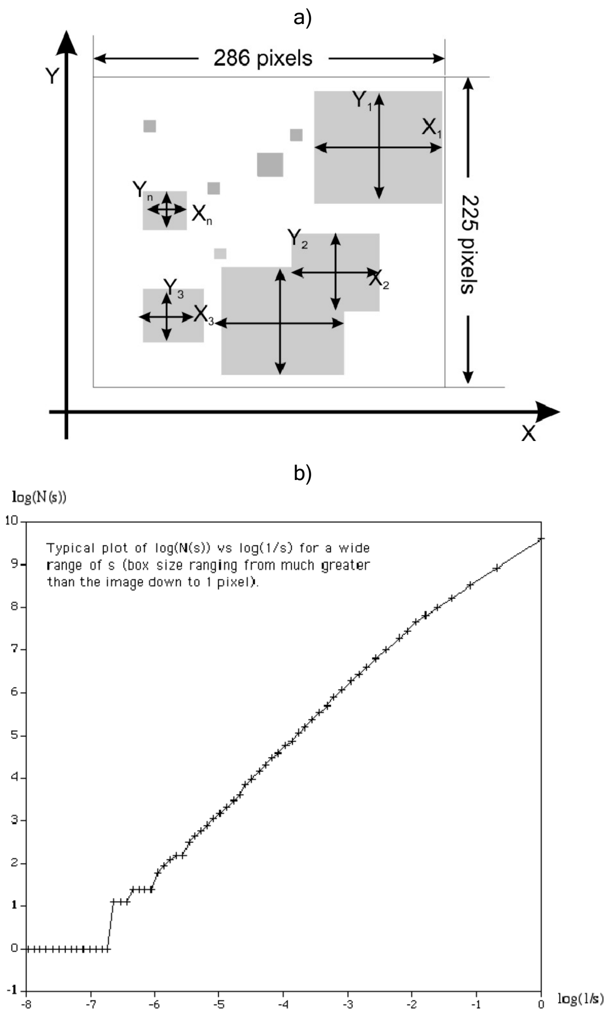

Figure 2. a) Measuring intensities in boxes of various sizes and b) corresponding fractal dimension.

RESULTS AND DISCUSION

The obtained results of measured fractal dimensions during the experiment (1200 h) are presented in Figure 3. The results of the observations clearly show tree periods of the emulsion life circle. The period of the first 300 h that could be designated as the emulsion starting life circle or meta-stable state. After a certain time, the emulsion starts its changes, in case of our experiments only under gravity influence, which could be designated as the transition state [6]. The characteristic of this state is that it is not predictable so we noticed higher variations in fractal dimensions, during time, than in previous state. After that, the fluctuations of fractal dimensions are smaller so the emulsion is again in some stable state which could be addressed as the stable state. The changes of fractal dimensions during time could be described by the four-parameter model presented as:

$$F_{\mathrm{d}} = \frac{A_1 - A_2}{1 + \left(\dfrac{x}{x_0}\right)^p} + A_2 \qquad (3)$$

In this case, parameters A_1 and A_2 represent the minimum and maximum fractal dimensions values, observed during the experiment. The results are presented in Figure 4 and the corresponding values for the parameters are presented in Table 1, together with the R square value.

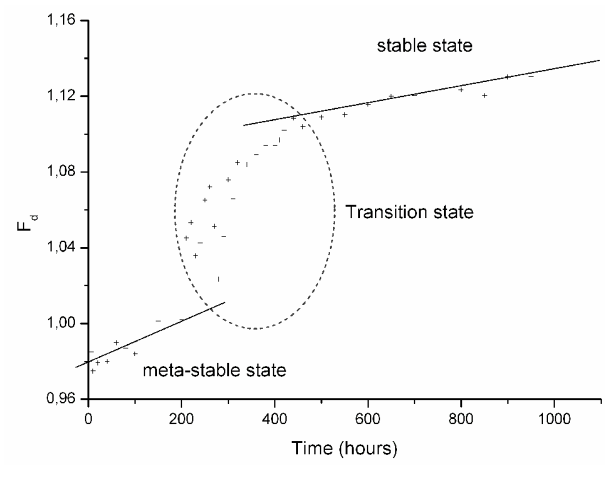

Figure 3. The results of the measured F_d during the experiment.

The simulation of the influence of parameter x_0 is presented in Figure 5. On the graph, the parameter x_0 is in the 218.3>x_0>391.3 range. This parameter of the emulsion behavior represents the time when the qualitative changes start to take place in the emulsion.

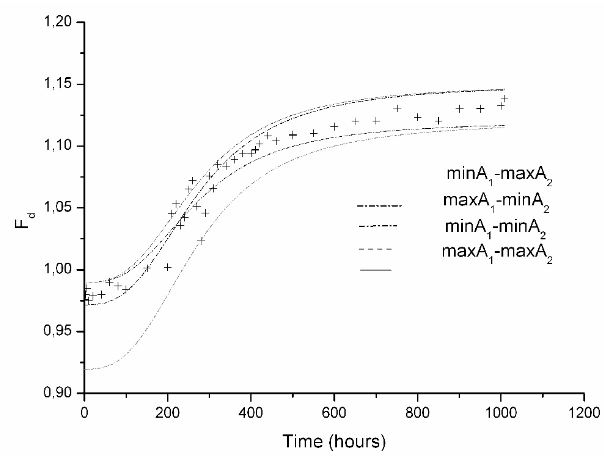

Figure 4. The model simulation for parameters A.

Table 1. Parameter values for the optimal model values

Parameter	Value	Error
A_1	0.979	0.0037
A_2	1.133	0.0055
x_0	270.7	11.004
p	2.768	0.3538
R^2	0.9663	

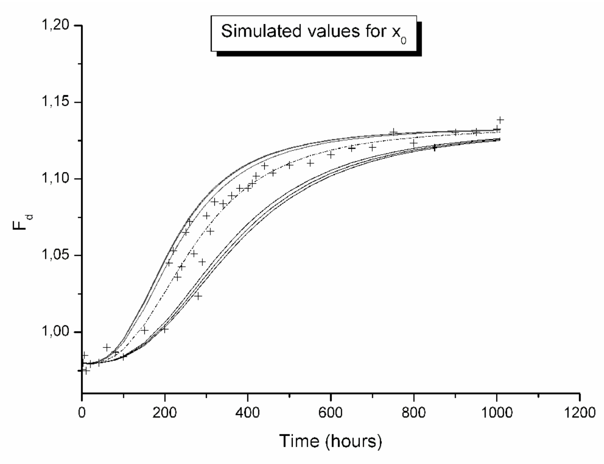

Figure 5. The model simulation for parameter x_0.

At the end, the last simulation was performed for the parameter p. This simulation is presented in Figure 6. The range for p was $4.1969 > p > 1.7969$.

The data presented in Figure 7 are optimal values of the parameter for the obtained model of the experimental emuslion. The values of parameters are presented in Table 1.

The chaos theory is defined as the study of the complex nonlinear dynamic systems. Complex implies just that, non-linear implies recursion and higher mathematical algorithms, and dynamic implies non constant and non-periodic, which could be the definition of the real emulsions. Thus the chaos theory is, very generally, the study of forever changing complex systems based on mathematical concepts of recursion, whether in the form of a recursive process or a set of differential equations modeling a physical system.

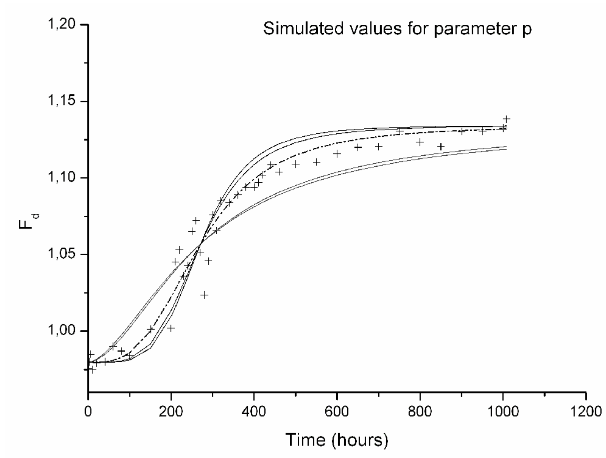

Figure 6. The model simulation for parameter p.

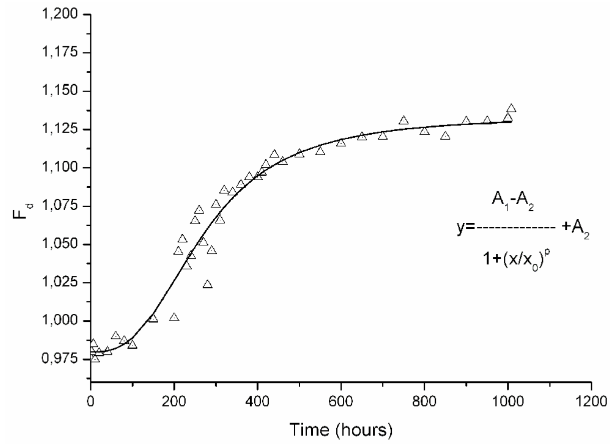

Figure 7. The optimal model for the experimental emulsion (Eq. (3)).

If we apply the principles of a dynamic system analysis to the obtained results and the ranges of the model values, we can define the frame of the emulsion existence (Figure 8).

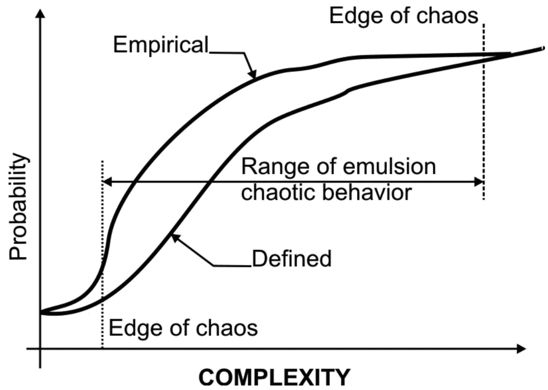

Figure 8. Probability-complexity relation for experimental emulsion.

CONCLUSION

The obtained model could be used for the simulation of the emulsion behavior during time in various conditions. As it was noticed before, the values of parameters A_1 and A_2 are the minimum and maximum values of the observed fractal dimensions. They present the range of the observed fractal dimensions for the emulsion in question. The real emulsion exists between A_1 and A_2 values.

The most sensitive parameter of the model is parameter p, which could be "connected" to the mechanisms of the emulsion destabilization, in this case only by gravitational influence. We assume that value of p can predict the dominant mechanism of the emulsion destabilization. The parameter x is connected to the time of the emulsion life circle.

First limitation in the emulsion changes is the range of fractal dimensions presented in the model with factor A. As the fractals are the measure of the irregularities in the system, this means that changes in emulsions have finite values after the new emulsion entity is formed.

The gravitationally-induced instability of weak depletion of attraction-induced networks has also been extensively investigated. However, for these systems there has been no investigation on the compression modulus, its relationship to the depletion attraction and its role in gravitational stability with changing. Understanding these effects is essential to fully exploit these means of stabilization.

The chaos theory is a way of looking at events which happen in the world differently from the more traditional strictly deterministic view which has dominated science from Newtonian times. Instead of a traditional 2D plot, scientists can now interpret phase-space diagrams which - rather than describing the exact position of some variable with respect to time – represent the overall behavior of a system. Instead of looking for strict equations conforming the statistical data, we can now look for dynamic systems with behavior similar in nature to the statistical data – systems, that is, with similar attractors.

List of symbols

A_1, A_2 - *Model parameters*
F_d - *Fractal dimensions*
l - *Length*
p - *Model parameters*
q - *Continuous index*
x, x_0 - *Time*

Greek symbols

ε - *Scale*

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